

1971

The crystal structure determinations of the perchlorate and chloride of pentaamminecyanocobalt(III)²⁺, 1,2,5-triphenylphosphole, and 1,2,5-triphenylpyrrole, and a method for phase determination

Willie Paul Ozbirn
Iowa State University

Follow this and additional works at: <https://lib.dr.iastate.edu/rtd>

 Part of the [Physical Chemistry Commons](#)

Recommended Citation

Ozbirn, Willie Paul, "The crystal structure determinations of the perchlorate and chloride of pentaamminecyanocobalt(III)²⁺, 1,2,5-triphenylphosphole, and 1,2,5-triphenylpyrrole, and a method for phase determination " (1971). *Retrospective Theses and Dissertations*. 4493.

<https://lib.dr.iastate.edu/rtd/4493>

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.

72-5241

OZBIRN, Willie Paul, 1944-

THE CRYSTAL STRUCTURE DETERMINATIONS OF THE
PERCHLORATE AND CHLORIDE OF PENTAAMINECYANOCOBALT
(III)²⁺, 1,2,5-TRIPHENYLPHOSPHOLE, AND 1,2,5-
TRIPHENYLPYRROLE, AND A METHOD FOR PHASE
DETERMINATION.

Iowa State University, Ph.D., 1971
Chemistry, physical

University Microfilms, A XEROX Company, Ann Arbor, Michigan

The crystal structure determinations of
the perchlorate and chloride of pentaaminecobalt(III)²⁺,
1,2,5-triphenylphosphole, and 1,2,5-triphenylpyrrole,
and
a method for phase determination

by

Willie Paul Ozbirn

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1971

PLEASE NOTE:

Some pages have small
and indistinct type.
Filmed as received.

University Microfilms

TABLE OF CONTENTS

	Page
INTRODUCTION	1
THE STRUCTURES OF THE PERCHLORATE AND CHLORIDE OF PENTAAMINECYANOCOBALT(III) ²⁺	3
Introduction	3
Data Taking Procedure	4
Experimental	5
Solution and Refinement	9
Discussion	17
THE STRUCTURE OF 1,2,5-TRIPHENYLPHOSPHOLE	25
Introduction	25
Experimental	26
Solution and Refinement	29
Discussion	30
THE STRUCTURE OF 1,2,5-TRIPHENYLPYRROLE	40
Introduction	40
Experimental	41
Solution and Refinement	43
Discussion	44
PHASE DETERMINATION	54
Introduction	54
Description of the Method	55
Application of the Method	57
Discussion	64

LITERATURE CITED

66

ACKNOWLEDGEMENTS

70

INTRODUCTION

The crystal structures of the perchlorate and chloride of pentaamminecyanocobalt(III)²⁺, 1,2,5-triphenylphosphole and 1,2,5-triphenylpyrrole were determined by single-crystal X-ray diffraction analysis. Points of interest ranging from the gross crystal structure to the detailed geometry of these compounds will be discussed. In addition a new method for determining phases is presented with some experimental results and comments regarding its use.

The crystal structure determinations in this thesis have evolved primarily from the use of the Patterson function and at times certain preconceived ideas of what the molecule under study should look like. The cobalt complexes are the first monocyano complexes of Co³⁺ studied by X-ray diffraction and have indicated the cyanide bonding mode to be Co-C-N. The structure of 1,2,5-triphenylphosphole was studied to examine the possible aromaticity of phospholes. Claims exist in the recent literature favoring both an aromatic and non-aromatic structure. The three dimensional geometry of 1,2,5-triphenylpyrrole was determined in order to examine the possibility that results obtained for the triphenylphosphole were an artifact of the crowding of the phenyl rings about phosphorus and to obtain a precise geometry of the pyrrole nucleus.

The integral of the absolute value of the electron density function was examined in order to determine its use as a purely mathematical method of determining phases. This technique has been successfully applied to three previously determined crystal structures.

THE STRUCTURES OF THE PERCHLORATE AND CHLORIDE
OF PENTAAMINECYANOCOBALT(III)²⁺

Introduction

Transition metal cyanide ion coordination has long been the subject of much conjecture between experimenters from various fields. In many cyanide complexes, metal to carbon bonding is often assumed and this assumption is found in many textbooks (1).

Spectral studies attempted thus far have been unable to unambiguously determine the cyanide ion coordination. Results of infrared studies on a series of cyanides favor the metal-ion to carbon atom coordination; however, the alternate coordination cannot be completely rejected (2,3). Kuroda and Gentile (4) have recently analyzed the visible and ultraviolet spectra of two cobalt-cyanide complexes and they interpret their results in terms of Co-N coordination.

Early X-ray diffraction studies of transition metal cyanide complexes, such as the ferrocyanide ion or $KAg(CN)_2$ (5), were interpreted to indicate that the metal ion is attached to the carbon atom. However even with today's modern instrumentation and high speed computers, atoms differing by only one electron can still be difficult to distinguish from one another. Even though neutron diffraction

is better suited to this type of problem, only the molecular structures of $K_3Co(CN)_6$ (6), $K_2Zn(CN)_4$ (7) and $Hg(CN)_2$ (8) have been attempted thus far by neutron diffraction. All of these studies have indicated metal to carbon bonding.

In 1968, Birk and Espenson (9) reported the chromium(II) oxidation by $[(NH_3)_5(CN)Co(III)]^{2+}$. The kinetics and mechanism of the reaction were explained in terms of a C-bonded cobalt(III); however, the N-bonded model is not entirely excluded. Therefore we decided to undertake the single-crystal X-ray diffraction analysis of $[(NH_3)_5(CN)Co(III)](ClO_4)_2 \cdot 0.5H_2O$.

During the refinement of the above complex the perchlorate ions were found to be disordered. Consequently we decided to carry on the single-crystal X-ray study of $[(NH_3)_5(CN)Co(III)]Cl_2$ in conjunction with the above analysis.

Data Taking Procedure

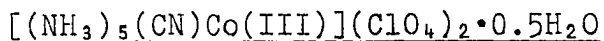
All X-ray intensity data were taken on a Hilger-Watts four-circle diffractometer interfaced to an SDS 910 computer in a real time mode. Zirconium-filtered molybdenum radiation was used, $\lambda = 0.7107\text{\AA}$.

Data were taken using a θ - 2θ step-scan procedure with steps of 0.01 degrees in theta and a counting time of 0.4096 seconds per step. The number of steps through a given

reflection varies with theta; $[50 + (2 \times \theta)]$ where θ is the peak center in degrees. Stationary-crystal, stationary-counter background measurements were made at the beginning and end of the step-scan, each measurement being made for one-half the total scan time.

As a general check on electronic and crystal stability, the intensities of three standard reflections were measured periodically during the data collection period. Approximately 25 reflections per hour were obtained and logged on an IBM seven track tape.

Experimental



Crystals of pentaaminecyanocobalt(III) perchlorate were prepared by the method of Siebert (10). Recrystallization from a water solution yielded red-orange crystals.

Preliminary precession photographs showed the unit cell to be orthorhombic with systematic absences $\underline{hk\bar{l}}$ when $\underline{h+k} = 2n+1$ and $\underline{h0\bar{l}}$ when $\underline{l} = 2n+1$. These absences are consistent with space groups Cmcm , $\text{Cmc}2_1$, or $\text{Ama}2$ (alternate setting). The unit cell parameters at 25°C are $\underline{a} = 8.164(1)$, $\underline{b} = 20.737(4)$, $\underline{c} = 7.724(1)\text{\AA}$. These parameters and their standard deviations were obtained by a least-squares fit to 15 independent reflections. The center of each reflection was found

by left-right top-bottom beam splitting on the previously described Hilger-Watts diffractometer. Any error in the instrumental zero was eliminated by centering the reflection at both $+2\theta$ and -2θ . The calculated density of 1.92gm/cc based on four molecules per unit cell agrees quite well with the observed density of 1.90gm/cc which was determined by flotation techniques.

For data collection a cylindrical crystal with radius 0.08mm and a height of 0.34mm was mounted on a glass fiber. The latter direction was the c crystal axis and was coincident with the spindle axis. Complete three-dimensional data to $\sin\theta/\lambda = 0.7035$ at 25°C were taken for the four octants with positive l index. The rest of the experimental arrangement for intensity collection has been discussed in some detail above.

The intensity data were corrected for Lorentz-polarization effects. The absorption coefficient, μ , is 18.14cm^{-1} . The maximum and minimum transmission factors are 78.58 and 77.16% respectively, which were calculated using a modified version of Busing and Levy's ABCOR program (11). Therefore no absorption correction was made.

Of the 4543 possible observations, 1488 were found to be less than three times the standard deviation in the background and were subsequently disregarded. The three sigma criteria was tested on 1154 symmetry extinct reflections and

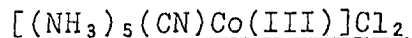
was found to hold 96% of the time. Since four octants of equivalent intensity data were collected, a confidence test (12) was applied. This test was used to determine if any piece of a set of equivalent data should be disregarded. Only 112 of the remaining 3055 possible observations failed this confidence test. The individual values of F_o^2 from the equivalent sets were then averaged to yield 750 independent F_o^2 values. The standard deviations of F_o^2 were estimated from the averages of the individual intensities and their standard deviations.

Also neutron data were collected for this compound on a crystal having approximate dimensions 2.33 x 1.07 x 4.69mm along the a, b and c crystal axes respectively. The crystal was mounted on a glass fiber such that the c crystal axis and the spindle axis were coincident.

Three-dimensional data were collected at room temperature with a neutron wavelength of 1.1588 \AA , utilizing a Mitsubishi diffractometer equipped with a two circle head and a BF_3 monitor counter. There were 125 observed reflections out of 197 unique observations. Each reflection required 50 steps in intervals of 0.2 of a degree in two-theta and each observed reflection was measured three times.

The intensities were corrected for Lorentz, absorption and background effects. Independent F_o^2 values and their

standard deviations were obtained in a manner similar to that described above.

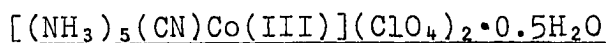


Crystals of pentaamminecyanocobalt(III) chloride, prepared by the method of Siebert (10) and recrystallized from a water solution, are orthorhombic with cell dimensions $\underline{a} = 10.190(1)$, $\underline{b} = 8.740(1)$, $\underline{c} = 10.335(2)\text{\AA}$, $D_m = 1.78\text{gm/cc}$ (by flotation), for $Z = 4$, $D_c = 1.76\text{gm/cc}$. Systematic absences (\underline{hkl} when $\underline{h+k} = 2n+1$ and $\underline{h0l}$ when $\underline{l} = 2n+1$) indicate space groups Cmcm , $\text{Cmcm}2_1$ or $\text{Ama}2$ (alternate setting).

Complete three-dimensional X-ray diffraction intensity data to $\sin\theta/\lambda = 0.9041$ were taken at room temperature (Mo K_α radiation) using a crystal with dimension $0.18 \times 0.28 \times 0.28\text{mm}$ along the \underline{a} , \underline{b} and \underline{c} crystal axes respectively, such that the \underline{c} axis was along the spindle axis. The rest of the experimental arrangement for intensity collection has been previously described.

The intensity data were corrected for Lorentz-polarization effects and effects due to absorption. The three sigma test was applied to the intensity data and 682 of the 2003 possible observable reflections were rejected.

Solution and Refinement



A Howells', Phillips' and Rogers' plot (13) was obtained using all the collected data and indicated the presence of a center of symmetry and the appropriate space group was assumed to be Cmc_m. An unsharpened Patterson function was calculated and a vector which was assumed to be a Co-Co vector resulting from the c-glide was located on the Harker line. The positions of the cobalt ligand atoms were also indicated from this three-dimensional Patterson function. However the direction of the cyanide group could not be determined; hence, the immediate ligand atoms were all assigned nitrogen scattering factors. Two cycles of positional refinement on the cobalt and immediate ligand atoms produced a conventional R-factor of 0.43.

The initial structure factor and electron density calculation indicated the direction of the cyanide group. It was also evident the perchlorate ions were in two four-fold sets (mm symmetry) instead of an eight-fold set and were disordered. After accounting for all the perchlorate oxygens in disordered positions there was still one peak left about the size of one-fourth an oxygen. This peak was assumed to be part of the water molecule. A difference Fourier was then computed, and it was verified that all non-hydrogen atoms had

been accounted for, and some anisotropic motion was evident.

A full matrix least-squares refinement minimizing the weighted R-factor was initiated with all atoms isotropic using the program of Busing et al. (11) and the atomic scattering factors of Hanson et al. (14). Two trial structures were assumed for refinement, one having the carbon atom of the cyanide group adjacent to the cobalt and the other having the nitrogen atom next to the cobalt. When the conventional R-factor in both cases fell below 0.15, anisotropic refinement on all atoms except the disordered oxygens was begun. Since the temperature factors are a function of the occupancy numbers, it did not seem justifiable to refine the oxygens anisotropically. At this time the weighting scheme was modified from one based on counting statistics such that a plot of $w\Delta^2$ versus F_o^2 was a constant. The final conventional and weighted R-factors are; 0.082 and 0.119 respectively for the Co-C-N model, 0.085 and 0.123 respectively for the Co-N-C model.

The observed and calculated structure factors for the Co-C-N model in space group Cmcm are given in Table 1a. The final positional, anisotropic temperature factors and standard errors are given in Table 2. In Table 2, Cl(2) and Cl(3) are the half chlorines and O(7) belongs to the water molecule. The more important interatomic distances,

angles and their errors (calculated using the function and error program of Busing et al. (11)) are summarized in Table 3.

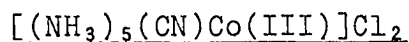
It may be noted here that the average effective isotropic B for the ammonia nitrogens is 4.2\AA^2 . In the Co-C-N model the effective isotropic B's for C and N are 4.4 and 7.5\AA^2 respectively, while in the Co-N-C model the effective isotropic B's for C and N are 6.0 and 6.0\AA^2 respectively. Also the experimental ratio of C:N integrated electron densities for the Co-C-N model is 0.864 while the calculated value is 0.857. For the Co-N-C model the experimental ratio of N:C integrated electron densities is 0.867.

Also the atomic parameters from the Co-C-N and Co-N-C models of the final X-ray least-squares refinement for space group Cmc₂m were used as input for refinement of the neutron data. Attempts to refine all the positional parameters were unsuccessful, probably due to the insufficient data. Also there were some experimental difficulties experienced toward the end of the data taking period. However the ammonia hydrogens were found approximately 1\AA from the nitrogens with bond angles between 105 and 118° .

Subsequent refinement using isotropic temperature factors for the hydrogen atoms gave weighted R-factors of 0.215 and 0.230 for the Co-C-N and Co-N-C models respectively. The larger value of the R-factor is to be expected as the

disorder of the perchlorate groups has more of an effect on the neutron intensities.

The observed and calculated structure factors for the Co-C-N model are given in Table 1b.



An unsharpened Patterson map was calculated using all observed reflections. All non-hydrogen atomic positional parameters were found and placed accordingly in the unit cell. The direction of the cyanide group was assumed to be the same as in the perchlorate case.

Using the full-matrix least-squares program of Busing et al. (11) and the scattering factors of Hanson et al. (14) an isotropic refinement was undertaken on all atoms. After four iterations using a Co-C-N model in space group Cmc the conventional and weighted R-factors were 0.094 and 0.112 respectively. After four cycles of anisotropic refinement the weighting scheme was modified such that a plot of $\omega\Delta^2$ versus F_o^2 was a constant. The final conventional and weighted R-factors are 0.076 and 0.101 respectively.

Refinement in space groups Cmc2₁ and Ama2 using a Co-C-N model gave weighted R-factors of 0.095 and 0.091 respectively. However both of these cases resulted in meaningless distortions of the cations and shifts in the anion positions. The centric space group Cmc was also indicated

Table 1b. Observed and calculated neutron structure factors (x10) for pentaaminecyanocobalt(III) perchlorate.

L = 0				6 12	34	-28	3 11	26	-19	4 2	91	112	
H	K	FO	FC	1 13	137	-133	0 12	55	-57	1 3	44	-81	
2 0	242	231		3 13	72	56	2 12	21	26	3 3	80	113	
4 0	53	61		5 13	61	-47				0 4	62	-57	
6 0	286	249		0 14	166	-151				3 5	44	-51	
3 1	35	-46		2 14	20	22	L = 2				0 6	125	102
5 1	85	53		3 17	99	-89	H	K	FO	FC	1 7	65	62
0 2	10	5		2 18	57	-52	0 0	189	-225	3 7	88	-96	
2 2	30	33		3 19	32	-23	4 0	105	-158	0 8	36	33	
1 3	19	15					3 1	51	-86	2 8	80	-86	
3 3	59	22					0 2	23	-27	3 9	50	-53	
5 3	45	-32		L = 1				1 3	16	-23	0 10	103	-87
0 4	55	61		H	K	FO	FC	0 4	74	-79	2 10	37	48
2 4	45	70		1 1	12	21	2 4	36	-51	1 11	33	32	
4 4	70	65		3 1	31	17	4 4	25	-27	0 12	112	-101	
6 4	82	-68		5 1	67	-39	1 5	63	-60				
1 5	17	36		0 2	23	28	5 5	91	-86	L = 4			
3 5	230	198		2 2	16	16	0 6	70	-55	H	K	FO	FC
0 6	51	-63		4 2	66	44	2 6	21	50	0 0	110	135	
4 6	26	-32		1 3	150	-157	4 6	36	28	4 0	129	127	
6 6	104	-87		3 3	39	17	1 7	24	32	3 1	43	65	
1 7	58	80		5 3	73	-42	0 8	61	34	0 2	31	31	
3 7	22	27		0 4	54	46	2 8	36	-37	0 4	87	74	
0 8	96	132		2 4	64	49	4 8	35	-30	2 4	28	56	
2 8	79	-80		4 4	91	73	1 9	26	10	1 5	52	70	
4 8	67	-45		1 5	85	73	3 9	107	-83	0 6	55	35	
6 8	78	50		3 5	30	-15	0 10	82	65	1 7	29	-33	
1 9	35	38		0 6	57	51	2 10	49	-41	1 9	31	24	
3 9	94	-62		2 6	18	-25	1 11	25	-28				
5 9	131	107		4 6	44	-28	2 11	21	-18	L = 5			
0 10	76	43		3 7	49	-28	2 12	74	61	H	K	FO	FC
2 10	54	-80		5 7	43	26				0 2	103	-71	
6 10	47	52		0 8	106	99				0 6	74	46	
1 11	38	26		1 9	45	65	L = 3						
3 11	25	-23		3 9	42	40	H	K	FO	FC	L = 6		
0 12	82	-88		0 10	22	-47	3 1	43	40	H	K	FO	FC
4 12	25	-22		1 11	105	-88	0 2	94	-92	0 0	165	-203	

Table 2. Fractional atomic coordinates ($\times 10^4$) and anisotropic temperature factors ($\times 10^5$) for pentaaminecyanocobalt(III) perchlorate. Values not followed by standard deviations in parenthesis are fixed by symmetry. The form of the anisotropic temperature factor is

$$\exp [-(\beta_{11}\underline{h}^2 + \beta_{22}\underline{k}^2 + \beta_{33}\underline{l}^2 + 2\beta_{12}\underline{hk} + 2\beta_{13}\underline{hl} + 2\beta_{23}\underline{kl})].$$

Atom	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0	1110 (1)	2500	716 (20)	197 (3)	919 (25)	0	0	0
Cl (1)	0	7453 (2)	2500	1799 (61)	261 (8)	1883 (63)	0	0	0
Cl (2)	0	4508 (4)	2500	838 (72)	390 (20)	1398 (98)	0	0	0
Cl (3)	0	3864 (3)	2500	1436 (6)	298 (18)	1979 (127)	0	0	0
C	0	201 (6)	2500	2723 (308)	227 (33)	1064 (181)	0	0	0
N (1)	0	2074 (5)	2500	1826 (196)	238 (27)	1526 (187)	0	0	0
N (2)	0	-347 (5)	2500	5392 (492)	228 (35)	1620 (219)	0	0	0
N (3)	1707 (6)	1100 (2)	693 (6)	1336 (79)	375 (16)	1559 (187)	3 (27)	374 (70)	-50 (28)
O (1)	1442 (24)	3483 (9)	2500	7.4 (4)					
O (2)	1360 (30)	4828 (12)	2500	9.5 (5)					
O (3)	0	4239 (6)	4000 (15)	9.8 (3)					
O (4)	1214 (20)	7373 (8)	1172 (15)	12.3 (3)					
O (5)	0	8113 (13)	2500	10.0 (6)					
O (6)	0	6767 (28)	2500	7.6 (3)					
O (7)	0	5569 (13)	2500	6.7 (5)					

Table 3. Distances (\AA) and angles (deg) with standard deviations in parenthesis for pentaaminecyano-cobalt(III) perchlorate. An atom with a superscript one implies a transformation of the atomic coordinates of Table 2 to $(-x,y,z)$. An atom with a superscript two implies a transformation to $(x,y,0.5-z)$.

Atoms	Distance	Atoms	Angle
Co-C	1.883(13)	C-Co-N(3)	89.3(2)
Co-N(1)	1.999(11)	N(3) ¹ -Co-N(3)	89.9(3)
Co-N(3)	1.972(5)	O(4)-Cl(1)-O(6)	83.3(7)
C-N(2)	1.138(17)	O(4)-Cl(1)-O(4) ¹	87.3(11)
Cl(1)-O(4)	1.435(15)	O(3)-Cl(2)-O(2)	102.8(5)
Cl(1)-O(5)	1.369(28)	O(2)-Cl(2)-O(2) ¹	118.3(24)
Cl(1)-O(6)	1.421(58)	O(3)-Cl(2)-O(3) ²	128.5(12)
Cl(2)-O(2)	1.293(26)	O(3)-Cl(3)-O(1)	108.1(4)
Cl(2)-O(3)	1.286(12)	O(1)-Cl(3)-O(1) ¹	112.2(16)
Cl(3)-O(1)	1.418(21)	O(3)-Cl(3)-O(3) ²	112.3(10)
Cl(3)-O(3)	1.395(13)		

by the HPR statistical test (13).

Also the refinement of a Co-N-C model was carried out in space group Cmc₂m. Final conventional and weighted R-factors in this case are 0.080 and 0.105 respectively.

The observed and calculated structure factors for the Co-C-N model in space group Cmc₂m are given in Table 4. The final positional, anisotropic temperature factors and standard errors are given in Table 5. The more important distances, angles and their errors are summarized in Table 6.

For this compound the average effective isotropic B of the ammonia nitrogens is 2.4\AA^2 . In the Co-C-N model the effective isotropic B's for C and N are 2.1 and 3.0\AA^2 respectively and the experimental ratio of C:N integrated electron densities is 0.873. In the Co-N-C model the effective isotropic B's for C and N are 2.5 and 2.6\AA^2 respectively, while the experimental ratio of N:C integrated electron densities is 0.900.

Discussion

The crystal structures of the perchlorate and chloride of pentaamminecyanocobalt(III) are depicted in Figures 1 and 2 respectively. In both cases the cobalt atom lies in a position of mm crystallographic symmetry with the cation

Table 4. Observed and calculated structure factors (x10) for pentaaminecyanocobalt(III) chloride.

Table with multiple columns containing numerical data for structure factors. The table is organized into several sections, each starting with a header row (e.g., L = 0, L = 1, L = 2) and followed by rows of observed and calculated values. The data is presented in a grid-like format with varying column widths and some text annotations interspersed.

Table 5. Fractional atomic coordinates ($\times 10^4$) and anisotropic temperature factors ($\times 10^5$) for pentaaminecyanocobalt(III) chloride. Values not followed by standard deviations in parenthesis are fixed by symmetry. The form of the anisotropic temperature factor is

$$\exp [-(\beta_{11}\underline{h}^2 + \beta_{22}\underline{k}^2 + \beta_{33}\underline{l}^2 + 2\beta_{12}\underline{hk} + 2\beta_{13}\underline{hl} + 2\beta_{23}\underline{kl})].$$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0	2159 (1)	2500	409 (5)	470 (6)	302 (4)	0	0	0
N (1)	0	4444 (5)	2500	857 (53)	579 (49)	488 (35)	0	0	0
N (2)	0	-1329 (7)	2500	1046 (66)	668 (57)	616 (43)	0	0	0
N (3)	1928 (3)	2176 (4)	2500	490 (25)	909 (42)	535 (26)	6 (26)	0	0
N (4)	0	2125 (4)	588 (3)	756 (33)	813 (37)	332 (20)	0	0	17 (23)
C	0	-23 (6)	2500	561 (43)	682 (53)	401 (35)	0	0	0
Cl	2838 (1)	0	0	556 (8)	735 (11)	494 (7)	0	0	20 (6)

Table 6. Distances (\AA) and angles (deg) with standard deviations in parenthesis for pentaaminecyano-cobalt(III) chloride.

Atoms	Distance	Atoms	Angle
Co-N(1)	1.996(1)	C-Co-N(3)	90.4(1)
Co-N(3)	1.965(4)	C-Co-N(4)	89.1(1)
Co-N(4)	1.975(3)	N(4)-Co-N(3)	90.0(1)
Co-C	1.908(6)		
C-N(2)	1.142(8)		

complex having approximately C_{4v} symmetry. In Figure 1 the mirror plane at a quarter in z bisects the four nitrogens in the equatorial plane while in Figure 2 the four-fold nitrogens lie in the mirror planes.

The disordered oxygens have been left out of Figure 2. The two chlorines labelled one-half in Figure 2 share two oxygen atoms. The disorder about the other chlorine leads to an approximately octahedral arrangement of oxygen atoms. This by no means indicates that the geometry of a perchlorate ion is anything other than tetrahedral. However since the perchlorate ion is spherical by nature, it is not surprising in this case that it has little preference regarding its orientation in packing.

The average values of Co-C, Co-N and C-N bond lengths agree quite well with previously reported values in the literature (15-17).

The main interest in these structure determinations lies in the attempt to distinguish between the Co-C-N and Co-N-C models. It was decided that the former is the correct bonding mode on the following evidence:

1. Integrated electron densities of both structures favored the Co-C-N model.

2. In all cases (X-ray and neutron), the Co-C-N model gave better agreement factors.

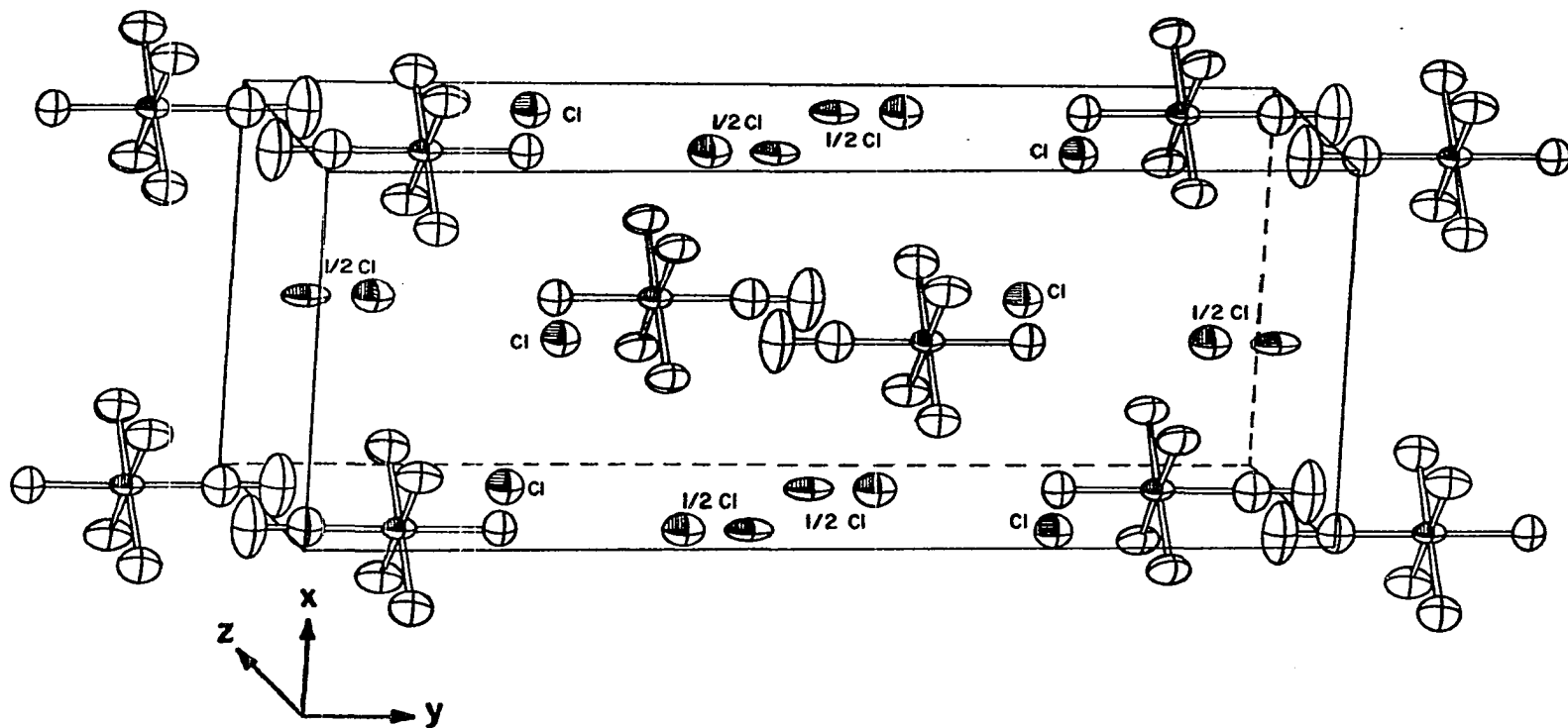


Figure 1. Illustration of molecular packing for pentaamminecyanocobalt(III) perchlorate. The oxygens are not shown and the disordered chlorines are labeled 1/2 Cl.

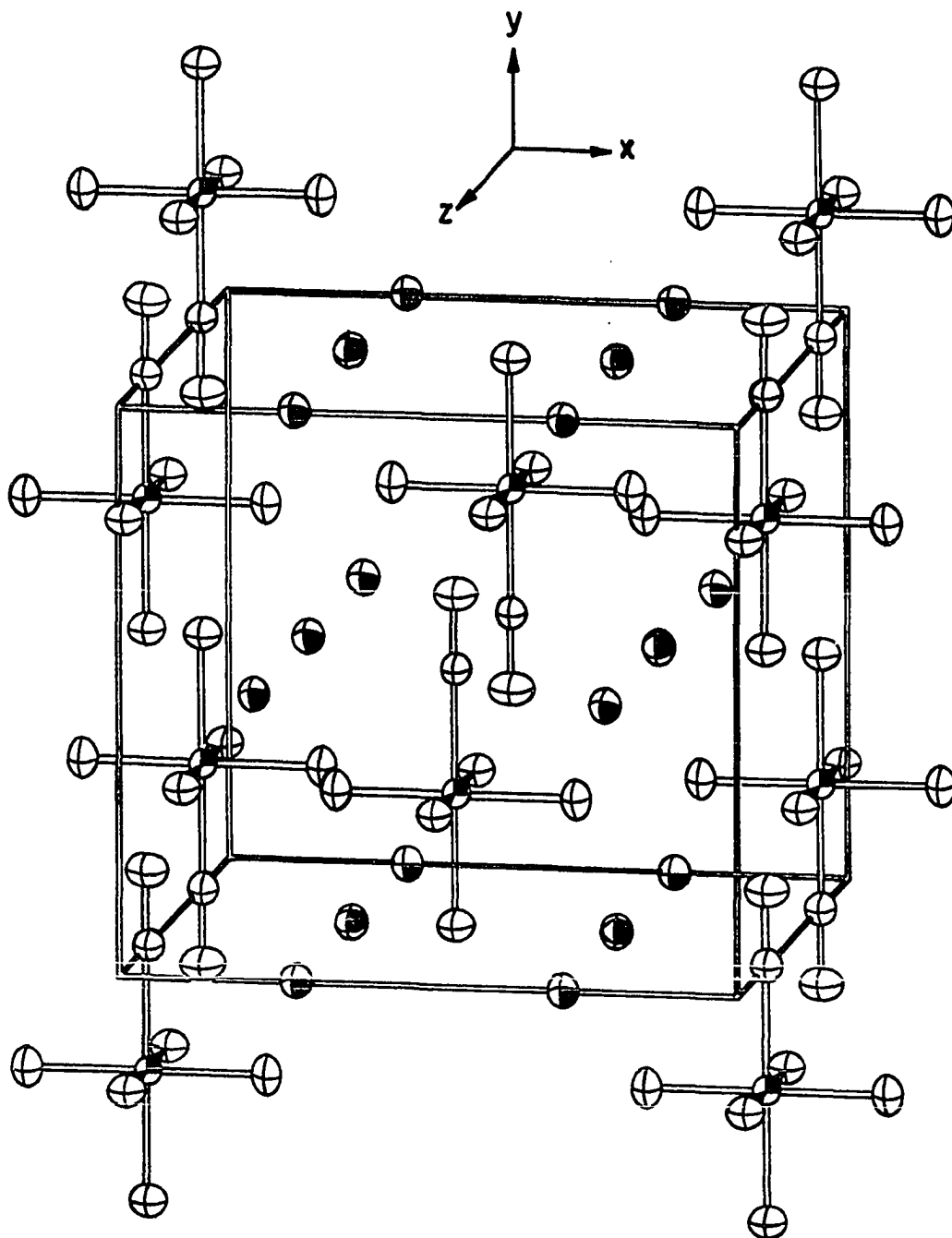


Figure 2. Illustration of molecular packing for pentaamminecyanocobalt(III) chloride.

3. In both structures, the effective isotropic temperature factor of the atom bonded to the cobalt atom had a tendency to increase when the Co-N-C model was invoked. The trend would, of course, be observed if a nitrogen were input where a carbon should be located.

THE STRUCTURE OF 1,2,5-TRIPHENYLPHOSPHOLE

Introduction

The potential aromatic character of the phosphole ring system has been the subject of considerable dispute in recent years. Pentaphenylphosphole (18) was synthesized in 1960, and later the phosphole ring system was prepared via the more general synthesis of Cookson (19), Markel (20) and Quin (21).

Much conflicting evidence exists concerning the degree of cyclic delocalization and aromatic character of the phosphole ring. Brown (22) has reported that HMO calculations on the planar phosphole ring gave a delocalization energy of 1.49 β as compared to 1.37 β for pyrrole. Mortimer (23) found that the heat of oxidation of pentaphenylphosphole to its oxide is abnormally low, 39kcal/mole less than that for trimethylphosphine. Quin (24) recently reported a significant shortening of the heterocyclic phosphorus-carbon bond lengths in the molecular structure of 1-benzylphosphole determined by X-ray film techniques. All this evidence as well as spectral data reported on the low-field absorption of the phosphole ring protons (20,21) and ^{31}P (21) indicated appreciable aromaticity of the ring. However 1,2,5-triphenylphosphole has been found to react with dimethylacetylenedicarboxylate (25) in an addition fashion to form

a 2:1 adduct containing one molecule of phosphole. The triphenylphosphole also undergoes rather facile photodimerization, a process that does not usually occur with aromatic heterocyclopentadienes (26). It has been estimated from vicinal PH coupling constants that the orientation of the lone pair of electrons on phosphorus relative to the π -bond in the plane of the ring is 45° (25). This evidence seemed to indicate little aromatic character in the phosphole ring.

In view of these contradictory indications, we undertook an accurate single-crystal X-ray investigation of 1,2,5-triphenylphosphole to attempt to resolve this dilemma.

After our structural work had been completed, further evidence for the non-planarity of the phosphole ring was reported by Mislow (27), who observed (nmr) inversion at phosphorus in 1-isopropyl-2-methyl-5-phenylphosphole. The abnormally low barrier to pyramidal inversion was interpreted as due to delocalization in the planar transition state.

Experimental

The crystals of 1,2,5-triphenylphosphole were prepared by the method of Cookson et al. (19) and were kindly furnished by Dr. T. J. Barton of this laboratory. Microscopic examination revealed that the crystals were clear yellow needles

with sharply defined faces. A suitable specimen (0.10 x 0.18 x 0.14mm) was cut from one such needle and mounted on a glass fiber. Preliminary Weissenberg and precession photographs exhibited 2/m Laue symmetry indicative of the monoclinic crystal system. The only observable systematic absences were for $0k0$ when $k = 2n+1$. Possible space groups consistent with this extinction condition are $P2_1$ and $P2_1/m$. The crystal was then transferred to a fully automated Hilger-Watts four-circle diffractometer. Accurate theta values were obtained for twelve independent reflections by a left-right, top-bottom beam splitting technique on this diffractometer. A least-squares fit of the cell constants to these angles gave $a = 12.129(2)$, $b = 5.926(4)$, $c = 12.678(2)\text{\AA}$ and $\beta = 115.85(4)^\circ$. The calculated density was 1.265gm/cc for $Z=2$.

All data in the hkl and $\bar{h}kl$ octants were collected within a theta sphere of 55° using a stationary-crystal, stationary-counter technique with Ni-filtered $\text{Cu } K_\alpha$ radiation, $\lambda = 1.5418\text{\AA}$. Intensities were measured by counting at the peak center $\theta(h, k, l)$ for ten seconds and subtracting two five-second background counts measured at $\theta(h, k, l) \pm [0.25 + (0.01 \times \theta(h, k, l))]$. A total of 1163 reflections were measured in this manner. As a general check on crystal and electronic stability, the intensities of three reflections were periodically monitored; no appreciable decomposition

was detected. Also 79 integrated intensities of previously measured reflections covering a range of values were obtained via the step-scan method (moving-crystal, moving-counter technique), for later use in a peak-height to integrated data conversion (28).

The intensity data were initially corrected for Lorentz and polarization factors. Since the absorption coefficient is only 1.42cm^{-1} for Cu K_{α} radiation, no correction for this effect was deemed necessary. Thirty-seven reflections were found to have net intensities less than three times the square-root of the background and were judged to be unobserved and omitted from the refinement. The estimated error in each intensity measurement was calculated by:

$$\sigma(I) = \sqrt{C_T + C_B + (K_T C_T)^2 + (K_B C_B)^2}$$

where C_T and C_B are the total and background counts respectively. In this formula, K_T and K_B are the relative random errors in the total and background intensities and are given values of 3 and 5% respectively. The finite difference method was used to derive the formula for the estimated standard error for each reflection:

$$\sigma(F) = (LP)^{-1/2} [(I + \sigma(I))^{1/2} - I^{1/2}]$$

where I is the calculated intensity and LP is the Lorentz-polarization correction. These standard errors were used

during refinement to weight the 1126 observed structure factors, where $\omega = 1/\sigma(F)^2$.

Solution and Refinement

A three-dimensional Patterson synthesis was computed from the observed data. The general absences of peaks on the <0V0> Harker line indicated that space group $P2_1$ with one molecule per asymmetric unit was the correct choice. The position of the phosphorus atom was readily established and despite some pseudo-symmetry a three-dimensional electron density synthesis revealed the 22 carbon atoms. Full matrix least-squares refinement with anisotropic temperature factors for all atoms, using the scattering factors of Hanson et al. (14), converged rapidly to a conventional R-factor of 0.082 and a weighted R-factor of 0.108. Hydrogen atom positions were obtained from a difference map, but only after the peak-height to integrated conversion of the data had been made (28). Subsequent isotropic refinement of the hydrogen atoms led to a significant (29) decrease in the conventional and weighted R-factors to 0.060 and 0.079 respectively. A final difference map revealed no peaks larger than 0.4 electrons/Å³. Refinements in which the phosphorus atom scattering factor was corrected for anomalous dispersion (30) led to no change in the R-factors and no change in molecular geometry.

Discussion

Observed and calculated structure factors are given in Table 7. Fractional coordinates and anisotropic temperature factors of the non-hydrogen atoms with standard deviations are summarized in Table 8. Table 9 contains the fractional coordinates and isotropic temperature factors of the hydrogen atoms, which are numbered similarly to the carbon atoms to which they are attached. Bond lengths and angles are given in Table 10. Figure 3 shows a stereoscopic view of the molecule and indicates the labeling of the atoms. Molecular packing is illustrated in Figure 4.

The equation of the least-squares plane of the four atoms (C(2), C(3), C(4), and C(5)) of the heterocyclic ring is

$$0.8835 X - 0.4266 Y - 0.1935 Z = 3.1942\text{\AA}$$

where the coefficients are direction cosines relative to \underline{a} , \underline{b} and \underline{c}^* . These four carbons are coplanar with root-mean-square deviation of 0.0006\AA . However the deviation of the phosphorus atom from this plane is 0.177\AA . The non-planarity of the ring is also illustrated by the ring torsion angles which are: P-C(2)-C(3)-C(4), -6.02 ; C(2)-C(3)-C(4)-C(5), 0.16 ; C(3)-C(4)-C(5)-P, 5.78 ; C(4)-C(5)-P-C(2), -7.63 ; and C(5)-P-C(2)-C(3), 7.74° .

Table 8. Heavy atom fractional coordinates ($\times 10^4$), anisotropic temperature factors ($\times 10^5$) and their standard deviations in parenthesis. Values not followed by a standard deviation are fixed by symmetry. The form of the anisotropic temperature factor is

$$\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	3734(1)	G	882(1)	977(13)	2839 (49)	893(12)	-14 (23)	538(10)	-4 (21)
C(2)	4748(4)	1956 (9)	1968(4)	819(44)	3372(199)	983(47)	-262 (81)	515(39)	-233 (90)
C(3)	4826(4)	3851(10)	1408(4)	1037(52)	3218(202)	1103(52)	-105 (86)	639(44)	-166 (89)
C(4)	4025(4)	3924(11)	173(4)	1248(58)	3421(205)	1028(50)	-185 (99)	679(46)	-9 (89)
C(5)	3302(4)	2088 (9)	-267(4)	1039(49)	3121(188)	920(46)	-36 (87)	586(40)	37 (82)
C(6)	2507(4)	1715(10)	-1512(4)	634(46)	3388(193)	1089(50)	298 (88)	586(41)	162 (92)
C(7)	2417(5)	3255(12)	-2374(4)	1162(56)	4385(258)	1036(51)	48(106)	590(46)	310(103)
C(8)	1666(6)	2862(14)	-3550(5)	1365(69)	5535(314)	1058(57)	78(138)	543(52)	495(128)
C(9)	992(5)	897(14)	-3903(5)	1391(70)	5797(355)	1040(58)	-105(132)	562(54)	-113(122)
C(10)	1050(5)	-645(13)	-3078(5)	1341(64)	5136(319)	1118(57)	-453(116)	580(49)	-40(117)
C(11)	1799(4)	-278(12)	-1890(4)	1401(62)	3988(257)	990(47)	-487(129)	689(46)	-196(112)
C(12)	5470(4)	1422(11)	3206(4)	1070(55)	3786(228)	1042(55)	14(100)	651(47)	-84 (99)
C(13)	6346(5)	2985(13)	3948(4)	1364(68)	4175(263)	1095(55)	-451(120)	509(52)	-123(111)
C(14)	7022(6)	2515(14)	5125(5)	1563(79)	5220(331)	1044(58)	-216(136)	410(55)	-195(127)
C(15)	6870(6)	546(13)	5608(5)	1449(72)	5867(398)	987(54)	117(141)	473(53)	137(123)
C(16)	6006(6)	-1035(14)	4890(5)	1729(82)	4715(281)	1187(64)	275(137)	800(63)	499(119)
C(17)	5321(5)	-572(11)	369 (4)	1152(56)	4342(285)	1028(52)	-119(100)	543(44)	165(101)
C(18)	2414(4)	-249 (9)	1217(3)	1012(47)	3129(198)	873(39)	-45 (98)	485(35)	179 (89)
C(19)	2094(4)	1449(11)	1767(5)	1108(52)	3494(217)	1236(55)	-32 (99)	669(47)	-266 (97)
C(20)	1094(5)	1209(13)	2015(5)	1206(67)	5142(295)	1476(71)	-315(136)	886(60)	-215(130)
C(21)	436(5)	-755(13)	1736(5)	1074(62)	5652(315)	1363(61)	-78(121)	780(53)	379(121)
C(22)	729(5)	-2496(13)	1166(5)	1156(62)	4838(289)	1274(64)	-489(115)	607(54)	106(121)
C(23)	1729(5)	-2250(12)	922(4)	1456(69)	3771(229)	1145(56)	-307(111)	701(54)	67(102)

Table 9. Hydrogen atom fractional coordinates ($\times 10^3$), isotropic temperature factors ($\times 10^2$) and their standard deviations in parenthesis.

Atom	x	y	z	B
H(3)	526(4)	511(13)	179(4)	389(117)
H(4)	404(4)	517(11)	-28(3)	246 (92)
H(7)	304(5)	458(13)	-212(4)	449(131)
H(8)	153(6)	379(15)	-413(5)	588(168)
H(9)	54(5)	56(13)	-482(6)	562(158)
H(10)	62(5)	-244(15)	-331(5)	620(172)
H(11)	166(4)	-147(12)	-148(4)	345(115)
H(13)	670(4)	430 (9)	364(3)	197 (94)
H(14)	768(6)	382(17)	559(6)	707(188)
H(15)	732(4)	12(13)	647(4)	395(119)
H(16)	585(6)	-267(15)	524(5)	635(175)
H(17)	491(5)	-191(13)	324(4)	449(132)
H(19)	273(6)	283(17)	208(6)	704(185)
H(20)	87(4)	254(10)	248(4)	277(105)
H(21)	-28(5)	-109(14)	188(5)	515(152)
H(22)	49(8)	-433(19)	105(8)	918(238)
H(23)	206(6)	-370(18)	60(6)	709(186)

Table 10. Bond distances (Å) and angles (deg) with their standard deviations in parenthesis.

P-C(2)	1.610(5)	C(2)-C(3)	1.354(8)	C(7)-H(7)	1.045(73)
P-C(5)	1.806(5)	C(3)-C(4)	1.439(7)	C(8)-H(8)	0.876(76)
P-C(18)	1.832(4)	C(4)-C(5)	1.356(8)	C(9)-H(9)	1.068(69)
C(6)-C(7)	1.390(7)	C(12)-C(13)	1.414(8)	C(10)-H(10)	1.164(87)
C(7)-C(8)	1.386(8)	C(13)-C(14)	1.382(8)	C(11)-H(11)	0.928(64)
C(8)-C(9)	1.380(10)	C(14)-C(15)	1.367(10)	C(13)-H(13)	1.047(49)
C(9)-C(10)	1.367(9)	C(15)-C(16)	1.404(10)	C(14)-H(14)	1.086(91)
C(10)-C(11)	1.395(7)	C(16)-C(17)	1.397(8)	C(15)-H(15)	1.020(52)
C(11)-C(6)	1.415(8)	C(17)-C(12)	1.385(9)	C(16)-H(16)	1.119(84)
C(16)-C(19)	1.372(7)	C(2)-C(12)	1.459(7)	C(17)-H(17)	0.979(73)
C(19)-C(20)	1.386(7)	C(5)-C(6)	1.464(6)	C(19)-H(19)	1.080(91)
C(20)-C(21)	1.368(10)	C(3)-H(3)	0.929(72)	C(20)-H(20)	1.082(56)
C(21)-C(22)	1.390(9)	C(4)-H(4)	0.951(60)	C(21)-H(21)	0.990(61)
C(22)-C(23)	1.384(8)			C(22)-H(22)	1.119(110)
C(23)-C(18)	1.402(9)			C(23)-H(23)	1.101(94)
C(5)-P-C(2)	92.1(2)	P-C(2)-C(3)	108.1(3)	C(4)-C(5)-C(6)	124.6(4)
C(5)-P-C(18)	105.4(2)	C(2)-C(3)-C(4)	115.3(5)	P-C(5)-C(6)	126.1(4)
C(2)-P-C(18)	104.3(2)	C(3)-C(4)-C(5)	115.6(5)	C(3)-C(2)-C(12)	126.6(4)
		C(4)-C(5)-P	108.0(4)	P-C(2)-C(12)	124.7(4)
C(18)-C(19)-C(20)	120.5(5)	C(11)-C(6)-C(7)	116.9(5)	C(17)-C(12)-C(13)	117.8(4)
C(19)-C(20)-C(21)	119.8(6)	C(6)-C(7)-C(8)	121.6(6)	C(12)-C(13)-C(14)	120.3(6)
C(20)-C(21)-C(22)	120.9(4)	C(7)-C(8)-C(9)	120.5(6)	C(13)-C(14)-C(15)	121.5(6)
C(21)-C(22)-C(23)	118.9(6)	C(8)-C(9)-C(10)	119.3(5)	C(14)-C(15)-C(16)	119.1(5)
C(22)-C(23)-C(18)	120.2(6)	C(9)-C(10)-C(11)	120.8(6)	C(15)-C(16)-C(17)	119.5(6)
C(23)-C(18)-C(19)	119.3(4)	C(10)-C(11)-C(6)	120.5(5)	C(16)-C(17)-C(12)	121.4(5)
C(5)-C(6)-C(7)	122.5(5)	C(5)-C(6)-C(11)	120.5(4)	C(2)-C(3)-H(3)	123.1(3.5)
C(2)-C(12)-C(13)	119.8(5)	C(2)-C(12)-C(17)	122.3(5)	C(4)-C(3)-H(3)	120.8(3.6)
P-C(18)-C(19)	121.8(5)	P-C(18)-C(23)	118.8(5)	C(3)-C(4)-H(4)	120.2(2.9)
				C(5)-C(4)-H(4)	124.1(2.9)
C(6)-C(7)-H(7)	117.3(3.4)	C(12)-C(13)-H(13)	123.7(2.4)	C(18)-C(19)-H(19)	115.4(4.2)
C(8)-C(7)-H(7)	120.2(3.2)	C(14)-C(13)-H(13)	113.8(2.4)	C(20)-C(19)-H(19)	123.3(4.2)
C(7)-C(8)-H(8)	126.3(5.1)	C(13)-C(14)-H(14)	113.1(4.4)	C(19)-C(20)-H(20)	119.4(3.6)
C(9)-C(8)-H(8)	113.0(5.0)	C(15)-C(14)-H(14)	125.2(4.4)	C(21)-C(20)-H(20)	120.6(3.0)
C(8)-C(9)-H(9)	117.1(4.1)	C(14)-C(15)-H(15)	125.0(4.1)	C(20)-C(21)-H(21)	125.9(4.6)
C(10)-C(9)-H(9)	122.9(4.3)	C(16)-C(15)-H(15)	115.7(4.1)	C(22)-C(21)-H(21)	113.0(4.6)
C(9)-C(10)-H(10)	123.1(3.2)	C(15)-C(16)-H(16)	121.7(3.6)	C(21)-C(22)-H(22)	132.3(4.9)
C(11)-C(10)-H(10)	115.1(3.2)	C(17)-C(16)-H(16)	118.6(3.6)	C(23)-C(22)-H(22)	106.2(4.8)
C(10)-C(11)-H(11)	106.5(3.3)	C(16)-C(17)-H(17)	112.6(3.6)	C(22)-C(23)-H(23)	119.7(4.3)
C(6)-C(11)-H(11)	132.7(3.3)	C(12)-C(17)-H(17)	123.9(3.6)	C(18)-C(23)-H(23)	119.4(4.2)

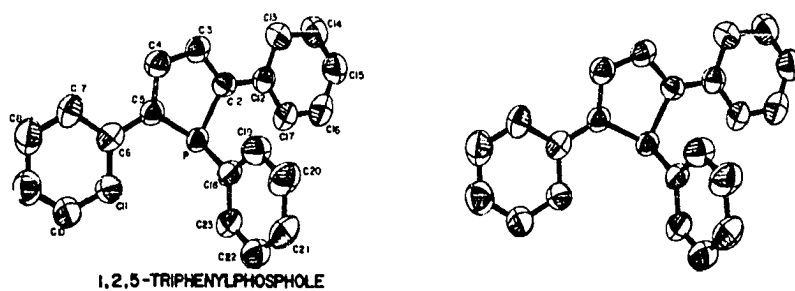


Figure 3. Stereoscopic view of 1,2,5-triphenylphosphole with 50% probability vibrational ellipsoids.

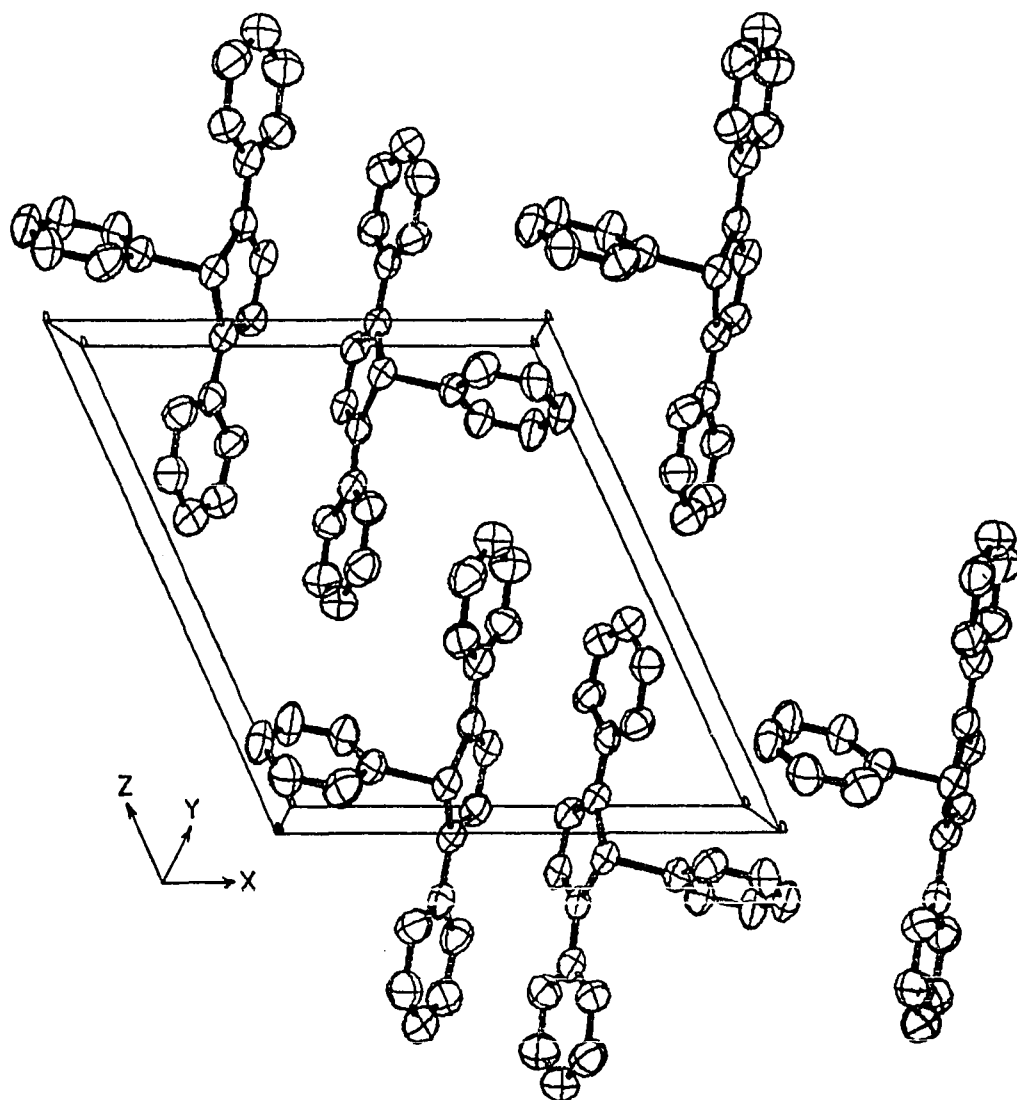


Figure 4. Illustration of molecular packing for 1,2,5-triphenylphosphole.

The phosphorus-carbon bond distances in the heterocyclic ring, 1.810 and 1.806Å, are significantly longer than those reported for: (a) 1,1-dimethyl-2,4,6-triphenylphosphorin (1.749Å) (31); (b) 2,6-dimethyl-4-phenylphosphorin (1.743Å) (32); (c) 1-benzylphosphole (1.783Å) (24). They do however compare favorably with the values reported for the phosphorus-carbon(Me) bonds of Me₃PO (1.813Å) (33) and 1,1-dimethyl-2,4,6-triphenylphosphorin (1.806Å) (32). The phosphorus-phenyl bond distance of 1.832Å agrees well with the value (1.828Å) found in triphenylphosphorin (34). Also the phosphole ring angles are very similar to those reported for 1-benzylphosphole (24).

The carbon-carbon bonds between the phosphole ring and the phenyl groups have an average length of 1.462Å, close to the value (1.488Å) found in 1,1-dimethyl-2,4,6-triphenylphosphorin (31). The C(3)-C(2)-C(12)-C(13) and C(4)-C(5)-C(6)-C(7) dihedral angles are -0.88 and 0.30° respectively. However the least-squares plane determined by C(2) through C(17) indicates that the phenyl groups are bent slightly out of the plane of the four carbon atoms of the phosphole ring. In Figure 3 the C(6) and C(12) phenyl groups are bent out towards the C(18) phenyl group and the phosphorus is bent back into the plane of the paper.

The plane bisecting the C(2)-P-C(5) angle contains C(18); however, this phenyl ring is twisted about the P-C(18) bond

and the C(2)-P-C(18)-C(19) dihedral angle is -26.37° . The direction of the twist is such that C(19) moves closer to C(17) and C(23) moves closer to C(11) to give intramolecular contacts of 3.79 and 3.78\AA respectively. Other intramolecular contacts of interest are: P-C(11), 3.27; P-C(17), 3.25; C(2)-C(18), 2.87; C(5)-C(18), 2.89; C(4)-C(7), 2.98; C(3)-C(13), 2.97; H(4)-H(7), 2.13; and H(3)-H(13), 2.27\AA .

The three phenyl groups, which are planar within the limits of error of this analysis, have average ring bond lengths and angles of 1.388\AA and 119.9° respectively.

The molecules pack together in a herring-bond fashion as illustrated in Figure 4. Looking down \underline{c}^* , P through C(17) and their symmetry related atoms give one herring-bond effect and looking down \underline{a} , C(18) through C(23) and their symmetry related atoms give another.

The van der Waals contacts of less than 4\AA show no unusual features, the shortest in each category being: C \cdots C, 3.73; C \cdots H, 2.84; H \cdots H, 2.46; P \cdots C, 3.76; and P \cdots H, 3.31\AA .

Although the steric effects of the bulky phenyl substituents on such ring systems are not clearly understood, it is evident that:

1. The carbon-carbon bond lengths in the heterocyclic ring are typical for butadiene (35) and therefore are not indicative of any ring delocalization effect.

2. The phosphorus-carbon bond lengths in the ring are suggestive of little if any π -character.

3. The phosphorus appears to be tetrahedrally coordinated, consequently decreasing the likelihood of delocalization of the lone pair of electrons throughout the ring. Hence it is concluded that electron delocalization plays no important role in the ground state molecular structure of 1,2,5-triphenylphosphole.

THE CRYSTAL STRUCTURE OF 1,2,5-TRIPHENYLPYRROLE

Introduction

During the determination of the molecular structure of 1,2,5-triphenylphosphole (36) it was recognized that the molecular geometry and apparent hybridization of the phosphorus atom could be an artifact of the steric crowding of the three bulky phenyl substituents. Consequently we decided to determine the crystal and molecular structure of 1,2,5-triphenylpyrrole.

Earlier research on pyrrole and its derivatives has been concerned mainly with the synthesis and reactions of these compounds (37,38). Mainly as a result of the instability or nonavailability of many pyrrole compounds the discussion of their physicochemical properties had been avoided and only as recently as the mid-1960's has any attempt been made to redress this neglect (39). Also recent improvements in synthetic and instrumental methods have enabled more accurate studies to be done and considerable spectral data exists in the literature for pyrrole and its derivatives.

Although the Raman and IR spectra (40) in the liquid phase of pyrrole favored the planar structure of C_{2v} symmetry, the nonplanar C_s structure was not rigorously excluded.

While the nonplanar pyrrole structures were thought to be excluded by microwave spectroscopy (41), there has been recent speculation (42) that a rapidly inverting nitrogen might equally well fit these spectral results.

As single-crystal X-ray studies of the pyrrole system have not been done other than in fused or porphyrin systems ample reasons exist for further investigations by X-ray diffraction techniques of the pyrrole system in the solid state.

Experimental

A sample of the compound was kindly supplied by Dr. T. J. Barton of this laboratory. Microscopic examination revealed that the crystals were needle shaped with sharply defined faces. As there was no observable decomposition in the atmosphere a crystal was mounted on a glass fiber and preliminary Weissenberg and precession photographs exhibited $2/m$ Laue symmetry indicating a monoclinic space group.

The only observed systematic absences were for hkl when $h+k = 2n+1$, which is consistent with space groups $C2$, Cm or $C2/m$. The unit cell parameters at room temperature are $a = 11.272(3)$, $b = 11.807(3)$, $c = 5.956(6)\text{\AA}$ and $\beta = 92.68(8)^\circ$. These parameters and their standard deviations were obtained via a least-squares fit to 12 independent reflection angles whose centers were determined by right-left, top-bottom beam

splitting on a previously aligned Hilger-Watts four-circle diffractometer (Cu K_{α} radiation, $\lambda = 1.5418\text{\AA}$). Any error in the instrumental zero was eliminated by centering the reflection at both plus two-theta and minus two-theta. For 2 molecules per unit cell the calculated density is 1.24gm/cc.

For data collection, a crystal having approximate dimensions 0.16 x 0.16 x 0.18mm along the a, b and c crystal axes respectively was mounted such that the b axis was coincident with the spindle axis.

All data in the hkl and $\bar{h}kl$ octants were collected within a theta sphere of 55° using a stationary-crystal, stationary-counter technique with Ni-filtered Cu K_{α} radiation, $\lambda = 1.5418\text{\AA}$. Intensities were measured by counting at the peak center $\theta(\underline{h}, \underline{k}, \underline{l})$ for ten seconds and subtracting two five-second background counts measured at $\theta(\underline{h}, \underline{k}, \underline{l}) \pm [0.25 + (0.01 \times \theta(\underline{h}, \underline{k}, \underline{l}))]$. A total of 531 reflections were measured in this manner. As a general check on crystal and electronic stability, the intensities of three reflections were periodically monitored; no appreciable decomposition was detected. Also 98 integrated intensities of previously measured reflections covering a range of values were obtained via the step-scan method (moving-crystal, moving-counter technique), for later use in a peak-height to integrated data conversion (28).

The intensity data were initially corrected for Lorentz and polarization factors. Since the absorption coefficient is only 5.56cm^{-1} for Cu K_{α} radiation, no correction for this effect was deemed necessary. Twelve reflections were found to have net intensities less than three times the square-root of the background and were judged to be unobserved and omitted from the refinement. The estimated error in each intensity measurement was calculated by:

$$\sigma(I) = \sqrt{C_T + C_B + (K_T C_T)^2 + (K_B C_B)^2}$$

where C_T and C_B are the total and background counts respectively. In this formula, K_T and K_B are the relative random errors in the total and background intensities and are given values of 3 and 5% respectively. The finite difference method was used to derive the formula for the estimated standard error for each reflection:

$$\sigma(F) = (LP)^{-1/2} [(I + \sigma(I))^{1/2} - I^{1/2}]$$

where I is the calculated intensity and LP is the Lorentz-polarization correction. These standard errors were used during refinement to weight the 519 observed structure factors, where $\omega = 1/\sigma(F)^2$.

Solution and Refinement

An unsharpened Patterson function was calculated using all observed reflections. The nitrogen and two carbons lying

on the crystallographic two-fold axis were readily found and placed such that the nitrogen was at the origin of the unit cell. The two carbons belong to the phenyl group attached to the nitrogen. This arrangement of atoms indicated space group C2 which was later confirmed by successful refinement. Three-dimensional electron density synthesis revealed the remaining non-hydrogen atoms and full-matrix least-squares refinement with anisotropic temperature factors for all atoms, using the scattering factors of Hanson et al. (14) converged rapidly to a conventional R-factor of 0.091 and a weighted R-Factor of 0.127. Hydrogen atom positions were obtained from a difference map and subsequent isotropic refinement of these atoms lead to a significant (29) decrease in the weighted and unweighted R-factors to 0.084 and 0.062 respectively. A final difference electron density map showed no peaks larger than $0.3 \text{ electrons}/\text{\AA}^3$, indicating that all the atoms had been accounted for. Observed and calculated structure factors ($\times 10$) for the final cycle of refinement are given in Table 11.

Discussion

The final positional and anisotropic temperature factors of the non-hydrogen atoms are given in Table 12, along with their standard deviations. Table 13 contains the fractional coordinates and isotropic temperature factors of the hydrogen

Table 12. Heavy atom fractional coordinates ($\times 10^4$), anisotropic temperature factors ($\times 10^5$) and their standard deviations in parenthesis. Values not followed by a standard deviation are fixed by symmetry. The form of the anisotropic temperature factor is

$$\exp [-(\beta_{11}\underline{h}^2 + \beta_{22}\underline{k}^2 + \beta_{33}\underline{l}^2 + 2\beta_{12}\underline{hk} + 2\beta_{13}\underline{hl} + 2\beta_{23}\underline{kl})].$$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N	C	O	O	1119 (62)	545 (43)	3948 (219)	C	-43 (98)	C
C(2)	702(5)	-672 (6)	-1271 (8)	1149 (60)	669(50)	3852(173)	-78(38)	-19C (8C)	-33 (76)
C(3)	442(4)	-1775 (7)	-787(10)	1156 (58)	892(58)	4296(204)	45(43)	-23 (78)	-2C3 (9C)
C(6)	-1599(4)	-261 (6)	2785 (9)	859 (47)	730(43)	4481(212)	-81(38)	-142 (74)	-79 (82)
C(7)	-1742(5)	-813 (8)	4801(10)	1068 (62)	960(53)	4075(192)	-170(45)	-34 (89)	233 (93)
C(8)	-2602(6)	-51C (7)	6256(11)	1232 (65)	1220(71)	4282(209)	-230(56)	95 (9C)	38(104)
C(9)	-3358(6)	392 (7)	5702(12)	1187 (67)	1082(67)	5097(263)	-4(51)	322(106)	-341(110)
C(10)	-3224(6)	972 (8)	3722(11)	121C (61)	941(54)	5453(248)	77(52)	207 (99)	-196(105)
C(11)	-2365(5)	654 (7)	2265(10)	114C (54)	942(59)	4399(202)	58(46)	103 (84)	-24 (97)
C(18)	C	1206 (9)	O	1121 (75)	813(67)	3291(255)	C	117(111)	C
C(19)	-439(4)	1787 (7)	-19C1 (9)	1074 (5C)	1C03(6C)	3774(260)	-43(44)	-209 (79)	113 (86)
C(2C)	-43C(5)	2959 (7)	-1884(11)	14C7 (65)	811(57)	4695(234)	68(50)	129(102)	338 (99)
C(21)	O	3544(1C)	C	1411(106)	897(86)	5026(366)	O	522(15C)	C

Table 13. Hydrogen atom fractional coordinates ($\times 10^3$), isotropic temperature factors ($\times 10^2$) and their standard deviations in parenthesis.

Atom	x	y	z	B
H(3)	81(4)	-241 (4)	-159 (7)	119 (94)
H(7)	-128(9)	-139 (9)	520(17)	776(281)
H(8)	-277(5)	-96 (5)	775(10)	320(130)
H(9)	-388(6)	65 (8)	688(12)	594(182)
H(10)	-380(6)	158 (5)	328(11)	415(150)
H(11)	-219(5)	106 (6)	66 (9)	391(131)
H(19)	-56(7)	119 (8)	-342(13)	536(172)
H(20)	-71(6)	330 (8)	-330(14)	527(177)
H(21)	0	435(17)	0	984(474)

atoms, which are numbered similarly to the carbon atoms to which they are attached. Bond distances and angles with standard deviations are summarized in Table 14. Figure 5 shows a stereoscopic view of the molecule and indicates the labeling of the atoms.

The analysis shows that in the solid state the 1,2,5-triphenylpyrrole molecule possesses a two fold symmetry axis which runs through N, C(18), C(21) and bisects the C(3)-C(4) bond. Thus the heterocyclic ring and the N(C₃) grouping are both required by symmetry to be planar.

As the distances (1.368 \AA) between carbon atoms 2 and 3, and 4 and 5 are greater than that between carbon atoms of ethylene (1.332 \AA) (43), as the distance between carbon atoms 3 and 4 (1.400 \AA) is less than that for carbon atoms in ethane (1.536 \AA) (44) and approaches the carbon-carbon distances in benzene (1.392 \AA) (45) and as the carbon-nitrogen distance of the heterocyclic ring (1.374 \AA) is less than those in trimethylamine (1.472 \AA) (46), the heterocyclic ring can not be adequately represented by a classical structure and must be treated as a resonance hybrid. The bond distances and angles reported here for the pyrrole ring are in good agreement with those determined by microwave spectroscopy (41).

The nitrogen-carbon 18 bond distance (1.424 \AA) is somewhat shorter than that taken as the pure nitrogen-carbon single bond (1.472 \AA) (47), but is in agreement with other

Table 14. Bond distances (\AA) and angles (deg) with their standard deviations in parenthesis.

N-C(2)	1.374(6)	C(2)-C(3)	1.368(8)	C(5)-C(6)	1.468(7)
N-C(18)	1.424(10)	C(3)-C(4)	1.400(12)		
C(6)-C(7)	1.382(8)	C(9)-C(10)	1.378(10)	C(18)-C(19)	1.395(6)
C(7)-C(8)	1.377(10)	C(10)-C(11)	1.381(8)	C(19)-C(20)	1.383(9)
C(8)-C(9)	1.394(10)	C(11)-C(6)	1.409(8)	C(20)-C(21)	1.386(8)
C(3)-H(3)	0.994(53)	C(9)-H(9)	0.993(82)	C(19)-H(19)	1.146(89)
C(7)-H(7)	0.886(110)	C(10)-H(10)	1.001(74)	C(20)-H(20)	0.981(95)
C(8)-H(8)	1.073(64)	C(11)-H(11)	1.094(62)	C(21)-H(21)	0.960(199)
C(2)-N-C(5)	109.3(5)	N-C(2)-C(3)	107.4(4)	C(4)-C(5)-C(6)	127.1(5)
C(2)-N-C(18)	125.3(2)	C(2)-C(3)-C(4)	107.9(3)	N-C(5)-C(6)	125.3(4)
C(5)-C(6)-C(7)	119.2(5)	C(6)-C(7)-C(8)	122.5(6)	C(9)-C(10)-C(11)	120.7(6)
C(5)-C(6)-C(11)	123.4(4)	C(7)-C(8)-C(9)	119.3(7)	C(10)-C(11)-C(6)	120.6(5)
N-C(18)-C(19)	119.4(5)	C(8)-C(9)-C(10)	119.4(7)	C(11)-C(6)-C(7)	117.2(5)
C(18)-C(19)-C(20)	118.9(6)	C(20)-C(21)-C(22)	120.2(8)	C(2)-C(3)-H(3)	121.3(2.7)
C(19)-C(20)-C(21)	120.4(6)	C(23)-C(18)-C(19)	121.0(7)	C(4)-C(3)-H(3)	130.5(2.7)
C(6)-C(7)-H(7)	120.7(6.6)	C(10)-C(9)-H(9)	122.7(5.0)	C(18)-C(19)-H(19)	111.6(4.4)
C(8)-C(7)-H(7)	116.6(6.6)	C(9)-C(10)-H(10)	118.9(3.8)	C(20)-C(19)-H(19)	127.9(4.4)
C(7)-C(8)-H(8)	123.8(3.2)	C(11)-C(10)-H(10)	120.0(3.9)	C(19)-C(20)-H(20)	114.2(5.5)
C(9)-C(8)-H(8)	116.5(3.2)	C(10)-C(11)-H(11)	125.7(3.8)	C(21)-C(20)-H(20)	125.3(5.5)
C(8)-C(9)-H(9)	117.1(4.8)	C(6)-C(11)-H(11)	113.5(3.8)	C(20)-C(21)-H(21)	119.8(5.4)

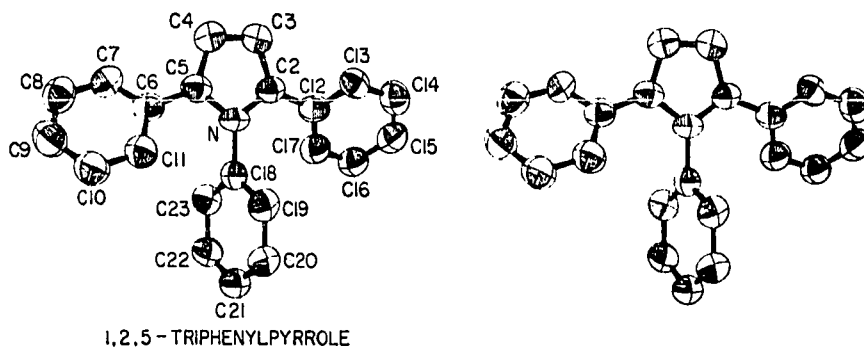


Figure 5. Stereoscopic view of 1,2,5-triphenylpyrrole with 50% probability ellipsoids.

carbon-nitrogen bonds adjacent to benzene rings (48). The distance (1.468 $\overset{\circ}{\text{Å}}$) between carbon atoms 5 and 6 agrees quite well with the average distances (1.462 $\overset{\circ}{\text{Å}}$) reported for the heterocyclic carbon to phenyl carbon atoms of 1,2,5-triphenylphosphole (36). Also the C(5)-C(6) distance is similar to those found in 1,1-dimethyl-2,5-diphenylsilole (49) and 2,5-diphenylselenophene (49), 1.490 $\overset{\circ}{\text{Å}}$ and 1.485 $\overset{\circ}{\text{Å}}$ respectively.

The phenyl groups, which are planar within the limits of error of this analysis, have average bond distances and angles of 1.387 $\overset{\circ}{\text{Å}}$ and 120.0 $^{\circ}$ respectively. Relevant dihedral angles are 40.7 $^{\circ}$ for C(4)-C(5)-C(6)-C(7) and 68.9 $^{\circ}$ for C(2)-N-C(18)-C(19).

The equation of the least-squares plane of the five atoms N, C(2), C(3), C(18) and C(21) is

$$0.6755 X - 0.0007 Y + 0.7373 Z = 0.0017\overset{\circ}{\text{Å}}$$

where the coefficients are direction cosines relative to \underline{a} , \underline{b} and \underline{c}^* . These five atoms are relatively planar with root-mean-square deviation of 0.0018 $\overset{\circ}{\text{Å}}$. However the C(6) and C(9) deviations from this plane are -0.0482 and -0.1608 $\overset{\circ}{\text{Å}}$ respectively, which indicates the carbon six phenyl group is bent back into the plane of Figure 5. The rotation of the phenyl rings and puckering of the C(6) phenyl group gives rise to intramolecular close contacts of: N-C(6), 2.52; N-C(11), 3.14; C(2)-C(18), 2.48; C(11)-C(18), 3.11;

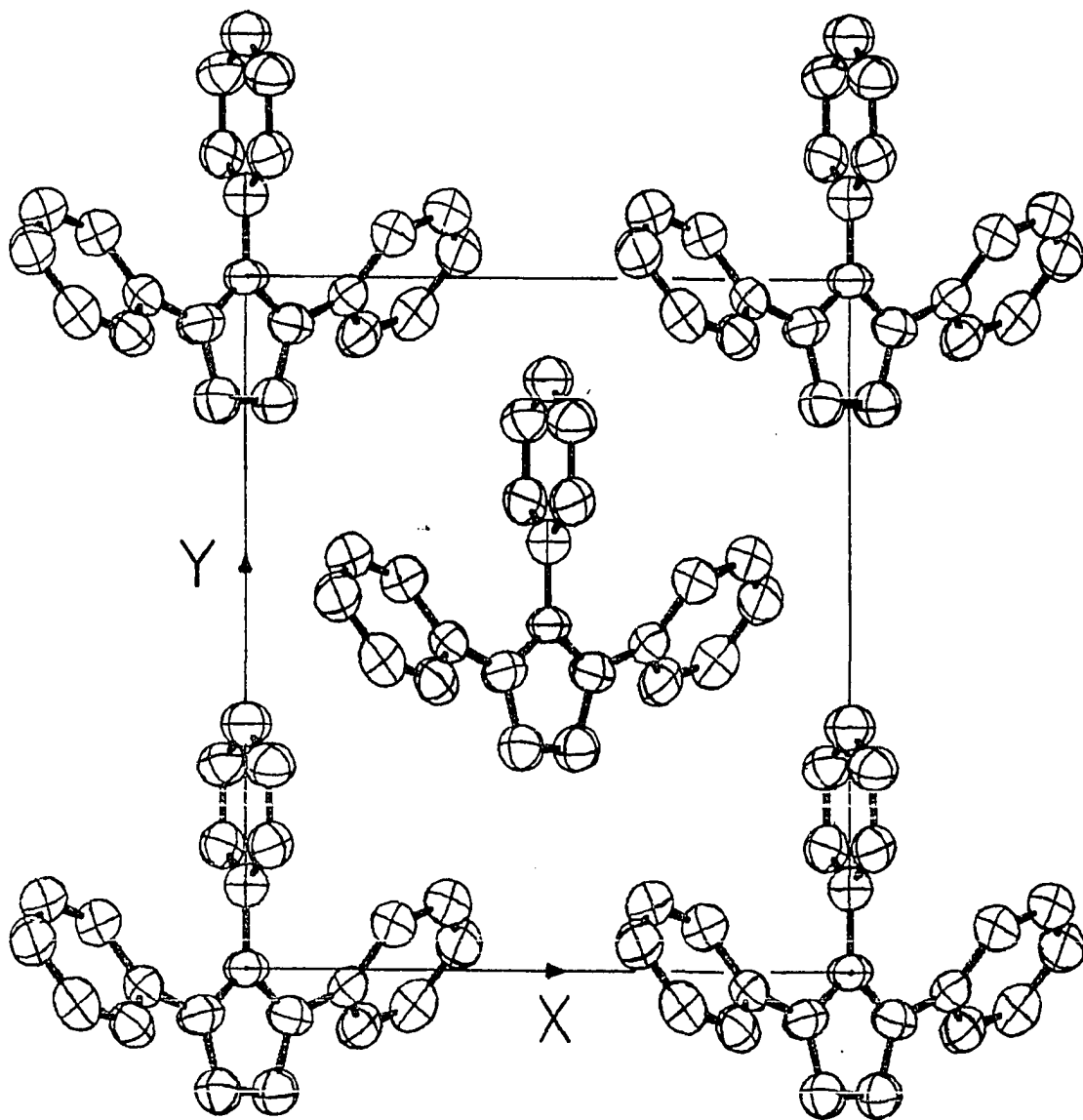


Figure 6. Illustration of molecular packing for 1,2,5-triphenylpyrrole.

C(6)-C(18), 3.04; C(18)-H(11), 2.52; and H(4)-H(7), 2.54Å.

Molecular packing is illustrated in Figure 6 and the van der Waals contacts of less than 4Å show no unusual features, the shortest in each category being: C···C, 3.59; C···H, 2.88; H···H, 2.70; N···C, 3.65; and N···H, 3.53Å.

This analysis confirms the conclusion given in the phosphole studies (36) and demonstrates that the speculation about the non-planarity of nitrogen in pyrrole (42) is without experimental foundation.

PHASE DETERMINATION

Introduction

It is well known that the electron density of a crystal can be obtained by a Fourier synthesis, and that the coefficients for the Fourier summations are the structure factors of the various diffraction spectra. In general each structure factor is a complex quantity composed of a magnitude, which is readily derived from the intensity, and a phase. Unfortunately the intensities are all the data that are normally afforded by the diffraction experiment. Hence it appears that crystal structures are indeterminate due to a lack of phase information. However it can be argued that if the structure can be deduced from the Patterson (50), which is the Fourier transform of the intensities, then it should be obtainable directly from the intensities themselves. It is this approach, that of generating a set of phases using a purely mathematical method and only the magnitudes of the structure factors, that is commonly referred to as "direct methods."

The crystallographer has at his disposal today a large number of computerized interpretative techniques of the so-called "direct methods". Most of these are based on the same fundamental principles (51, 52) but differ in the manner of

handling the data and extracting the phases. In general the phases of only a relatively few properly chosen reflections are required to be known in order to proceed with the phase determination. In some cases expanding the starting set of phases beyond those required for specifying the origin (53, 54) leads to the wrong physical solution or no solution at all. Hence in order to develop a new method of expanding the starting set of phases and possibly deduce a new "direct methods" technique, it was decided to investigate the integral of the absolute value of the electron density function, ρ , to test phases. The discussion of this method will be limited, only by application, to centrosymmetric space groups, that is those in which the phasing consists of assigning a plus or minus sign to each observed structure factor.

Description of the Method

This method is based on the following arguments and assumptions:

1. The electron density at any point in a crystal may be zero or positive but never negative.
2. The electron density function can be rather accurately represented by a partial set of signed structure factors. In this instance "partial set" refers to all the data normally afforded by the X-ray experiment.

3. It can be shown from fundamental definitions that the integral of the electron density function, $\rho(\vec{r})$, over the entire volume of the unit cell is equal to $F(000)$, which is the number of electrons in the unit cell. Furthermore this is true regardless of the signs selected or the number of structure factors used to calculate the electron density map.

4. In view of statements 1 and 2, replacing the integrand, $\rho(\vec{r})$, by its absolute value, $|\rho(\vec{r})|$, will not change the results for a correct physical solution. However considering the pseudo electron density function, $\rho'(\vec{r})$, (which is the result of a Fourier series expansion containing some incorrectly signed structure factors) the results are somewhat altered. The integral of $\rho'(\vec{r})$ over the entire volume of the unit cell is again equal to $F(000)$ as this integral is insensitive to the signs of the structure factors (except $F(000)$ which is defined to be positive). However if $\rho'(\vec{r})$ is replaced with its absolute value, $|\rho'(\vec{r})|$, the results of the integration will in general be larger than $F(000)$ since the pseudo electron density function is not restricted to zero or positive values.

5. It can be shown that for a small number of structure factors $\rho(\vec{r})$ cannot be accurately represented and the integral of $|\rho(\vec{r})|$ will also be greater than $F(000)$. However the initial impetus for this method was the assumption that for a small number of correctly signed structure factors the

value of the integral of the absolute value of the electron density function, $|\rho(\vec{r})|$, over the entire volume of the unit cell would be less than the value obtained if $\rho(\vec{r})$ is replaced by $\rho'(\vec{r})$. Furthermore it is assumed that to a good approximation the value of these integrals can be obtained by numerical integration, providing a sufficiently small grid is chosen.

Application of the Method

First attempts to apply the method were on the previously completed structures of hydrogen fluoride (55) and pentaamminecobalt(III) chloride (56). In both cases the calculated structure factors were used as Fourier coefficients. Signs were determined for enough of the structure factors to give complete physical solutions in both cases.

Since the method did show promise the next structure solution undertaken was for β -picoline-N-oxide fumaric acid adduct (57). The adduct, $C_{16}H_{18}N_2O_6$, is monoclinic, space group $P2_1/c$, with one molecule per asymmetric unit and its solution is considered a moderately difficult task for this method. In this case it was decided to normalize the structure factors (58) and use these E's as Fourier coefficients. This substitution does not alter the arguments or assumptions made for this method; however, the normalization procedure does remove the $\sin\theta/\lambda$ dependence of the structure factors.

The adduct structure solution is divided into six major steps which may be used as a guide for those who wish to make further application of this method.

1. The signs of three reflections with large E values were assigned as plus in order to specify the origin. The reflections chosen in this instance are $E(1,0,2)$, $E(-1,2,7)$ and $E(-2,11,5)$ which have corresponding magnitudes of 4.16, 2.08 and 3.31.

2. Four reflections with large E values are selected and the results of the summation of the absolute value of the electron density function for the 16 combinations of signs are calculated. It should be noted that in this step it is possible to get the same lowest value of the summation for more than one sign combination as it can be shown that the smaller the number of input reflections the smaller the number of sign interactions. In the adduct case four reflections were found that gave only two sign combinations with the same low value for the summation, Table 15. However there were other sets of four reflections that gave as many as four sign combinations with the same lowest value. It was decided to use the set of four reflections with only two possible sign combinations, one of which was correct, set 1 of Table 15, and the other contained two incorrect signs, set 10 of Table 15.

Table 15. Summation of the absolute value of the electron density function over the entire volume, SAR, for the sixteen sets of sign combinations generated by the four reflections ($A=(2,0,4)$, $B=(-1,10,6)$, $C=(-1,11,7)$ and $D=(-2,10,4)$), with $E(\underline{A})=3.10$, $E(\underline{B})=3.19$, $E(\underline{C})=3.15$ and $E(\underline{D})=3.26$. The three origin determining reflections and $E(000)$ are also input for the calculation of this table.

No.	A B C D	SAR
1	+ + + +	12.60
2	- - - -	14.00
3	- + + +	13.10
4	+ - - -	13.86
5	- - + +	13.95
6	+ + - -	14.57
7	- - - +	14.24
8	+ + + -	13.75
9	- + - +	13.99
10	+ - + -	12.60
11	- + - -	14.24
12	+ - + +	13.75
13	- + + -	13.95
14	+ - - +	14.56
15	- - + -	13.10
16	+ + - +	13.86

3. Attempts were then made to add two reflections at a time to both sets of sign combinations. Four more reflections were signed in this manner to give a total of eleven reflections for both starting sets, see Table 16. It should be noted that this step could be eliminated and step 4 initiated immediately. Hereafter the sets of reflections containing the signs determined in this and the previous step will be referred to as CS and IS, acronyms for correct set and incorrect set.

4. Next one reflection at a time was added to both CS and IS, first with a positive sign, then with a minus sign, and the summations of the $|\rho(\vec{r})|$ over the entire volume of the unit cell were calculated. If the difference between the two summations was greater than 1.5% the reflection was immediately added to the starting set with the indicated sign. The percent difference was always calculated by taking the absolute value of the difference between the two summations and dividing by the smallest summation. Table 17 contains the results of this step for both CS and IS and the reflections are arranged in the order that they were tested. After 38 tries 22 reflections had been added to both CS and IS to give a total of 33 reflections in each starting set. All 22 of the reflections added to the CS set of sign combinations had been assigned a correct sign. Of the 16 reflections that were not added to the CS set of sign

Table 16. Summation of the absolute value of the electron density function over the entire volume, SAR, for the four sets of sign combinations generated by the four reflections ($\underline{A}=(0,0,14)$, $\underline{B}=(-1,0,12)$, $\underline{C}=(1,8,2)$ and $\underline{D}=(2,1,1)$), when (a) \underline{A} and \underline{B} are added to set 1 of Table 15, (b) \underline{A} and \underline{B} are added to set 10 of Table 15, (c) \underline{C} and \underline{D} are added to set 1 of Table 15 and (d) \underline{C} and \underline{D} are added to set 10 of Table 15. The values of E are: $E(\underline{A})=4.29$, $E(\underline{B})=2.80$, $E(\underline{C})=2.57$ and $E(\underline{D})=2.51$.

No.	A B	SAR	No.	A B	SAR		
1	+	+	13.85	1	+	+	13.85
2	-	-	13.58	2	-	-	13.58
3	+	-	14.54	3	+	-	14.55
4	-	+	14.47	4	-	+	14.45
	(a)			(b)			

No.	C D	SAR	No.	C D	SAR		
1	+	+	15.13	1	+	+	14.98
2	-	-	15.02	2	-	-	15.09
3	+	-	14.89	3	+	-	15.12
4	-	+	15.10	4	-	+	15.04
	(c)			(d)			

Table 17. Reflection indices (h, k, l) and signed E observed values, SEO, listed in the order in which they were tested; (a) additions were made to the CS set of phase combinations and (b) additions were made to the IS set of phase combinations. SARP and SARM are the summations of the absolute value of the electron density function with the E value having a plus, P, or minus, M, sign. Percent differences between SARP and SARM are listed under %D.

h	k	l	SEO	SARP	SARM	%D	SARP	SARM	%D
-2	0	10	-2.41	15.41	15.11	2.0	15.45	15.07	2.5
-1	1	1	-2.35	15.73	15.25	3.1	15.28	15.68	2.6
0	12	0	-2.07	15.50	15.63	0.8	15.47	15.63	1.0
0	7	2	-2.00	15.74	15.76	0.1	15.70	15.74	0.3
0	1	3	-1.67	15.79	15.42	2.4	15.40	15.84	2.9
0	8	0	1.98	15.22	15.80	3.8	15.20	15.79	3.9
1	4	2	-1.70	15.52	15.63	0.7	15.52	15.63	0.7
1	5	0	1.67	15.59	15.56	0.2	15.54	15.59	0.3
-1	4	5	-1.60	15.49	15.52	0.2	15.48	15.51	0.2
-2	2	5	1.82	15.45	15.75	1.9	15.44	15.73	1.9
0	4	7	-1.99	15.64	15.64	0.0	15.62	15.60	0.1
-1	7	3	1.97	15.68	15.66	0.1	15.66	15.64	0.1
1	6	2	1.55	15.68	15.71	0.2	15.66	15.69	0.2
-1	3	7	1.51	15.64	15.76	0.8	15.63	15.74	0.7
0	7	5	1.86	15.81	15.81	0.0	15.81	15.75	0.4
1	7	0	1.83	15.78	15.81	0.2	15.74	15.85	0.7
0	11	9	3.03	15.65	17.10	9.3	15.68	17.08	8.9
0	12	4	-2.96	16.29	16.33	0.2	16.36	16.27	0.6
0	11	5	-2.82	16.73	16.16	3.5	16.81	16.16	4.0
0	10	8	2.73	15.52	17.01	9.6	17.02	15.53	9.6
-3	10	2	2.37	15.52	16.81	8.3	16.83	15.57	8.1
0	10	6	-2.24	16.31	15.97	2.1	16.01	16.36	2.2
-1	8	12	-2.84	17.47	17.09	2.2	17.45	17.05	2.3
1	10	8	-2.74	17.78	16.74	6.2	16.73	17.72	5.9
-1	11	3	-2.41	17.56	16.61	5.7	17.53	16.53	6.0
3	1	3	-2.55	17.62	16.68	5.6	16.66	17.60	5.6
0	7	12	-2.17	18.03	18.09	0.3	17.99	18.06	0.4
-1	10	7	2.39	18.17	18.17	0.0	18.16	18.10	0.3
1	11	7	-2.56	18.73	17.62	6.3	18.77	17.56	6.9
-2	8	10	-2.65	18.57	17.84	4.1	18.53	17.86	3.8
1	12	8	-1.98	18.39	18.20	1.0	18.18	18.41	1.3
-2	1	13	1.93	18.06	18.46	2.2	18.45	18.03	2.3
2	8	4	1.93	18.01	18.36	1.9	17.98	18.40	2.3
1	10	10	1.85	17.95	18.44	2.7	18.41	17.98	2.4
-2	11	1	-1.62	18.75	18.24	2.8	18.75	18.22	2.9
-1	10	4	-1.66	18.84	18.17	3.7	18.15	18.83	3.7
-3	9	5	-1.77	18.61	18.49	0.6	18.65	18.46	1.0
-3	0	8	-1.79	18.57	18.24	1.8	18.57	18.28	1.6

(a)

(b)

combinations, eight were calculated with wrong signs and three were not picked at all. Of the eight wrong choices the largest percent difference was 0.8% and the average was 0.3%.

5. The absolute value of the electron density function was calculated for both CS and IS which now contain the 33 previously signed reflections. The Fourier transform of this function was then calculated and in the beginning only the reflections that had an observed E, E_0 , greater than 1.5 and an E transform value, E_T , greater than 0.4 were added. As more reflections were signed these restrictions were gradually relaxed until E_T values of greater than 0.1 with corresponding E_0 values greater than or equal to 1.5 and E_T values of 0.3 with corresponding E_0 values greater than or equal to 1.0 were accepted. Also if a reflection was previously added and failed these tests in a subsequent step it was removed from the set of assigned signs.

6. When there were more input reflections failing the criteria of step 5 than there were new reflections being determined it was decided to accept all signs calculated by the Fourier transform procedure. Of the 534 observed reflections 270 had E_0 values greater than or equal to 1.0 which were signed and used to calculate a new absolute value of the electron density function and the Fourier transform was again calculated. This procedure was reiterated until there were only a relatively few sign changes.

Discussion

From the final electron density map using the 270 signed EO values as Fourier coefficients for the CS combination of signs the correct physical solution was obtained. Of the 270 EO values for the CS combination only 14 were assigned the wrong sign.

Although the EO map calculated for the IS combination of signs afforded some atomic positions, different from the CS positions, they could not be interpreted to make "chemical sense". Also it was observed during steps 5 and 6 for the IS data set many of the EO values that were previously signed were failing the criteria of step 5 and being removed or they were changing signs in step 6. In the final cycle of Step 6 there was one sign change for the CS combination and 25 sign changes for the IS combination. Perhaps this lack of convergence in determining signs and the number of sign changes is indicative of an incorrect starting set of signs. Also after the last cycle of Step 6 the summation of $|\rho(\vec{r})|$ for CS and IS is 34.06 and 36.90 respectively.

Although it has not rigorously been shown that for a correct sign choice or set of signs this method should give a lower value of the summation than that calculated for an incorrect set, it has indeed been found to be true for the three structures attempted by this author. However the

crucial test for this method will be the solution of a previously unsolved structure preferably in the triclinic crystal system.

LITERATURE CITED

1. L. Pauling, "The Nature of the Chemical Bond," 3rd. ed., Cornell University Press, Ithaca, New York, 1960, pp 333-339.
2. L. Jones, J. Chem. Phys., 26, 1578 (1957).
3. L. Jones, J. Chem. Phys., 27, 468 (1957).
4. K. Kuroda and P. S. Gentile, Inorg. Nucl. Chem. Letters, 3, 151 (1967).
5. N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. 1, Clarendon Press, Oxford, England, 1950, p 671.
6. N. A. Curry and W. A. Runciman, Acta Cryst., 12, 674 (1958).
7. A. Sequeria and R. Chidamboram, Acta Cryst., 20, 910 (1966).
8. R. C. Seccombe and C. H. Kennard, J. Organometal. Chem., 18, 243 (1969).
9. J. P. Birk and J. H. Espenson, J. Amer. Chem. Soc., 90, 1153 (1968).
10. H. Siebert, Z. Anorg. Allgem. Chem., 327, 63 (1964).
11. In addition to programs written in this laboratory for the IBM 360-65, other programs used in this work were Johnson's ORTEP to prepare drawings of molecules and unit cells, Busing and Levy's ORFFE to calculate errors, and Busing, Martin, and Levy's ORFLS, modified to allow mixing of isotropic and anisotropic temperature factors.
12. R. B. Dean and W. J. Dixon, Anal. Chem., 23, 636 (1951).
13. E. R. Howells, D. C. Phillips, and D. Rogers, Acta Cryst., 3, 210 (1950).
14. H. P. Hanson, F. Herman, J. D. Lee, and S. Skillman, Acta Cryst., 17, 1040 (1964).
15. N. A. Curry and W. A. Runciman, Acta Cryst., 12, 674 (1959).

16. Y. Tanito, Y. Saito, and H. Kuroya, Bull. Chem. Soc. Japan, 25, 188 (1952).
17. Y. Tanito, Y. Saito, and H. Kuroya, Bull. Chem. Soc. Japan, 26, 420 (1953).
18. F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, J. Amer. Chem. Soc., 82, 5099 (1960).
19. I.G.M. Campbell, R. C. Cookson, M. B. Hocking, and A. N. Hughes, J. Chem. Soc., 2184 (1965).
20. G. Markel and R. Potthast, Tetrahedron Letters, 1755 (1968).
21. L. D. Quin, J. G. Bryson, and C. G. Moreland, J. Amer. Chem. Soc., 91, 3308 (1969).
22. D. A. Brown, J. Chem. Soc., 929, (1962).
23. A. F. Bedford, D. M. Heinekey, I. T. Millar, and C. T. Mortimer, J. Chem. Soc., 2932 (1962).
24. P. Coggon, J. F. Engel, A. T. McPhail, and L. D. Quin, J. Amer. Chem. Soc., 92, 5779 (1970).
25. N. E. Waite and J. C. Tebby, J. Chem. Soc., C, 386 (1970).
26. T. J. Barton and A. J. Nelson, Tetrahedron Letters, 5037 (1969).
27. W. Egan, R. Tang, G. Zon, and K. Mislow, J. Amer. Chem. Soc., 92, 1442 (1970).
28. L. E. Alexander and G. S. Smith, Acta Cryst., 15, 983 (1962).
29. W. C. Hamilton, Acta Cryst., 18, 502 (1965).
30. K. Lonsdale, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1968, p 214, Table 3.3.2B.
31. J. J. Daly, J. Chem. Soc., A, 1832 (1970).
32. J.C.J. Bart and J. J. Daly, J. Chem. Soc., A, 567 (1970).
33. H. K. Wang, Acta Chem. Scand., 19, 879 (1965).

34. J. J. Daly, J. Chem. Soc., 3799 (1964).
35. M.J.S. Dewar and H. M. Schmeising, Tetrahedron, 5, 166 (1959).
36. W. P. Ozbirn, R. A. Jacobson, and J. C. Clardy, submitted for publication in J. Amer. Chem. Soc.
37. A. H. Corwin, in "Heterocyclic Compounds," Vol. 1, R. C. Elderfield, Ed., John Wiley and Sons, New York, N.Y., 1950, pp 277-342.
38. E. Baltazzi and L. I. Krimen, Chem. Rev., 63, 511 (1963).
39. K. Schofield, "Heteroaromatic Nitrogen Compounds: Pyrroles and Pyridines," Plenum Press, New York, N.Y., 1967.
40. R. A. Jones in "Advances in Heterocyclic Chemistry", Vol. 11, A. R. Katritzky and A. J. Boulton, Eds., Academic Press Inc., New York, N.Y., 1970, Sec. 111.B.1, pp 443-459.
41. L. Nygaard, J. T. Nielsen, J. Kirchheiner, G. Maltesen, J. Rastrup-Anderson, and G. O. Sorensen, J. Mol. Structure, 3, 491 (1969).
42. M.J.S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Inc., New York, N.Y., 1969, pp 409-410.
43. L. S. Bartell and R. S. Bonham, J. Chem. Phy., 31, 400 (1959).
44. H. C. Allen, Jr. and E. K. Plyler, J. Chem. Phy., 31, 1062 (1959).
45. E. G. Cox, D.W.J. Cruickshank, and J.A.S. Smith, Proc. Roy. Soc. (London), 247, 1 (1958).
46. D. R. Lide, Jr. and D. E. Mann, J. Chem. Phy., 28, 572 (1958).
47. L. Pauling, "The Nature of the Chemical Bond," 3rd. ed., Cornell University Press, Ithaca, New York, 1960, p 224.
48. C. J. Brown, Acta Cryst., 2, 228 (1949).
49. J. C. Clardy, Iowa State University, personal communication, 1969.

50. A. L. Patterson, Z. Krist., A, 90, 517 (1935).
51. A. I. Kitaigorodskii, "The Theory of Crystal Structure Analysis," Consultants Bureau, New York, N.Y., 1961.
52. M. M. Woolfson, "Direct Methods in Crystallography," Oxford University Press, New York, N.Y., 1961.
53. H. Hauptman and J. Karle, "Solution of the Phase Problem, I. The Centrosymmetric Crystal," A. C. A. Monograph No. 3, Polycrystal Book Service, Brooklyn, N.Y., 1953.
54. H. Hauptman and J. Karle, Acta Cryst., 12, 93 (1959).
55. A. Masao and W. N. Lipscomb, Acta Cryst., 7, 173 (1954).
56. W. Ozbirn and R. A. Jacobson, Inorg. Chim. Acta, 4, 377 (1970).
57. B. T. Gorres, Ph.D., Thesis, Princeton University, Princeton, New Jersey, 1964.
58. G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan Co., London, England, 1968, p 320.

ACKNOWLEDGEMENTS

I am grateful to the following:

Dr. R. A. Jacobson for his understanding of the art of crystallography and for his inspiration and advice throughout this work.

Dr. J. W. Patterson for many interesting discussions and assistance on many projects not related to this work.

Dr. J. C. Clardy for his knowledge of crystallography and many helpful discussions.

Dr. T. J. Barton for the preparation of the phosphole and pyrrole compounds.

Faculty and graduate students for their assistance and discussions, and a special acknowledgement to the members of X-ray Groups I and II.

J. R. Clark, J. E. Benson and H. F. Hollenbeck for their invaluable technical assistance.

Finally, I am indebted to my wife for the persistent aid and encouragement she has given me throughout my thesis work.