I. THE CRYSTAL STRUCTURE OF DIMETHYL PHOSPHINOBORINE TRIMER

II. THE METHOD OF LEAST SQUARES IN ELECTRON DIFFRACTION

III. SOME STRUCTURAL STUDIES BY THE ELECTRON DIFFRACTION BY GAS MOLECULES

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Walter Clark Hamilton

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ABSTRACT

I

The crystal structure of dimethyl phosphinoborine trimer, $[(CH_3)_2PBH_2]_3$, has been determined by analysis of its x-ray diffraction maxima. Use was made of a three-dimensional Patterson function, least squares on the structure factors, and a three-dimensional electron-density difference map. The space group is P_{nma}; the unit cell constants are a = 11.16 Å, b = 13.16 Å, and c = 10.53 Å. There are four molecules per unit cell. The molecule has a cyclohexane-like ring of alternating phosphorus and boron atoms, with two methyl groups attached to each phosphorus atom. It has a plane of symmetry, and the environment of each phosphorus atom is C_{2v}. The following average structural parameters were found:

P-B	1.934 Å
P-C	1.835
∡ P-B-P	112° 17'
∡ B-P-B	117° 58'
∡ B-P-C	109° 7'
∡ C-P-C	100° 26'

Some attention is given to the determination of temperature factors from the difference map and to fitting of atomic form factors by Gaussians. The R factor for the final structure is 0.169.

II

The advantages of the method of least squares, as contrasted to the usual correlation treatment, in electron diffraction investigations of molecular structure are outlined. Special attention is given to visual data and to the weighting of observations, including remarks on the use of a non-diagonal weight matrix and the derivation of weights from the goodness of fit, and to obtaining reliable estimates of error, and of error correlation, for the parameters.

III

The method of least squares has been applied to electron diffraction photographs of bicycloheptadiene, C_7H_8, and bicyclo-octane, C_8H_{14}. In the case of bicycloheptadiene, a simple valence-force potential function adequately explains the values found for the structural parameters. The structure of difluoromethane has been reinvestigated by electron diffraction.

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I. The Crystal Structure of Dimethyl Phosphino-borine Trimer

Dimethyl phosphino-borine trimer, $[(CH_3)_2PBH_2]_3$, prepared by the reaction of dimethyl phosphine with diborane and subsequent polymerization of the product, has been described by Burg as being perhaps the most stable of all B-H compounds. (1) It is extremely stable toward both hydrolysis and thermal decomposition. Burg has postulated that the structure is a hexatomic ring with six equivalent P-B bonds, and that the resistance toward hydrolysis is primarily due to the special nature of the bonding required to explain such a structure, rather than to steric hindrance by the methyl groups which may also play an important role.

It seemed of interest to attempt a complete crystal structure determination* of this unusual compound, both to test the hypothesized hexatomic ring structure and to determine interatomic distances and bond angles in the hope that these would help elucidate the nature of the bonding involved.

The crystal lattice is orthorhombic, and the preferred crystal form is needle-like, although on

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*Previous x-ray diffraction work by Burg and co-workers extended only to determination of the lattice type and the cell constants.

recrystallization from methanol it is possible to obtain almost square plates perpendicular to the needle axis, b. The crystals used in the preparation of the x-ray diffraction photographs were 0.2 - 0.3 mm. in maximum dimension with the exception of the needles, which were sometimes 1 mm. long. Because of the high sublimation pressure of the compound at room temperature, it was found necessary to mount the crystals in non-absorbing glass capillary tubes for all x-ray work.

From rotation and Weissenberg photographs about the a and b axes and precession photographs about all axes, using Cu K_α ($\lambda = 1.542$ Å) and Mo K_α ($\lambda = 0.711$ Å) radiation, the cell constants were found to be:

$a = 11.16 \pm 0.014$ Å

$b = 13.16 \pm 0.016$ Å

$c = 10.53 \pm 0.014$ Å

The unit cell volume is 1546.5 $Å^3$, while that calculated for four molecules per unit cell and the density, 0.96 g/cc (1), is 1533 $Å^3$.

The only systematic absences are

hk0 h odd

0kl k+l odd

indicating an (001) glide plane with component a/2 and a (100) glide plane with component b/2 + c/2.

The possible space groups are P_{nma} (D_{2h}^{16}) and, with a relabeling of axes, P_{na2_1} (C_{2v}^{9}). It was decided to attempt a differentiation between these on the basis of the N(z) test (2), i.e., on the distribution of intensities to be expected for the centrosymmetric as contrasted to the acentric space group.

After all data had been collected and corrected for Lorentz, polarization, and film factors, and correlated as is discussed in detail below, the reflections were divided into groups of about sixty reflections each at small intervals of $\sin^2\theta$*. The average intensity in each group of approximately constant $\sin^2\theta$ was calculated. For each reflection $z' = I/\bar{I}$ was calculated. A plot of N(z), the fraction of the total number of reflections having $z' \leq z$, versus z was then made (fig. 1). As may be seen, the points fall nicely along the curve $N(z) = \mathrm{erf}(\frac{1}{2}z)^{\frac{1}{2}}$, the theoretical curve for the space group $\bar{1}$. The agreement is remarkably good for $z > 0.3$, the theoretical and observed values differing by no more

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*The average values of $\sin^2\theta$ in the various groups were 0.06, 0.12, 0.17, 0.22, 0.27, 0.32, 0.36, 0.41, 0.45, 0.48, 0.52, 0.55, 0.59, 0.62, 0.66, 0.70, 0.72, and 0.74

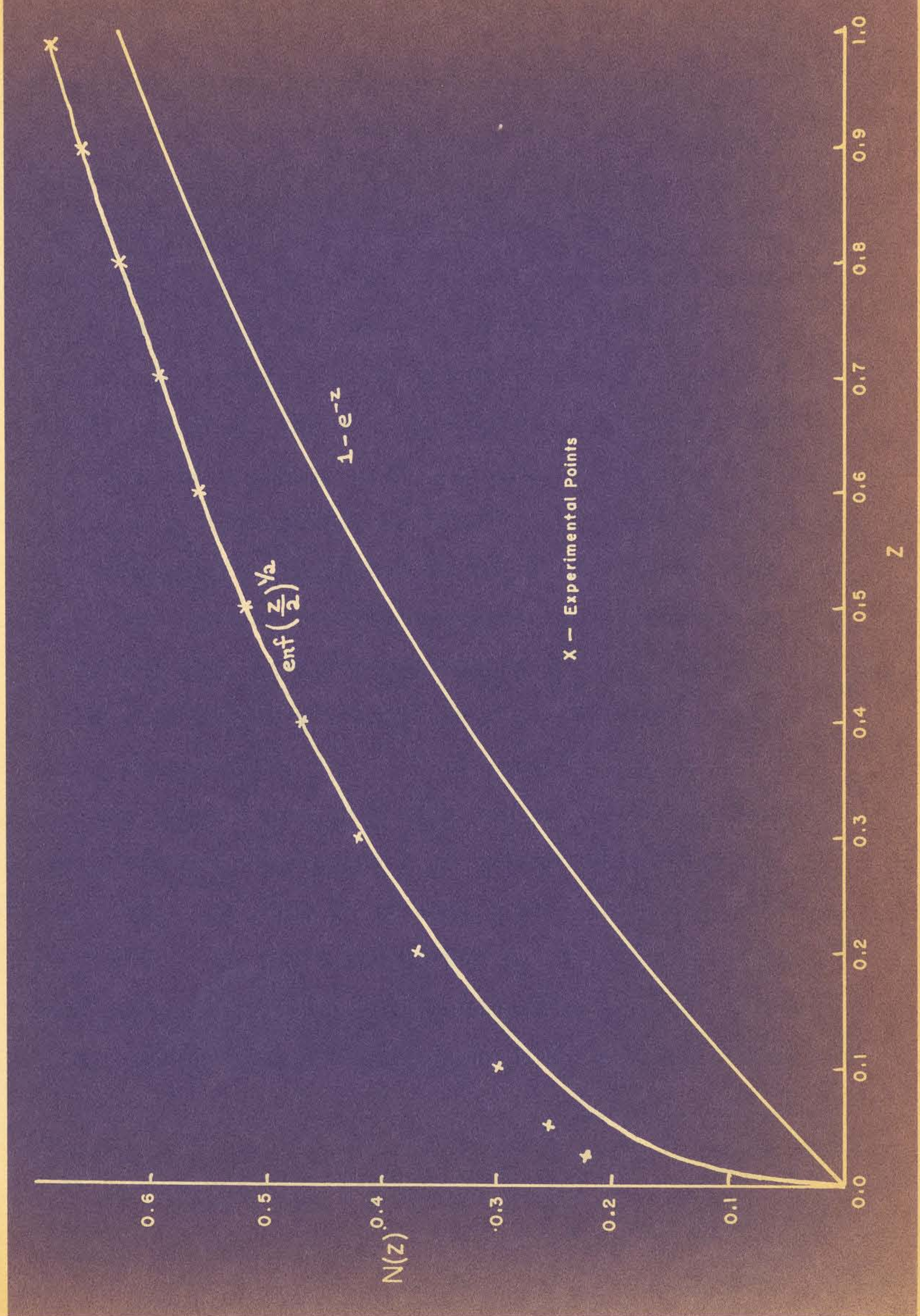
N(Z)
0.1
0.2
0.3
0.4
0.5
0.6
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Z
$\mathrm{erf}\left(\frac{z}{2}\right)^{1/2}$
$1-e^{-z}$
X – Experimental Points

Figure 1

than 0.005[*]. The indicated space group is D_{2h}^{16}, which was confirmed by the concentrations of peaks found in the Patterson.

Since D_{2h}^{16} has eight-fold general positions and there are only four molecules per unit cell, some of the atoms must lie in special positions. It was deemed most probable that the atoms in the special positions lie on the space-group imposed mirror plane and that the molecule has a plane of symmetry coinciding with this plane. A (100) Patterson projection was difficult to interpret in terms of a layer structure with the entire ring lying in the mirror plane, so it appeared that the molecule probably lies perpendicular to the mirror plane with one P and one B lying in the plane.

Although it may have been possible to determine the phosphorus positions from two-dimensional analysis, the unit cell is of such a size and the overlap so great in any projection that the likelihood of obtaining good light atom positions from zonal data alone seemed small. Consequently, it was decided to

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[*] The N(z) curves for the h0l and 0kl projections were also made and exhibited the same general behavior as for the entire group of reflections. There was, however, considerably more scatter of the points about the ideal curve.

carry out a complete three-dimensional analysis.

Equi-inclination Weissenberg photographs were taken with Cu K_α radiation around the a and b axes, the layers extending to 10 kl and h8l. The maximum sin Θ observed was 0.884. Within this limit, 1210 reflections are allowed by the space group, and, of these, 249 were unobservably small. All intensities were visually estimated from multiple-film photographs by comparison with standard intensity strips prepared from the same crystals. All but the weakest reflections were estimated from two, or even three, films. The film factors were estimated separately for each set of photographs. No correction was made for the Cox and Shaw factor (3) for variation of film factor with angle of incidence, but an average value was taken for each layer.

The intensities, the indices, and $\sin^2\Theta$ were punched on IBM cards for the succeeding calculations*. After correction for Lorentz and polarization factors, correlations between the various sets of films were

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*IBM equipment was used as fully as possible, both in the initial reduction of data and in the subsequent refinement, including least squares, structure factor calculations, and Fourier syntheses.

made by comparison of the approximately 800 intensities which had been measured on photographs around both the a and b axes. The ratio of the two intensities was calculated for each reflection, and averages were made for the 99 inter-set comparisons which could be made, i.e., for groups of reflections with given h and k. From these, the effective relative exposures for the twenty sets of films were calculated, and all intensities were corrected for these correlation factors to place them on the same relative scale. For those reflections which were observed twice, the average was taken.

To get a rough estimate of the accuracy with which the intensities had been estimated, the ratio $(I_a - I_b)/\bar{I}$ was calculated. For the 800 relevant reflections, the unweighted average value of this ratio was 0.207, the worst agreement, as expected, being for the very intense and the very weak reflections.

The next step was reduction of the intensities to an absolute scale and estimation of an overall temperature factor, again by a statistical method. Wilson has shown (4) that in a spherical shell of approximately constant $\sin^2\Theta$ the average intensity is equal to $\sum_i f_i^2 \exp(-2b \sin^2\Theta)$, the sum being taken over all the atoms in the unit cell. Values of f, the atomic scattering factor[*], for each atom were punched on the cards and $\sum_i f_i^2$ calculated. Reciprocal space was again divided into shells of approximately constant $\sin^2\Theta$, and in each group $\Sigma I / \Sigma(\sum_i f_i^2)$ was calculated. Since $E(I) = \sum_i f_i^2 \exp(-2b \sin^2\Theta)$, if $\log_e \left[\Sigma I/\Sigma(\sum_i f_i^2)\right]$ is plotted versus $\sin^2\Theta$ a straight line should result, the slope of which is the temperature factor parameter, -2b, and the intercept, the appropriate factor which reduces the intensities to an absolute scale. In the averaging, the unobserved planes were put in at half their estimated minimum observable value[**]. The effect of omitting these is to cause the line to curve downward at high values of $\sin^2\Theta$. The best straight line (fig. 2) was obtained by a least squares fit to the points, giving the first point zero weight. This line has a slope of 3.121 and an intercept at -log 7.87. The temperature factor for

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[*] James and Brindley form factors were used throughout (5).

[**] This is not the expected value for the intensities of these planes if they follow the theoretical statistical distribution (see figure 1). However, the approximation used here should not seriously affect the results of the method.

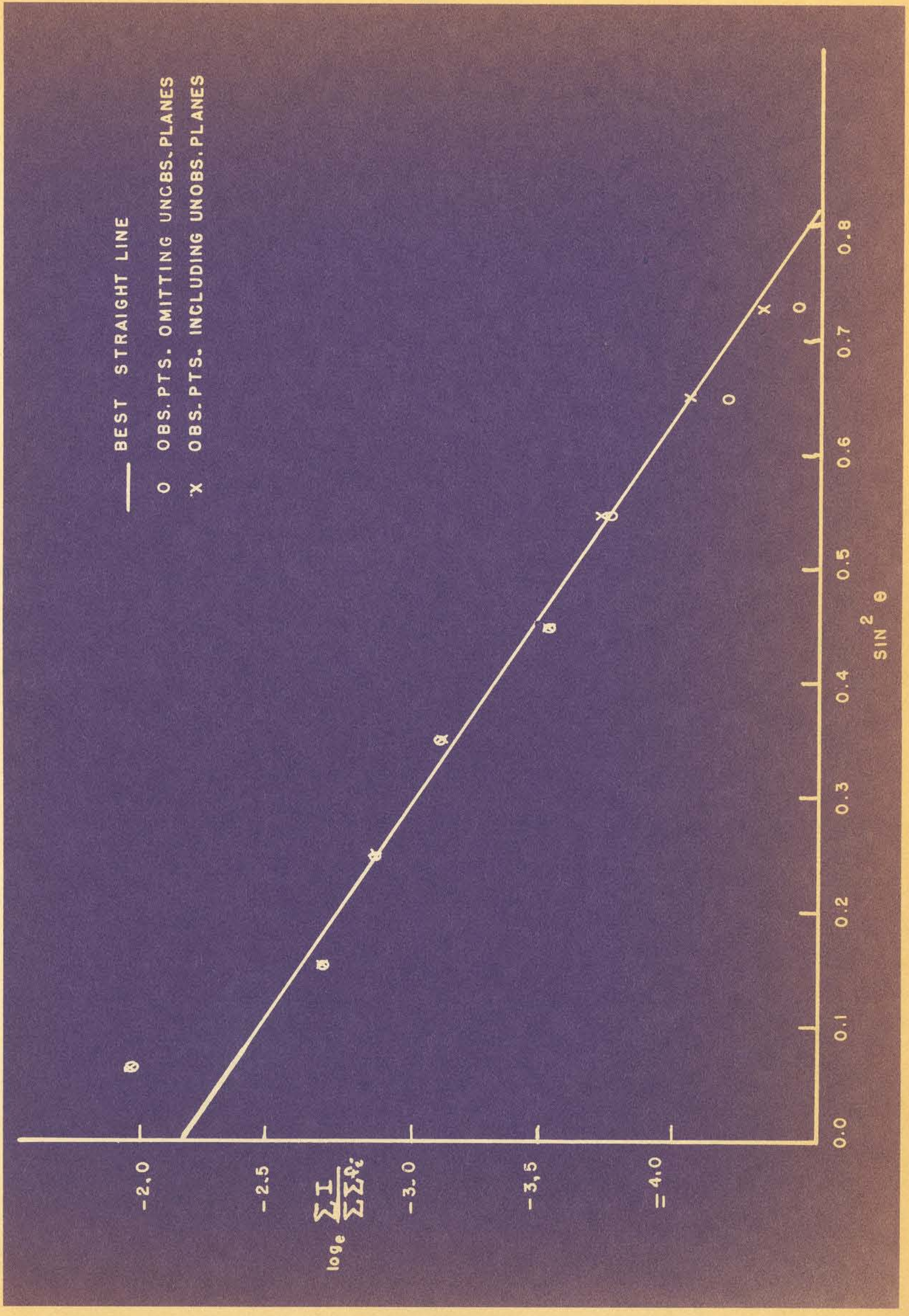
BEST STRAIGHT LINE
O OBS. PTS. OMITTING UNOBS. PLANES
X OBS. PTS. INCLUDING UNOBS. PLANES
-2.0
-2.5
-3.0
-3.5
-4.0
$\log_e \frac{\sum I}{\sum\sum f_i^2}$
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
$\sin^2\theta$

Figure 2

the F^2's is then $\exp(-3.121 \sin^2 \Theta)$ and for the F's, $\exp(-1.560 \sin^2 \Theta) = \exp(-3.711 \sin^2 \Theta / \lambda^2)$*.

After reduction of the intensities to an absolute scale, a three-dimensional Patterson,

$$P\ (UVW) = 1/V \sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty} A \cos 2\pi hU \cos 2\pi kV \cos 2\pi lW$$

was calculated. The coefficients, A, were taken as $F^2(hkl) - (\sum f_i)^2$ in order to remove the peak at the origin. $F^2(000)$ was not included. Other than removal of the peak at the origin, no other modification function was applied. The intervals in U, V, and W were taken as sixtieths of a cell edge, and the function was calculated to $U_{max} = V_{max} = W_{max} = \frac{1}{2}$, the asymmetric unit of Patterson space for this space group.

The peak concentrations were those expected for the space group D_{2h}^{16}, the most notable concentrations being along the line (0V0) and in the plane ($\frac{1}{2}$VW) (fig. 3). The positions of the phosphorus atoms were immediately obvious, and reasonable light atom

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*For the final structure, the best overall temperature factor, on neglecting the hydrogen atoms, was 3.581, rather than 3.711. For this structure, the scale factor had to be increased by 6%, no doubt partly because the hydrogen contributions, although considered in the above original determination of the scale factor, were omitted from the calculated structure factors.

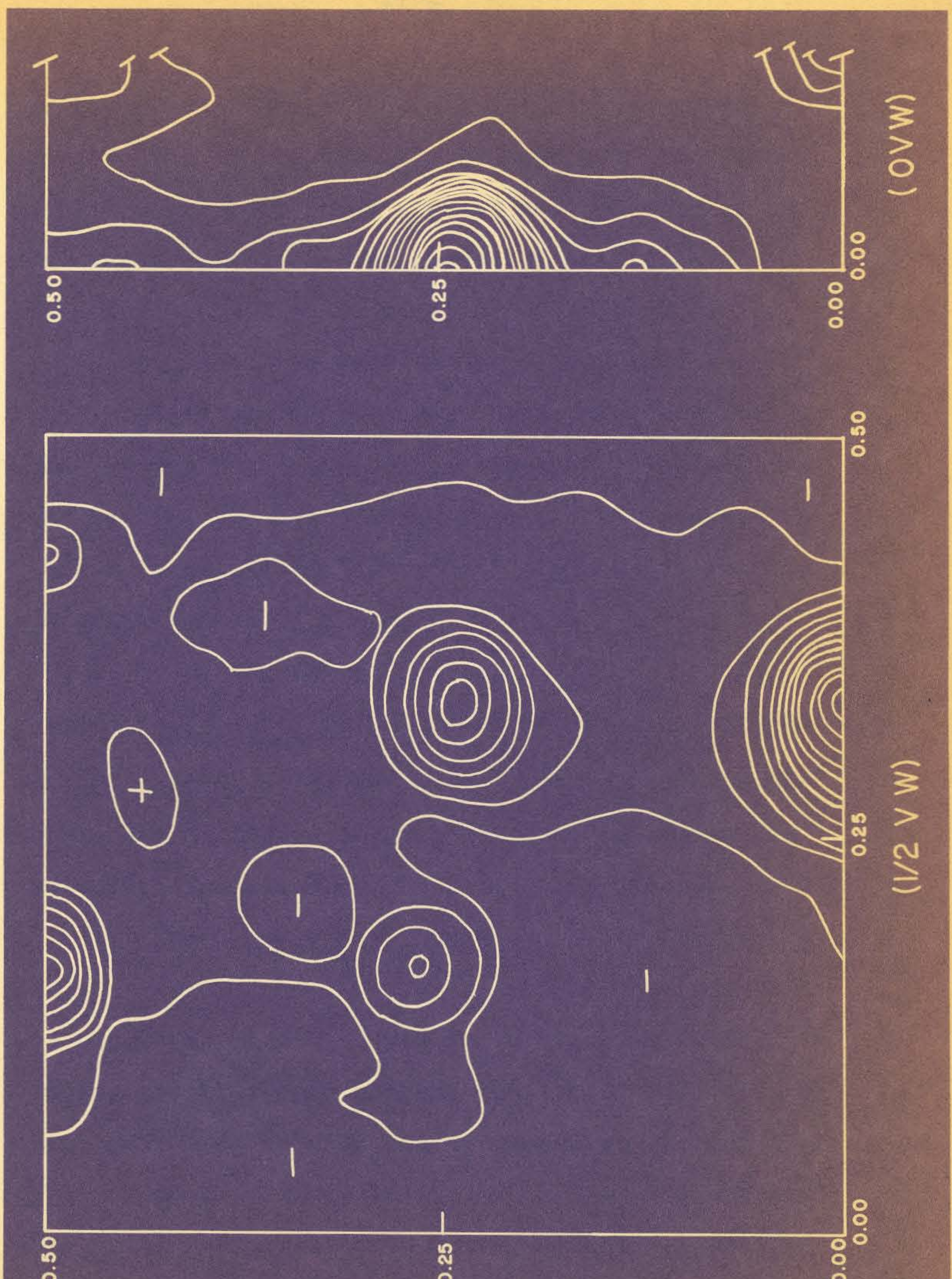

Figure 3

positions were obtained by a least squares treatment of peak positions. All P-C and P-B peaks were easily recognizable, but a great deal of overlap in some cases caused the assignment of atomic parameters for B and C to be more uncertain than for P. The positions of the B-B, C-C, and B-C peaks were calculated; these lie, in most cases, in positive areas of the Patterson, but, except where several overlap, they do not produce recognizable peaks. Table I (page 13) exhibits the Patterson-determined parameter values.

A set of structure factors,

$$F\,(hkl) = \sum_{\text{unit cell}} f_i(hkl)\ \cos 2\pi(hx_i+ky_i+lz_i)\ \exp(-b\sin^2\theta)$$

was calculated, using the overall temperature factor previously derived. No hydrogen contributions were included. The value of the reliability factor,

$$R = \frac{\sum |F_{obs} - F_{calc}|}{\sum |F_{obs}|}$$

was 0.3263 for the observed reflections or 0.3323 including the fifty-two unobservably small reflections which gave a calculated structure factor greater than the minimum observable value. This value is agreeably small for a trial structure, and it was decided to start initial refinement by the least squares method, neglecting off-diagonal terms. Weighting in

Table I

Parameter Values from Patterson

Atom Number	Atom	x	y	z
1	P	0.226	0.130	0.083
2	B	0.159	0.140	-0.077
3	C	0.133	0.102	0.220
4	C	0.320	0.018	0.087
5	P	0.069	0.250	-0.117
6	B	0.300	0.250	0.108
7	C	0.034	0.250	-0.285
8	C	-0.083	0.250	-0.058

the first least squares was proportional to F_{calc} and in the later adjustments inversely proportional to F^2_{obs} for $|F|_{obs} > 12$ and constant for $|F|_{obs} \leq 12$.

The first least squares gave shifts averaging 0.003 for phosphorus and 0.008 for boron and carbon. A new set of structure factors gave an R factor of 0.281. Since the shifts were large and it was felt that several refinements would be necessary, it was decided that it would be practical to carry out a few stages of refinement on a smaller group of reflections. Three hundred fifty-eight reflections with $|F|_{obs} \geq 15$ were chosen. Two least squares adjustments were made on these, the R factor dropping from 0.281 to 0.224 to 0.218 for all reflections, the factor for the selected group alone being in each case about 0.03 less. Several off-diagonal terms were calculated and found to be small, as is expected in three-dimensional work.

Since there still appeared to be large errors ($|F|_{obs} \ll |F|_{calc}$) in some of the strong low-order reflections, these were given even smaller weights than $1/F^2$, as it is quite probable that extinction is important. The reflections so treated were 240, 080, 004, 006, 111, 102, 302, 031, 211, and 213.

The next least squares adjustment was made on the entire 1210 reflections, and gave parameter shifts less than the corresponding standard deviations for twelve of the twenty positional parameters, indicating that the structure was approaching the final stages of refinement. The overall temperature factor and scale factor were also adjusted at this time. The R factor for the resulting structure was 0.192. A second adjustment gave parameter shifts less than the corresponding standard deviations for all atoms but atom 2, the boron atom in a general position. As the shifts for this atom had been large throughout the refinement, it was considered probable that the initial position had been poorly chosen. Consequently, the position of this atom was changed to satisfy three-fold molecular symmetry, assuming that the other atoms were correctly placed. Having changed this position, a new adjustment was made of scale and temperature factor, but the R factor for the resulting structure remained at about 0.19. A further least squares resulted in shifts less than or equal to the least squares standard deviationsfor all parameters, so it seemed apparent that no further improvement could be obtained by least squares on the positional parameters alone.

In order to determine what factors would improve the agreement, it was decided that at this point a three-dimensional electron density difference map would be useful (6, 7). The series,

$$D = 1/V \sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}_{hkl} (F_{obs} - F_{calc}) \cos 2\pi(hx+ky+lz)$$

was calculated. The intervals and ranges of x, y, and z were as follows:

$$0 \leq x \leq 60/120, \quad 30/120 \leq y \leq 90/120, \quad 0 \leq z \leq 30/60.$$

The principal features on the difference map were peaks about 0.7 $e\text{-}\text{Å}^{-3}$ high and negative areas about 1.5 $e\text{-}\text{Å}^{-3}$ deep, which indicated changes in the temperature factors and introduction of hydrogen atoms, but no gross shifts of atomic positions. The principal temperature factor effect was the introduction of a much higher temperature factor for carbon than the one assumed. All hydrogen atoms were identified, and their approximate positions were determined.

Figures 4 and 5 show two typical sections of the difference map. The positive contours are drawn at intervals of about 1/8 $e\text{-}\text{Å}^{-3}$ and the negative contours at about twice this interval. All contours of interest are shown. Figure 4 illustrates well the general behavior in the neighborhood of a carbon atom, being taken through the center of C_3 (lower left) and somewhat below the center of C_7 (extreme upper right).

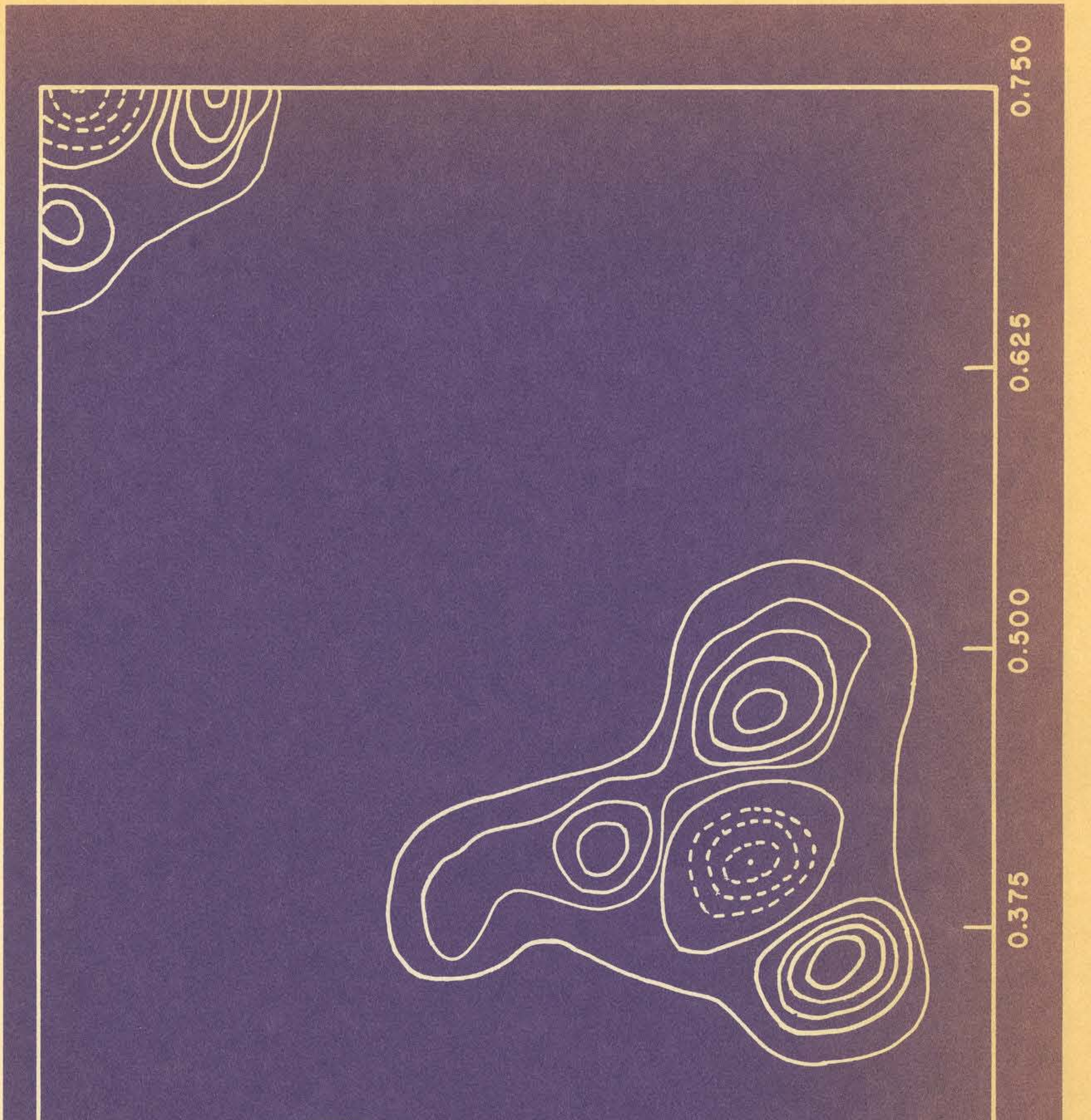

Figure 4

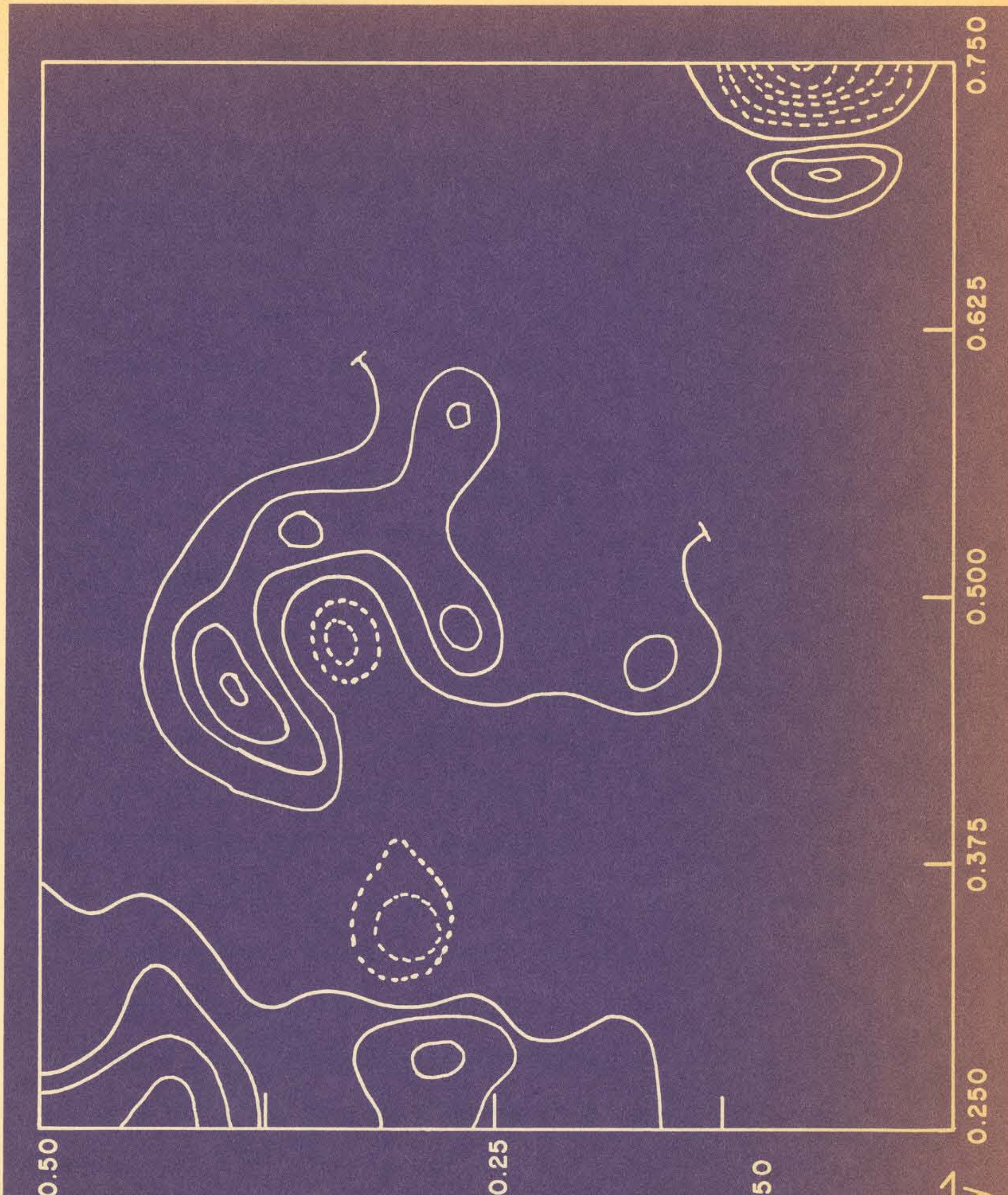

Figure 5

The neighborhood of C_3 is especially illustrative. There is a depression about 1 e-$Å^{-3}$ deep at the atomic center, surrounded by a low positive ring, corresponding very nicely to an underestimation of temperature factor. No significant anisotropy is evident, the three peaks superimposed on the positive ring being interpretable as hydrogen atoms (whose centers are, of course, not in this plane). The smaller peak in the upper left represents a hydrogen atom bonded to boron.

Figure 5 shows the same situation around C_4, somewhat different in this case, as the P-C bond lies in a plane parallel to the section, rather than considerably skewed as in figure 4. Below and to the left is an indicated shift in P_1, principally in the y direction, the maximum amount of this shift not being indicated here, as this plane lies somewhat below the atomic center. To the upper left is another hydrogen atom. This general area illustrates well some of the difficulties that arise from false detail in the neighborhood of gross features, as well as from overlap of these features. In the lower right hand corner of this figure is C_8 with a bonded hydrogen.

For determination of atomic shifts and temperature factors, it was assumed that the electron density in the neighborhood of atomic positions could be approximated by a Gaussian,

$$\rho(xyz) = \rho^{\circ}\exp\left[-(ax^2+by^2+cz^2+2dxy+2fxz+2gyz)\right]$$
$$\equiv \rho^{\circ}\exp\left[-X'AX\right]$$

where

$$X = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad \text{and} \quad A = \begin{pmatrix} a & d & f \\ d & b & g \\ f & g & c \end{pmatrix}$$

Then,

$$\left(\frac{\partial \Delta\rho}{\partial x}\right)_{r=0} = -2a\rho^{\circ}\Delta x$$
$$\left(\frac{\partial^2 \Delta\rho}{\partial x^2}\right)_{r=0} = -2a\Delta\rho^{\circ} - 2\rho^{\circ}\Delta a$$
$$\left(\frac{\partial^2 \Delta\rho}{\partial x\partial y}\right)_{r=0} = -2\rho^{\circ}\Delta d$$

Thus, if the Gaussian approximation is assumed to be valid, errors in both positions and temperature factors may be determined by evaluation of first and second derivatives at the atomic origins.

To determine the best Gaussian fit to the electron density, the following procedure was used. The Fourier transform of

$$f = f_o(s)\ \exp(-bs^2)$$

was calculated numerically by a series approximation to the Fourier integral (8). The interval taken was $s = \pi/10$, and the series was terminated at $s = 23\pi/10$, the limit for the data in the present work. Here, $f_o(s)$ is the assumed atom form factor and b is the assumed temperature factor, 0.0227 in this case. The resulting peak heights were taken as ρ^o, and the parameter in the Gaussian was chosen to make the integrated electron density equal to Z. The results were very pleasing (fig. 6). The following expressions were found:

$$\begin{aligned} &P: \rho(r) = 25 \exp(-4.43r^2) \\ &C: \rho(r) = 6.5 \exp(-3.32r^2) \\ &B: \rho(r) = 6.1 \exp(-3.60r^2) \end{aligned}$$

This result is equivalent to the assumption that the atomic form factors may also be approximated by Gaussians as follows:

$$\begin{aligned} &P: f_o(s) = 15 \exp(-0.0336s^2) \\ &C: f_o(s) = 6 \exp(-0.0528s^2) \\ &B: f_o(s) = 5 \exp(-0.0468s^2) \end{aligned}$$

Although the fit is quite good for the electron density curves, it seems to be very poor for the form factor curves. (fig. 7)* Indeed, if the

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*Also given in figure 7 are curves for a formula given by Yakel (9), $f_o(s) = Z \exp(-0.0203s^2)$; the approximation in the present work certainly gives a much better fit to the transforms of the real f curves, taken to the practical copper limit.

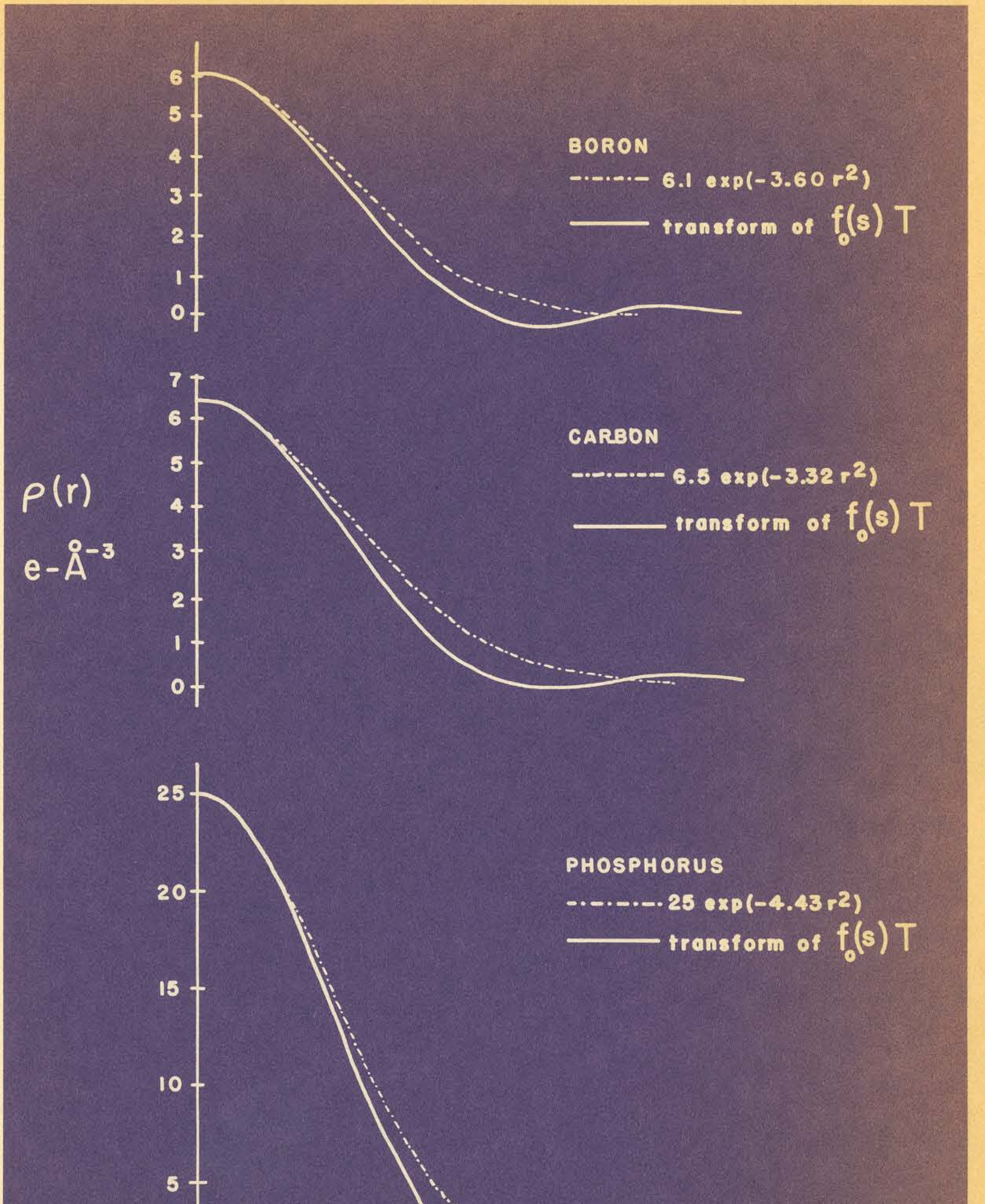
ρ(r)
e-Å^{-3}
BORON
6.1 exp(-3.60 r^2)
transform of f$_0$(s) T
CARBON
6.5 exp(-3.32 r^2)
transform of f$_0$(s) T
PHOSPHORUS
25 exp(-4.43 r^2)
transform of f$_0$(s) T
0
1
2
3
4
5
6
7
10
15
20
25
0.25
0.50
0.75
1.00
1.25
1.50
r Å

Figure 6

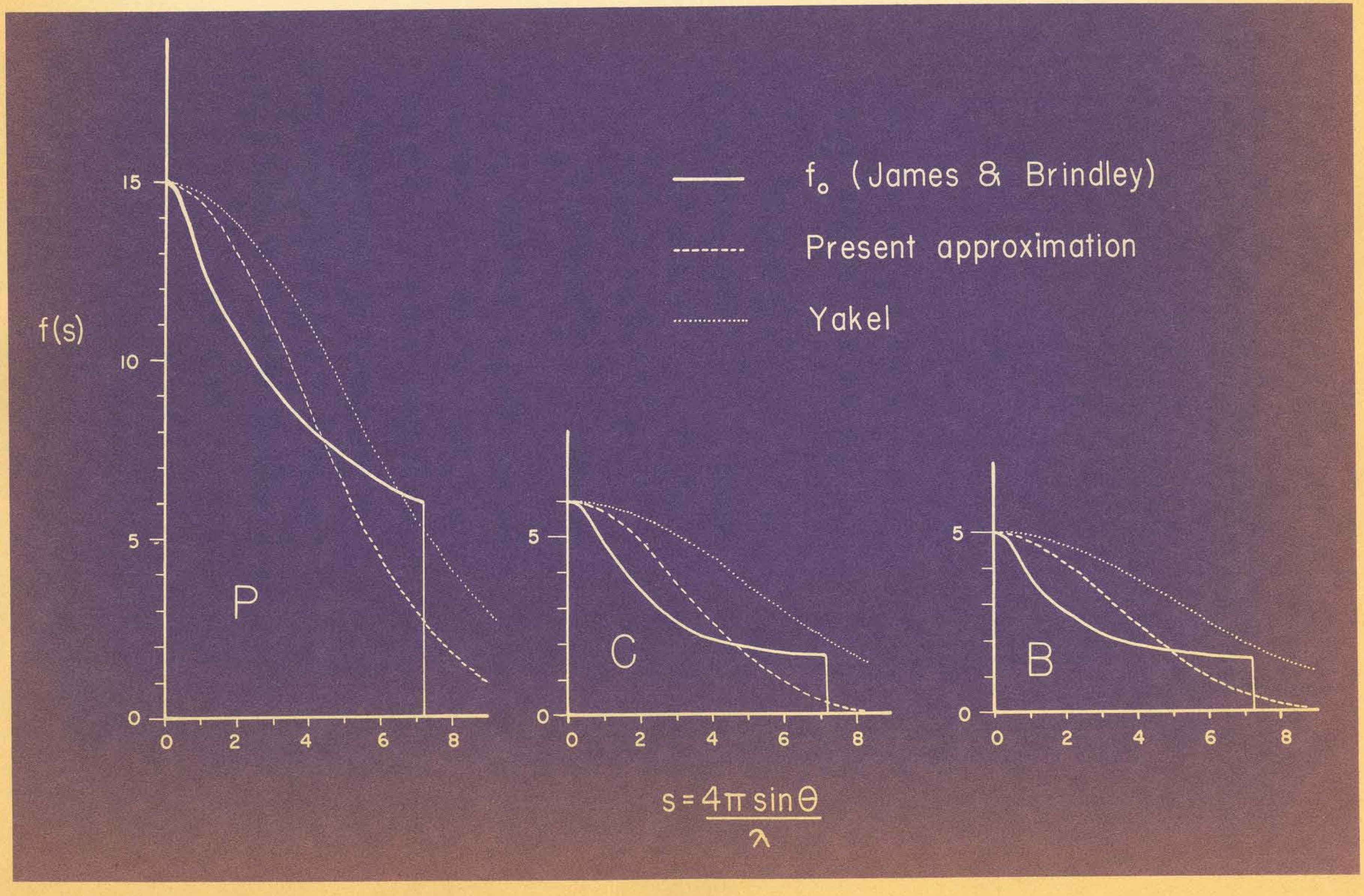
f(s)
15
10
5
0
P
C
B
0
2
4
6
8
f_o (James & Brindley)
Present approximation
Yakel
$s = \frac{4\pi \sin\theta}{\lambda}$

Figure 7

approximation to f were to be used in any sense except in the transform, it would be of little or no value. Nevertheless, it has great value in approximating the electron density, i.e., the transform of f, over a wide range of real temperature factors.

To confirm this, fits were made to the transforms of combinations of f_o with several temperature factors. For carbon, the parameter, a, in the approximation to f_o has the following values:

T factor	a
$\exp(-0.00s^2)$	0.0528
$\exp(-0.01s^2)$	0.0513
$\exp(-0.02s^2)$	0.0528
$\exp(-0.04s^2)$	0.0515

so that the same fit is good over the entire range of temperature factors ordinarily met with in experiment. Consequently, changes in temperature factor estimated from changes in peak shape have a maximum error of about 10%, a value which is certainly as good as could be expected from any method of estimation from a difference map.

Using the fits obtained above and derivatives approximated by differences obtained from the difference map, changes in peak shape were estimated.

In table II are given the components of the matrix A for each atom. These values cannot be considered accurate to more than about 10%, so that is seems unreasonable to consider any small, indicated anisotropies which may be indicated. It was decided that the most reasonable thing to do at this stage was to calculate the best isotropic temperature factor for each atom. These were chosen in a way which would make the peak height of the electron density distribution (or the area under the f curve) the same as for the anisotropic values found. In other words, in the expression,

$$\rho(r) = \rho^{\circ}\exp(-Br^2)$$

B was chosen so that

$$B^3 = |A|$$

These values of B are also given in table II. Now, if

$$\rho(r) = \rho^{\circ}\exp(-Br^2)$$
$$f_o(s) = Z\exp(-as^2)$$
$$T(s) = \exp(-bs^2)$$

and $\rho(r)$ is the transform of $f_o(s)\cdot T(s)$,

$$4B = (a+b)^{-1}$$

Table II*

Components of Peak Shape

Atom	a	b	c	d	f	g	B
P_1	4.66	4.38	4.61	0.03	0.00	0.05	4.6
B_2	3.52	3.60	3.48	0.00	0.00	0.07	3.5
C_3	2.80	2.68	2.71	-0.14	-0.23	0.25	2.7
C_4	2.09	2.74	3.18	0.58	0.12	0.21	2.6
P_5	4.69	4.21	4.69	0.00	-0.33	0.00	4.5
B_6	3.48	2.96	3.85	0.00	1.31	0.00	3.3
C_7	2.85	2.84	3.08	0.00	-0.69	0.00	2.9
C_8	2.44	3.02	2.44	0.00	0.31	0.00	2.6

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*If the anisotropies are to be regarded as meaningful, it must be noted that the values given here apply to the atoms which lie in the octant bounded by $x = 0$, $x = \frac{1}{2}$, $y = \frac{1}{4}$, $y = 3/4$, $z = 0$, $z = \frac{1}{2}$. The matrix must obviously be transformed to apply to the atoms related by symmetry.

From this expression, and with the knowledge of B and a, b was calculated for each atom. These values are presented in table III. The average values for P, B, and C are 0.0214, 0.0268, and 0.0400, as contrasted to the assumed overall value of 0.0227.

That the differential method of determination of corrections in peak shape is applicable in this particular case is illustrated in figure 8. The solid line is a plot of

$$4.9 \exp(-2.6r^2) - 6.5 \exp(-3.60r^2)$$

while the other lines give actual cross-sections of the difference map in the directions of the crystallographic axes through the center of carbon atom 8. The fit is seen to represent quite adequately the average of the three line sections, the discrepancies in the x and y sections at about 0.8 Å being largely due to overlap of hydrogen atoms near these positions.

Atomic shifts were also calculated by the above formula and were found to be in every case less than or only slightly greater than the least squares standard deviations. Table IV (page 30) presents the final values of the atomic parameters for P, B, and C as well as the values at some of the intermediate stages of refinement. The standard deviations are

Table III

Final Temperature Factors

Atom	b
P_1	0.0208
B_2	0.0247
C_3	0.0398
C_4	0.0434
P_5	0.0220
B_6	0.0289
C_7	0.0335
C_8	0.0434

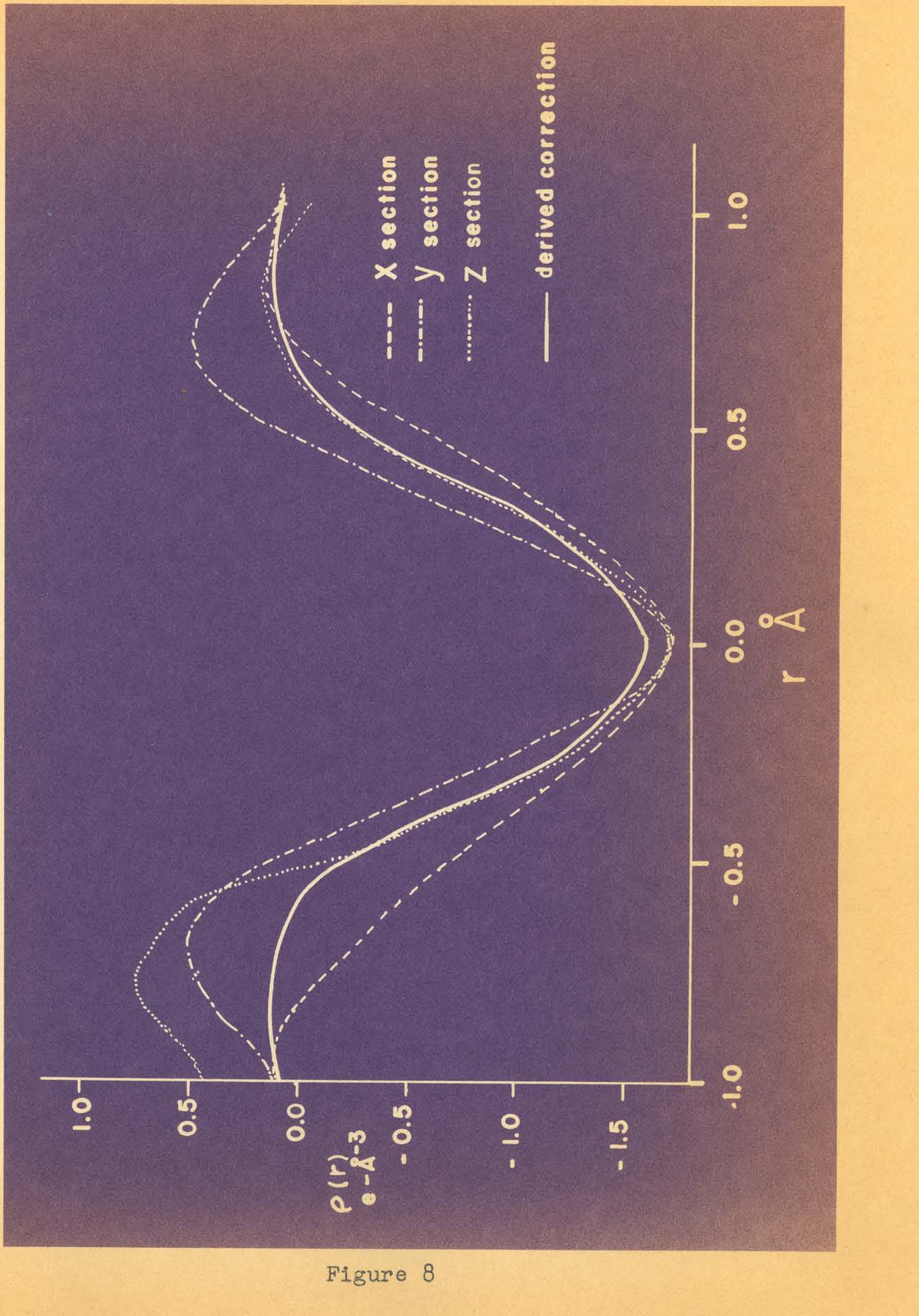
ρ(r)
e-Å-3
1.0
0.5
0.0
- 0.5
- 1.0
- 1.5
-1.0
-0.5
0.0
0.5
1.0
r Å
X section
y section
Z section
derived correction

Figure 8

Table IV

Atomic Parameters for Heavy Atoms

Parameter		Patterson	Least Squares First	Least Squares Final	Final	σ
P_1	x	0.226	0.235	0.2345	0.2345	0.0003
	y	0.130	0.129	0.1286	0.1281	0.0003
	z	0.083	0.082	0.0820	0.0822	0.0003
B_2	x	0.159	0.149	0.1518	0.1513	0.0011
	y	0.140	0.122	0.1245	0.1244	0.0009
	z	0.923	0.918	0.9213	0.9200	0.0011
C_3	x	0.133	0.126	0.1257	0.1257	0.0009
	y	0.102	0.096	0.0975	0.0975	0.0008
	z	0.220	0.210	0.2092	0.2102	0.0010
C_4	x	0.320	0.335	0.3355	0.3340	0.0009
	y	0.018	0.021	0.0204	0.0199	0.0008
	z	0.087	0.086	0.0864	0.0864	0.0009
P_5^*	x	0.069	0.071	0.0707	0.0712	0.0003
	z	0.883	0.881	0.8816	0.8818	0.0004
B_6^*	x	0.300	0.321	0.3226	0.3236	0.0015
	z	0.108	0.118	0.1241	0.1236	0.0016
C_7^*	x	0.034	0.025	0.0236	0.0226	0.0013
	z	0.715	0.716	0.7155	0.7155	0.0014
C_8^*	x	0.917	0.923	0.9234	0.9219	0.0013
	z	0.942	0.953	0.9584	0.9584	0.0014

---

*The value of y was assumed to be 0.2500 for these atoms.

those obtained from the final least squares. The average differences between the Patterson values and final values are 0.003, 0.013, and 0.007 for P, B, and C, respectively.

All hydrogen atoms were identified, and, although overlap from atomic shift and temperature factor effects often made assignment of accurate positions impossible, the values obtained were accurate enough to indicate the general orientation of these atoms, if not to give reliable interatomic distances. Table V presents the parameter values for these atoms.

Although inclusion of hydrogen contributions would presumably improve considerably the agreement between observed and calculated structure factors, it was felt that the amount of labor involved would not be justified. A final set of structure factors omitting hydrogen contributions, but including revised parameter and temperature factor values, was calculated*. The overall R factor is 0.169, the variation with $\sin^2\theta$ being given in table VI (page 33). This variation may be interpreted on the basis of remaining errors in temperature factors affecting the high

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*These are tabulated in the appendix, along with the observed structure factors.

Table V

Hydrogen Atom Positions

Bonded Atom	H Number	x	y	z
B_2	1	0.217	0.117	0.853
	2	0.075	0.067	0.933
B_6	3	0.417	0.250	0.050
	4	0.340	0.250	0.233
C_7	5	0.083	0.250	0.667
	6	0.992	0.192	0.733
C_8	7	0.900	0.300	0.933
	8	0.925	0.250	0.033
C_3	9	0.126	0.475	0.200
	10	0.083	0.358	0.233
	11	0.167	0.417	0.283
C_4	12	0.367	0.458	0.167
	13	0.400	0.467	0.033
	14	0.333	0.542	0.083

Table VI

Variation of R Factor with $\sin^2\theta$

$\sin^2\theta$	Number of Planes	R
0.0-0.1	63	0.245
0.1-0.2	103	0.154
0.2-0.3	124	0.147
0.3-0.4	140	0.138
0.4-0.5	151	0.148
0.5-0.6	156	0.161
0.6-0.7	149	0.214
0.7-0.8	75	0.202

angle data, and extinction effects, as well as omission of hydrogen contributions, affecting the low angle data.

A drawing of the molecule is presented in figure 9. The methyl groups are so oriented that, on both the top and bottom of the molecule, one hydrogen atom from each methyl group is directed inward toward the three-fold axis of the molecule. The hydrogen atoms are not in close contact, the average separation being 2.95 Å around the top of the molecule, 2.75 Å between hydrogens on methyls bonded to the same P, and 2.96 Å between methyl hydrogens and boron hydrogens around the bottom of the molecule.

In table VII (page 35) are exhibited a number of intramolecular interatomic distances of interest. The standard deviations are those estimated from the least squares standard deviations for the coordinates. No standard deviations are given for distances involving hydrogen, since there was no method of reliable estimation of error available. The errors here are probably several times larger than for the heavy atom distances.

In table VIII (page 36) are given the bond angles calculated for the structure. No values are given for angles involving hydrogen bonded to carbon, for, although there was considerable deviation from

Table VII

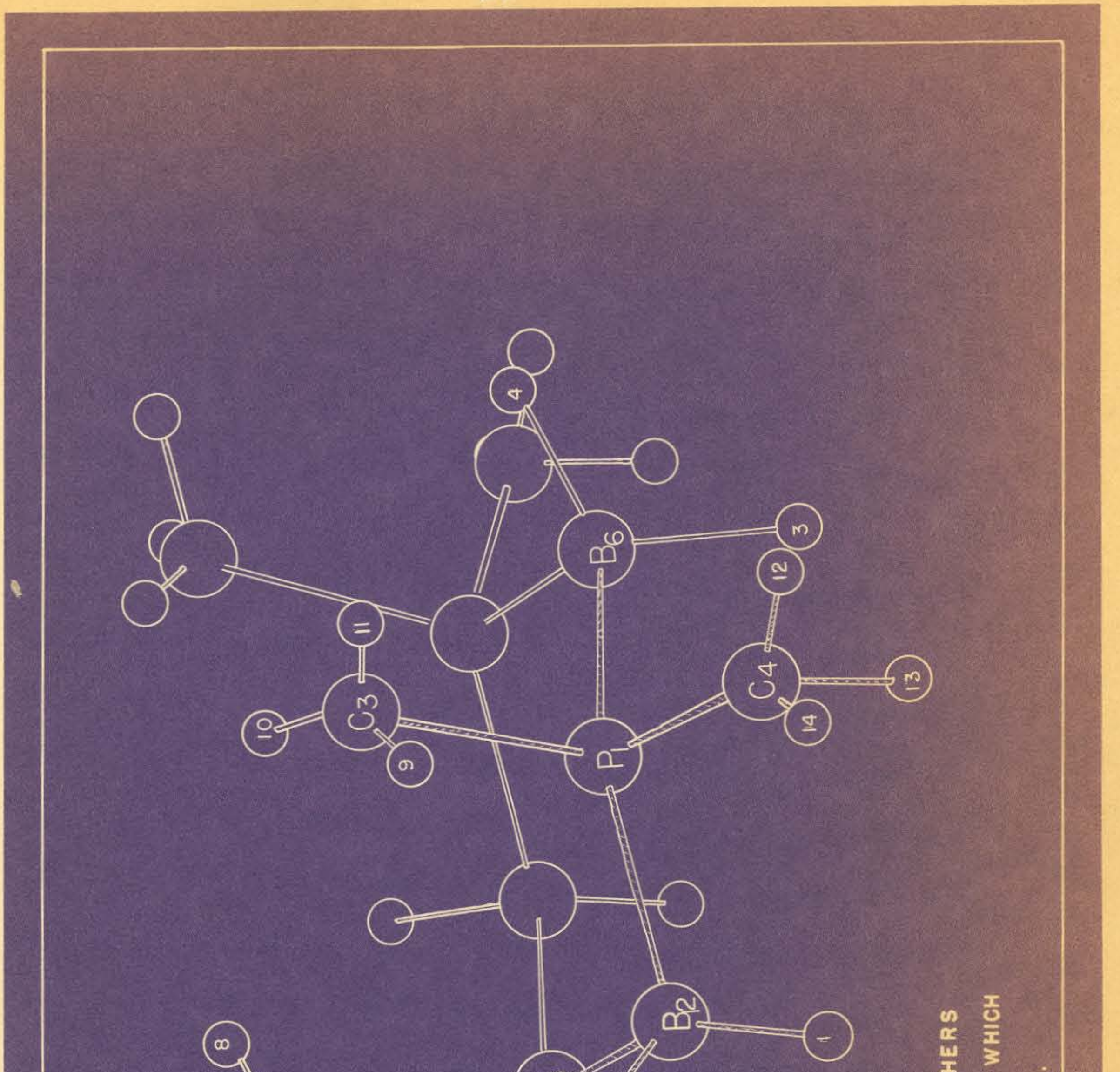
Intramolecular Interatomic Distances

Distance	Value	σ	Average
P_1-P_5	3.216	0.006	
P_1-P_1	3.208	0.006	3.212
B_2-B_6	3.321	0.020	
B_2-B_2	3.306	0.017	3.313
P_1-B_2	1.945	0.013	
P_5-B_2	1.922	0.013	
P_1-B_6	1.937	0.017	1.935
P_1-C_3	1.858	0.011	
P_1-C_4	1.806	0.011	
P_5-C_7	1.833	0.015	
P_5-C_8	1.851	0.015	1.837
C_3-C_8	4.028	0.017	
C_3-C_3	4.014	0.014	4.021
B_2-H_1	1.18		
B_2-H_2	1.15		
B_6-H_3	1.30		
B_6-H_4	1.17		1.20
C_7-H_5	0.8		
C_7-H_6	0.9		
C_8-H_7	1.0		
C_8-H_8	0.8		
C_3-H_9	1.0		
C_3-H_{10}	0.8		
C_3-H_{11}	0.9		
C_4-H_{12}	0.9		
C_4-H_{13}	0.8		
C_4-H_{14}	0.8		0.87

Table VIII

Bond Angles

Angle	Value	Average
C_3-P_1-C_4	102° 19'	
C_7-P_5-C_8	98° 34'	100° 26'
B_2-P_1-B_6	117° 38'	
B_2-P_5-B_2	118° 38'	118° 8'
P_1-B_6-P_1	111° 48'	
P_5-B_2-P_1	112° 32'	112° 10'
B_2-P_1-C_3	108° 40'	
B_2-P_1-C_4	107° 11'	
B_6-P_1-C_3	110° 38'	
B_6-P_1-C_4	109° 22'	
B_2-P_5-C_7	109° 43'	
B_2-P_5-C_8	109° 7'	109° 7'
H_1-B_2-H_2	119° 6'	
H_3-B_6-H_4	119° 30'	119° 18'



UNLABLED ATOMS ARE RELATED TO OTHERS BY REFLECTION IN THE MIRROR PLANE WHICH PASSES THROUGH P5, B6, C7 AND C8.

Figure 9

tetrahedrality in a few cases, it was felt that the accuracy of the hydrogen atom position determination was so low that these deviations would be meaningless. There did not appear to be any significant trend for these angles to be other than tetrahedral as in the case of the H-B-H angle. The environments of the phosphorus and the boron atoms are not significantly different from C_{2v}.

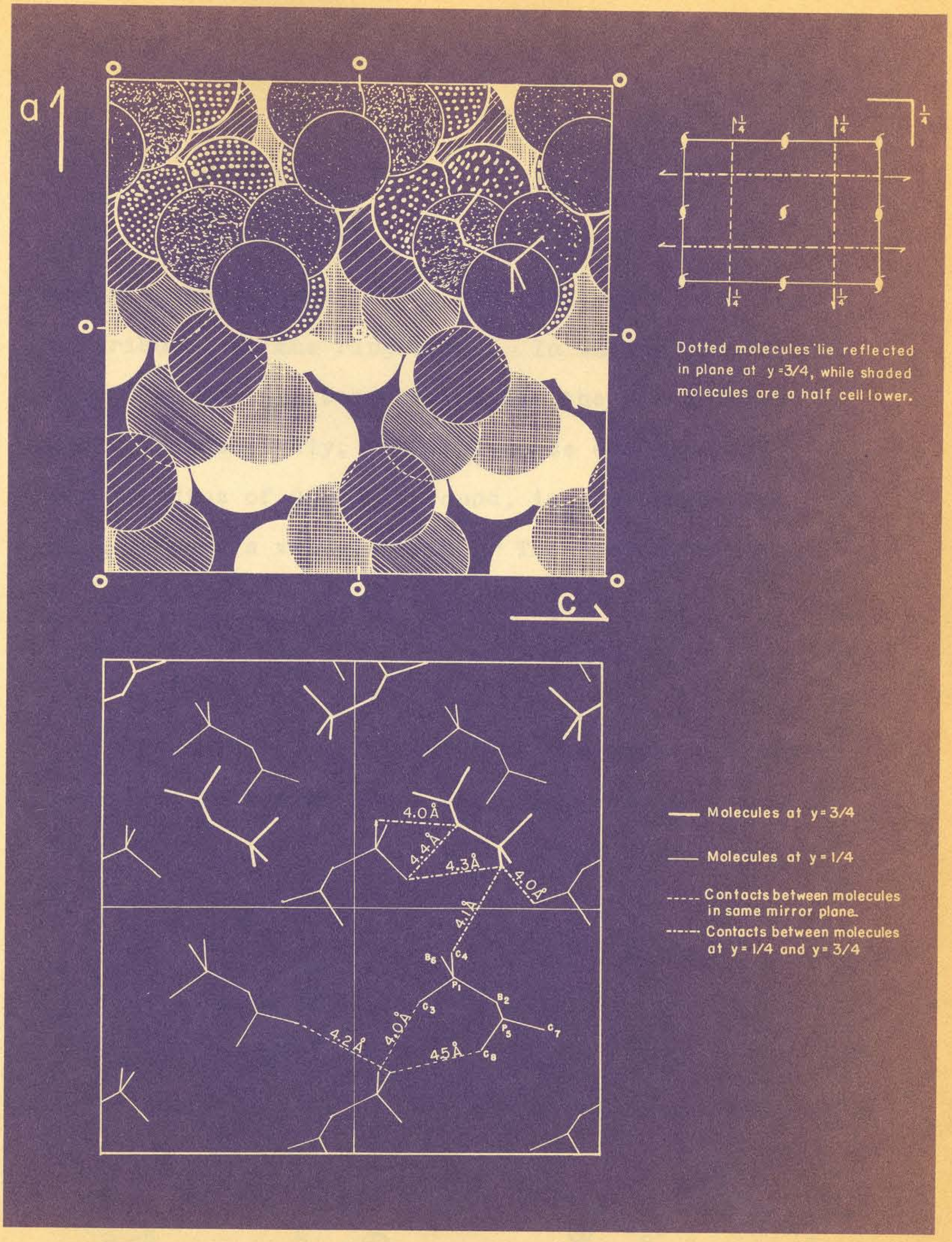
There are four intermolecular C-C contacts at about the proper distance for van der Waals contact, 4.05, 4.15, 4.28, and 4.00 Å. The corresponding inter-hydrogen distances are 2.35, 2.40, 3.10, and 3.03 Å, so that the latter two may not be important if a van der Waals radius of about 1 Å is assumed for hydrogen. Packing also seems to be governed by B-C contacts, the distances being 4.5, 4.2, 4.0, and 4.4 Å. Here, the shortest H-H contacts are 2.64, 2.94, 3.02, and 3.02, respectively. It would appear here that perhaps only the first is important. However, since the hydrogen positions are not known with great accuracy, it would seem reasonable to regard the C-C and C-B distances as being more meaningful than the H-H distances as packing criteria. Taking 2.0 Å as the van der Waals radius for methyl and 2.2 Å for B-H, all of these contacts may be considered to be important. A drawing of the packing is given in figure 10. An area of four unit cells is shown, the plane of the projection being normal to b. Two layers of molecules are shown, one at $y = \frac{1}{4}$ and the other at $y = 3/4$. The lower drawing is identical to the upper except that only the skeletons of the molecules are shown to better indicate the packing distances. Only one contact of each type is shown; others are related by symmetry and produce chains of molecules along several of the screw axes of the space group.

The P-C distance, 1.837, is normal according to the Schomaker-Stevenson rule (10).

$$\begin{aligned} \text{P-C} &= 1.10 + 0.77 - 0.09(0.4) \\ &= 1.834 \end{aligned}$$

However, Springall and Brockway (11) have reported a value of 1.87 in trimethyl phosphine, the only compound for which this bond length has been determined, so that there appears to be some discrepancy.

The P-B bond length should be 1.89, assuming a radius of 1.10 for P and 0.80 for B, so that it would appear that there is somewhat less than single-bond character in this compound, as the average value is 1.945. In Hedberg's discussion (12) of the boron radius, a method of calculation of bond orders is used which may be useful here. We may write the



Dotted molecules lie reflected in plane at y = 3/4, while shaded molecules are a half cell lower.

—— Molecules at y = 3/4

—— Molecules at y = 1/4

----- Contacts between molecules in same mirror plane.

------ Contacts between molecules at y = 1/4 and y = 3/4

Figure 10

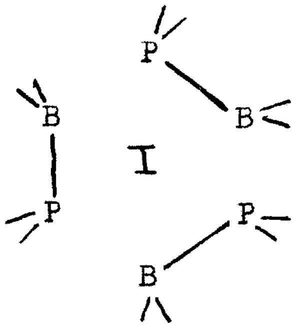
equations,

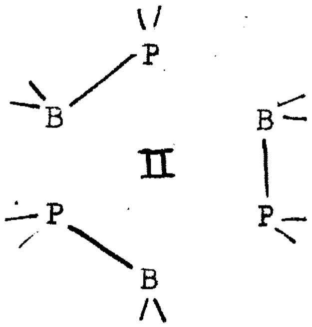
$$1.10 + r_B - 0.01 - 0.6 \log n_1 = 1.945$$
$$0.30 + r_B - 0.01 - 0.6 \log n_2 = 1.20$$
$$2(6n_1 + 6n_2) = 18,$$

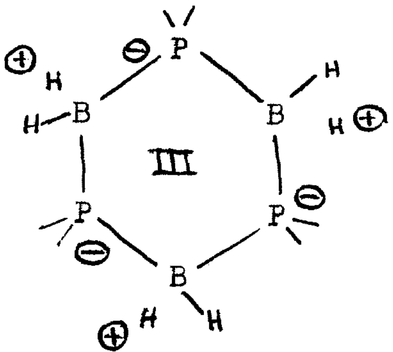
assuming that there is but one electron per P atom contributed to the ring bonds. In these expressions, n_1 and n_2 are the bond orders for the P-B and B-H bonds, respectively. Solving these equations, a boron radius of 0.803 is found, in good agreement with Hedberg's value of 0.80. The bond orders are

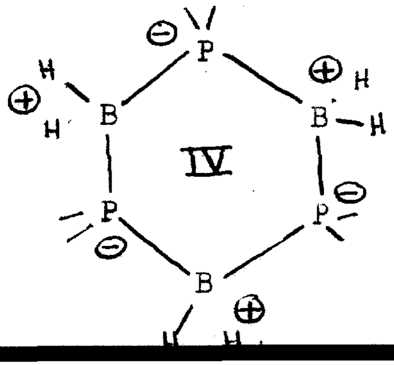
$$n_1 = 0.83$$
$$n_2 = 0.67$$

It would appear, then, that the structure may be described in terms of the following resonance structures:

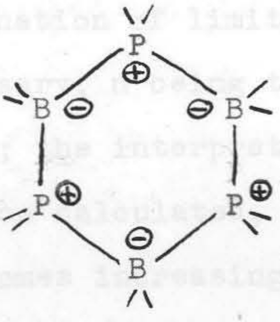








With structures I and II contributing 1/3 of the electron density and III and IV 2/3, the bond orders found are perfectly explained. According to Schomaker (13), the no-bond single-bond resonance between structures I and II, by analogy with PCl_5, probably leads to a lower energy for the molecule than would a structure involving promotion of the unshared pair on P into bonding orbitals to give the following structure:



These structures also account satisfactorily, in a qualitative way, for the ring bond angles found in this investigation. Since the C-P-C and the H-B-H angles have values which would be characteristic of the monomeric segments of structures I and II, i.e., the angles are approximately those found in compounds of the types PX_3 and BX_3 (14), and since the C-P-B and H-B-P angles also tend to achieve these values, the P-B-P angle becomes small and the B-P-B angle becomes large in accordance.

II. The Method of Least Squares in Electron Diffraction

The correlation procedure commonly used in electron diffraction investigations of molecular structure is unsatisfactory for molecules of any great complexity, that is to say, with about five or more independent parameters. There are three principal reasons for this: The labor involved in the calculation of theoretical intensity curves becomes prohibitive, since for reliable determination of limits of error, about 3^n curves are necessary, n being the number of independent shape parameters; the interpretation and correlation of these curves, once calculated, becomes extremely difficult; and it becomes increasingly difficult both to determine limits of error and to express these, with their interdependencies, either graphically or numerically. For a five or six parameter problem, the situation is practically hopeless.

It would be desirable to have a procedure for deriving parameter values and estimates of error directly from the experimental data. The obvious suggestion, the radial distribution method being less than satisfactory in several respects, is the method of least squares, but, probably because of the special nature of visual electron diffraction data, this seems not to have been used in a systematic way heretofore. In the following application (bicycloheptadiene), which it is believed will prove typical, the method has afforded a complete parameter determination, including a complete and concise statement of estimated errors. Only half a dozen theoretical intensity curves were calculated instead of the hundred or more which would have been required by the correlation procedure.

As early as 1936, Bauer, in trial applications of his analytic method (15), used least squares on just the measured positions of intensity maxima and minima. This limited treatment will lead to the correct results in very special cases, where virtually only frequencies (as contrasted to amplitudes) are important; generally, however, other aspects of the diffraction pattern, many of them essentially qualitative, are much more important and must be considered also. Such are the relative intensities, widths, spacings, or shapes of two or more maxima or minima; in short, just those features on which the shape determination in the correlation procedure is almost always based[*]. In fact, every observation must be used in the least squares adjustment, each with its appropriate weight, and the choice of these weights is perhaps the most difficult part of the whole treatment. It is discussed in detail below.

Matrix notation makes possible a concise and remarkably conspicuous presentation of least squares theory (16,17), of which the parts essential to this treatment are reproduced here.

Denoting an n x m matrix $\{a_{ij}\}$ by A_{nm} (or simply A) and its transpose by A', the least squares problem may be stated as follows: Given a set of observations F^{o}_{n1} whose true but unknown values are $E\{F^{o}\} \equiv F_{n1}$, a set of unknown parameters X_{m1} $(m \leqslant n)$, and a matrix of known coefficients A_{nm} such that

$$F = AX$$

it is desired to find H_{1n} such that (a) $E\{HF^{o}\} \equiv HAX$ is

---

[*] In the case of accurate sector-microphotometer data, the ordinates of the sI(s) vs. s curve may well be taken as the primary observations. However, for visual data, to which the detailed discussions here are devoted, these ordinates are usually considerably less certain than most of the visual observations on which, together with various necessary assumptions and guesses, they are based; it is the direct visual comparisons, therefore, which logically must be used in the least squares adjustment.

equal to $G_{1m}X$, a certain desired linear function of X, and that (b) the variance of HF^o,

$$E\left\{(HF^o - HF)^2\right\} \equiv E\left\{H(F^o-F)(F^o-F)'H'\right\}$$
$$\equiv HE\left\{(F^o-F)(F^o-F)'\right\}H'$$
$$\equiv HM_FH'$$

shall be a minimum; in short, the requirements on H are (a)

$$HA = G$$

(since X is arbitrary) and (b)

$$\delta(HM_FH') = 0$$

M_F, the moment matrix of the observations is assumed to be known. The solution is found by introducing LaGrange multipliers, Λ_{1m}, requiring that

$$HM_FH' + 2\Lambda(G' - A'H')$$

have an extreme value with respect to variations in H, and subsequently adjusting Λ to satisfy

$$HA = G.$$

Since M_F is symmetric,

$$\delta H\ M_FH' = HM_F\ \delta H'$$

and the sequence becomes simply

$$\delta(HM_FH') - 2\Lambda A'\delta H' = 0$$

$$HM_F - \Lambda A' = 0$$

$$H = \Lambda A'M_F^{-1} = G(A'M_F^{-1}A)^{-1}A'M_F^{-1}$$

The desired best quantity HF^o may be written as $G\bar{X}$, with $\bar{X}$ the solution of the least squares normal equations,

$$B\bar{X} \equiv A'M_F^{-1}A\bar{X} = A'M_F^{-1}F^o$$

The reciprocal moment matrix, M_F^{-1}, is also called the weight matrix, P, and $V_{nl} \equiv F^o - A\bar{X}$ is called the matrix of residuals. It is easily shown that if $\bar{X}$ satisfies the normal equations,

$$\delta(V'PV) = 0$$

i.e., that the weighted quadratic form of the residuals is a minimum*.

It is also of importance to know the moment (error) matrix M_X for the derived quantities $\bar{X}$.

$$\bar{X} = B^{-1}A'M_F^{-1}F^o$$

---

* In the case of a diagonal weight matrix, this is equivalent to saying that the weighted sum of the squared residuals is a minimum.

$$X = B^{-1}A' M_F^{-1}F$$

$$(\bar{X}-X) = B^{-1}A'P(F^o-F)$$

$$M_X = E\{(\bar{X}-X)(\bar{X}-X)'\} = B^{-1}A'PE\{(F^o-F)(F^o-F)'\}PAB^{-1'}$$

$$= B^{-1}A'PP^{-1}PAB^{-1'}$$

$$= B^{-1}BB^{-1'}$$

$$M_X = B^{-1'} = B^{-1}$$

That is, the error matrix for the parameters is simply the inverse of the matrix of coefficients in the normal equations*.

The elements of $M_X \equiv \{\mu_{ij}\}$ have the following significance

$$\mu_{ij} = \begin{cases} \sigma_i^2 & i=j \\ \sigma_i\sigma_j\rho_{ij} & i\neq j \end{cases}$$

σ_i being the marginal standard deviation in x_i, and ρ_{ij},

---

*In performing calculations on a real problem, the following point must be noted: The weight matrix used in calculation may not be the actual inverse of the error matrix for the observations, but rather this matrix multiplied by an arbitrary constant, γ. In this case, the matrix of coefficients for the normal equations will not be B, but $B_\gamma = \gamma B$. The correct value for M_X will then be γB_γ. If γ is unknown and if the errors are assumed to be normally distributed, an unbiased estimate of γ is given by

$$\gamma \approx \frac{V'PV}{n-m}$$

which, if the weight matrix is properly normalized, has an expected value of unity.

the correlation coefficient between x_i and x_j.

Now if it is assumed that the errors in the observations have a multiple Gaussian distribution (an assumption which is in no way demanded by the previous discussion):

$$d\,\Phi = C'\exp\left[-\tfrac{1}{2}(F^{o}-F)'M_F^{-1}(F^{o}-F)\right]\,df_1\cdots df_n$$

the errors in the estimated parameters $\overline{X}$ also have a Gaussian distribution

$$d\,\Phi = C\exp\left[-\tfrac{1}{2}(\overline{X}-X)'M_X^{-1}(\overline{X}-X)\right]\,dx_1\cdots dx_m$$

where $C = \dfrac{|M_X^{-1}|^{\frac{1}{2}}}{(2\pi)^{\frac{1}{2}m}}$

in order that $\underset{m}{\int_{-\infty}^{+\infty}} d\,\Phi = 1$ *

---

* That this is the proper normalization may be shown as follows: Let us find the orthogonal transformation, T_{mm}, such that

$$T'M^{-1}T = D, \text{ a diagonal matrix.}$$

Then $X = TY$, and $X'M^{-1}X = Y'DY$.

$$dx_1\cdots dx_m = |J(x,y)|\;dy_1\cdots dy_m$$
$$= |T|\,dy_1\cdots dy_m = dy_1\cdots dy_m$$

since T is orthogonal. It follows that

$$1 = C\underset{m}{\int_{-\infty}^{+\infty}}\exp\left[-\tfrac{1}{2}(d_{11}y_1^{2} + \ldots + d_{mm}y_m^{2})\right]dy_1\cdots dy_m$$
$$= \frac{C(2\pi)^{\frac{1}{2}m}}{(d_{11}\cdots d_{mm})^{\frac{1}{2}}} = \frac{C(2\pi)^{\frac{1}{2}m}}{|D|^{\frac{1}{2}}}$$

But $|D| = |M^{-1}|$, and therefore $C = \dfrac{|M^{-1}|^{\frac{1}{2}}}{(2\pi)^{\frac{1}{2}m}}$

In general, it will also be interesting to report a moment matrix for parameters other than those chosen for the adjustment. If these may be expressed as a linear combination of the parameters used in the adjustment[*]

$$Y_{pl} = R^{o}_{pl} + R_{pm}X_{ml}$$

then the following relation holds:

$$M_Y = RM_XR'$$

It is also convenient in expressing results to define a correlation matrix, $C \equiv \{\rho_{ij}\}$, which will, of course, have diagonal elements equal to unity.

The moment matrix may be given the following physical interpretation. If a hyper-ellipsoid of standard deviation is defined in parameter space, its equation will be

$$(X-\overline{X})' M_X^{-1}(X-\overline{X}) = 1$$

---

[*] This assumption is one which is convenient to make also in deriving the coefficients for the observational equations, and it is just as valid as the assumption that the changes in the observables, F, are linear in the parameter increments, an assumption that is demanded by the application of a least squares procedure. Both assumptions are, in general, valid over the small range of parameter values in which the probability mass is concentrated.

Since this ellipsoid is difficult to visualize, it is instructive to consider its projection on the x_i, x_j plane, or, what is equivalent, to consider the case of two independent parameters, x_i and x_j. In this case, the latter equation reduces to

$$\frac{x_i^2}{\sigma_i^2} + \frac{x_j^2}{\sigma_j^2} - \frac{2\rho_{ij}x_i x_j}{\sigma_i \sigma_j} = 1 - \rho_{ij}^2$$

with the origin taken at the point $(\bar{x}_i, \bar{x}_j)$. It is easily seen that the projections of this ellipse on the x_i and x_j axes are exactly equal to twice the corresponding marginal standard deviations. The lines denoted A and B in figure 11 are termed the regression lines of x_i on x_j and of x_j on x_i respectively. Their slopes are given by $\frac{1}{\rho_{ij}}\frac{\sigma_j}{\sigma_i}$ and $\rho_{ij}\frac{\sigma_j}{\sigma_i}$. For a given value of x_j, the most probable value of x_i is given by a point on A; a similar statement holds for x_i, x_j, and B. It is obvious that for a given x_j, the conditional standard deviation of x_i is less than σ_i. In a general sense, then, the correlation coefficients may be interpreted as giving the probable direction of an error in one parameter associated with a given error in another.

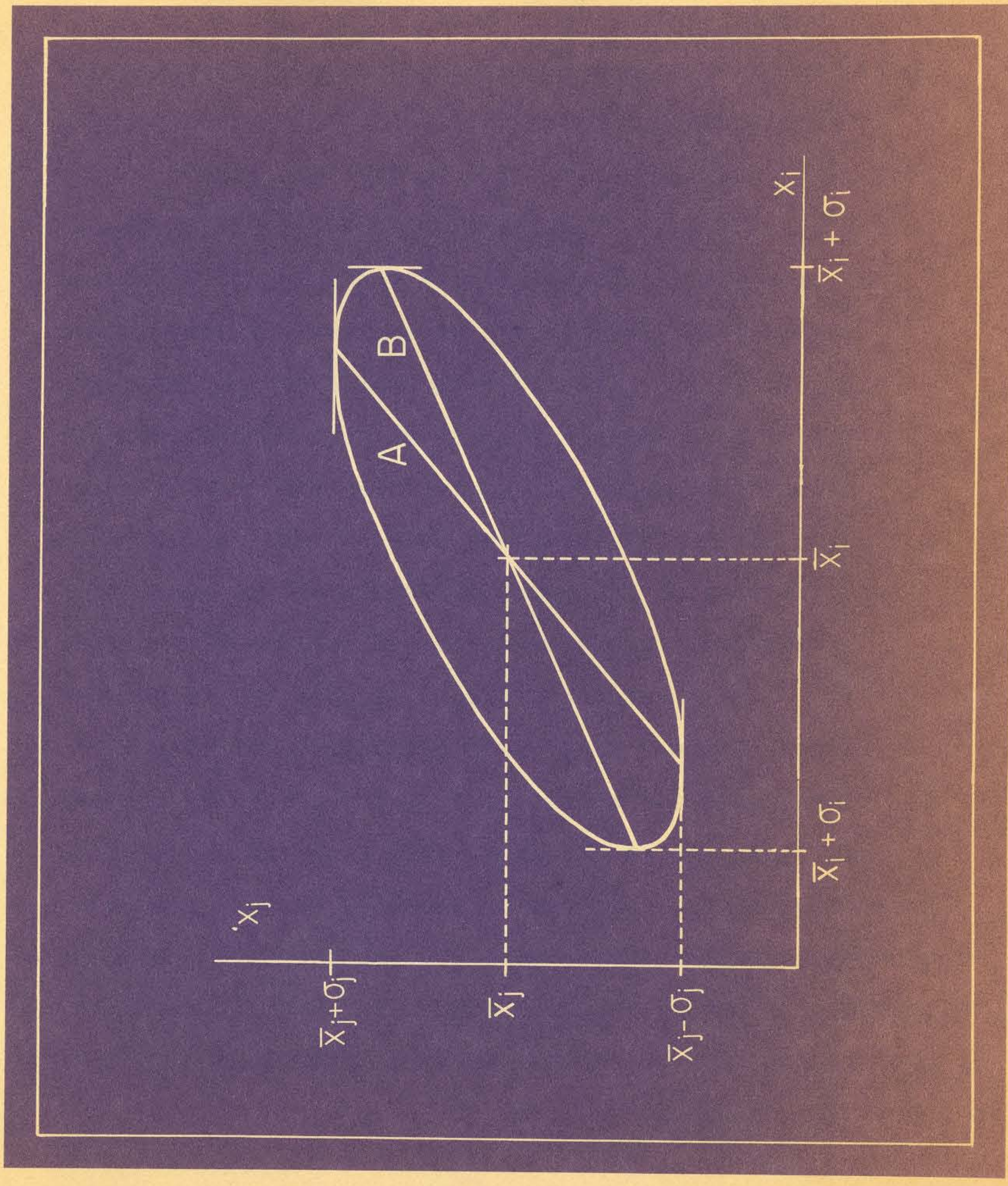

X_j
$\bar{X}_j+\sigma_j$
$\bar{X}_j$
$\bar{X}_j-\sigma_j$
A
B
$\bar{X}_i+\sigma_i$
$\bar{X}_i$
$\bar{X}_i+\sigma_i$
X_i

Figure 11

Associated with the ellipsoid of standard deviation are concentric ellipsoidal surfaces representing equi-probability surfaces for the determination. Use may be made of the matrix $B \equiv M^{-1}$ in determining on which probability surface a given model, with parameter values X_d, lies. If we define $(X_d-\overline{X})'B(X_d-\overline{X})$ as T^2, T^2 has the χ^2 distribution with m degrees of freedom, and the probability surface in question may be found by consultation of tables of χ^2. This calculation is of great convenience in determining the acceptability of various models, _e.g._, those from other methods of determination or those resulting from small changes in certain of the parameter values. This latter use will be illustrated in the discussions of bicycloheptadiene and bicyclo (2,2,2) octane.

It is interesting to note that if one diagonalizes the matrix M_X, that is, if one finds the orthogonal transformation such that $T\, M_X\, T'$ is diagonal, the variables $Z = TX$, linear combinations of the parameters used in the adjustment, will be experimentally independent quantities. These will have been determined independently of one another, and, as such, should be well suited toward reporting the results of an investigation. The variances of these parameters, Z, would be merely the eigenvalues of the matrix M_X, and the interesting geometrical constants of the molecule would have variances which could be expressed as sums of these eigenvalues. Although this diagonalization (reduction of the ellipsoid of error to normal form) would lead to an especially simple and clear method of expressing all the information derivable from the diffraction experiment, the considerable labor involved in the process (including the solution of a "secular equation" whose order is the number of parameters) makes it of doubtful value in most electron diffraction problems where it is necessary to use the least squares procedure. Much of the information which could be obtained in this way may be arrived at directly or indirectly from the other considerations detailed above.

Let us now proceed to the problem of deriving the observational equations from the visual electron diffraction data. The first step is the calculation of a theoretical curve which should represent the most reasonable assumptions as to the values of the structural parameters. These values will, in general, be derived from the radial distribution curve obtained from the visual curve by Fourier inversion (8).

This theoretical curve is the curve to be adjusted to fit the data, and it is important that it have parameter values near those of the correct model. The closer the first guess, the fewer adjustments necessary to give a satisfactory model with meaningful limits of error.

For each observation that we are able to make on the photographs, a function F may be defined (for computational simplicity, a function which may be represented as a linear combination of intensities at two or more values of q). The following examples may be given:

Type of Observation	F
Relative heights of maxima at q_1 and q_2	$I(q_1) - I(q_2)$
Same for three features	$\frac{I(q_1) + I(q_3)}{2} - I(q_2)$

For observations dealing with shift in position of maxima or minima, the function may be of the same type as the first listed in the table above, as expressions for the curvature near the points where $dI/dq = 0$ may be written in this form conveniently. It is also possible to define the function here merely as the position itself, q_{max} or q_{min}, but this necessitates calculation of complete theoretical curves when calculating increments due to individual parameters.

Now let $\Delta F = F_{obs} - F_{calc}$ be the change required to bring the feature on the theoretical curve into agreement with the observed feature. In this connection, it is well to remark that the visual curve, assumed to be plotted to the same scale as the theoretical, is used as a guide in placing the estimation of the ΔF's on the same relative scale. On no account, however, must one fall into the trap of taking the ΔF's as the exact differences between ordinates of the visual and theoretical curves.

Now, since $F = F(x_1, x_2, \cdots, x_m)$, where the x_i are the independent parameters chosen for the adjustment, we may immediately write the following:

$$\Delta F = \sum_{i=1}^{m} \frac{\partial F}{\partial x_i} \Delta x_i$$

and, since F was chosen as a linear combination of intensities,

$$F = a_1 I(q_1) + \cdots + a_k I(q_k)$$

$$\frac{\partial F}{\partial x_i} = a_1 \frac{I(q_1)}{x_i} + \cdots + a_k \frac{I(q_k)}{x_i}$$

The partial derivatives entering into the above equations are in practice approximated by the corresponding finite differences,

$$\frac{\partial I(q_k)}{\partial x_i} \approx \frac{I_{x_i+\delta x_i}(q_k) - I_{x_i}(q_k)}{\delta x_i}$$

These differences are to be calculated for δx_i small (usually 0.01 Å if x_i is a distance, which is most conveniently, but not necessarily, the case),holding all other parameters fixed. It is obvious that, in calculating these increments, changes in non-independent interatomic distances brought about by a change in x_i must also be included.

These differences are easily calculated by punched-card methods, using the same card file and methods used for the calculation of the theoretical intensity curves (18).

If it has been decided to use n functions, F, for the adjustment, there will be a set of n equations similar to (1) in the $m \leq n$ increments of the independent parameters. These n equations may be solved for the best values of the parameters as soon as weights have been assigned to them.

It is common practice in the visual technique to use information regarding relative intensities of three or four maxima or minima as well as relations between only two adjacent features. When both types of observations are made in deriving the observational equations, they are not likely to be independent; they are, on the contrary, observationally correlated. Thus, as we have seen, a non-diagonal weight matrix should be introduced. However, if use of a non-diagonal weight matrix is contemplated, the moment matrix for the observations must first be obtained. The correlation coefficients between the observed features must of course, in this application, be estimated; the near impossibility of accurate estimation here makes the use of a non-diagonal weight matrix unfeasible in our work. At the present time, then, it seems unrealistic to demand the use of such a procedure. Accordingly, it would seem desirable to limit errors by some other method, for example, by having each observation made by an independent observer, as the problem does not arise if the observations are really made independently of one another. As this is obviously impractical, in making observations which are likely to be correlated, one should attempt to estimate desired changes in the curve forgetting completely the numbers which have been assigned to any closely related features. In cases where this is nearly impossible, and two observations of different features give exactly the same information with the same weight, i.e., if the correlation coefficient is practically unity, one of these should be discarded. The following discussion will be limited to uncorrelated observations.

The assignment of weights to the observational equations is the most difficult step in the application of the least squares method to visual electron diffraction data, primarily because the data in general do not include the measures of standard deviation for a single measurement which are commonly used for weight assignment in most other problems. In examining the functions F which have been defined above it is easily seen that the observations on which they are based will have been made with different degrees of confidence. In an attempt to translate this into a quantitative expression, the most reasonable method would seem to be the following. Estimates of the deviation to be allowed in ΔF are made from observations on the photographs, i.e., observation of maximum and minimum acceptable values of ΔF are made at the same time as estimated desired values of ΔF. The weights are then chosen as the reciprocals of the squares of these allowed deviations.

The above method seems to be satisfactory for the qualitative observations, but a different approach is needed for observations of position. In general, it is probably acceptable to determine the weights for such observations on the same basis that the weights are chosen for finding the mean value of q/q_o in the usual adjustment of scale parameter. Such items as standard deviation of measurements for a single feature, position of the feature in the pattern, and symmetry of the feature may be taken into consideration. However, trial and error may have to determine the weights of the positional observations in relation to the weights of the qualitative features.

It should be pointed out that the decision as to whether a weight assignment is reasonable should be made on the basis of the so-called w^2 test. The observational equations are divided into groups, e.g., maxima *vs.* minima, qualitative *vs.* positional, symmetrical features *vs.* unsymmetrical etc. For the two groups, the estimated sample variance, $s_i^2 = \frac{V_i' P_i V_i}{n_i - m}$ is computed. For the two groups to be compared, the quotient $\omega^2 = s_1^2/s_2^2$ is calculated. Selecting a level of significance, α , the appropriate value of

w^2 is obtained from a table of such values* and compared with ω^2. Since $P(\omega^2 < w^2) = 1-\alpha$, the weighting is said to be reasonable if $\omega^2 < w^2$. In short, the criterion is that the differences in variances calculated for the several sub-samples shall not be statistically significant. If the weighting is found to be unreasonable for a group of features by this criterion, the weights for this group should be multiplied by a constant factor and another least squares adjustment carried out.

The question now arises as to what is the most reasonable adjustment of weights to be made. Let us assume that we have n measurements, x_{ij}, of a quantity with unknown value x_o. Furthermore, let these n observations be divided into m groups of size n_i, such that $\sum_{i=1}^{m} n_i = n$. Let these groups be selected from populations with identical mean but different variances, σ_i^2.

$$\begin{array}{llll} x_{11} & x_{12} & \cdots & x_{1n_1} \\ x_{21} & x_{22} & \cdots & x_{2n_2} \\ \vdots & & & \\ x_{m1} & x_{m2} & \cdots & x_{mn_m} \end{array}$$

---

*Tables of w^2 for several levels of significance and degrees of freedom are to be found in numerous compilations of statistical tables, e.g., (19, 16).

We wish to determine the appropriate weights for the m groups relative to one another. We define the following quantities:

$$E(x_{ij} - x_o) = 0$$

$$E(x_{ij} - x_o)^2 = \sigma_i^2$$

$$\mu = \frac{\sum_{ij} w_i x_{ij}}{\sum_i w_i n_i} = \frac{\sum_i w_i n_i \mu_i}{\sum_i w_i n_i}$$

$$\mu_i = \frac{1}{n_i} \sum_j x_{ij}$$

$$s_i^2 = \frac{1}{n_i} \sum_j (x_{ij} - \mu_i)^2$$

$$S_i^2 = \frac{1}{n_i} \sum_j (x_{ij} - \mu)^2$$

$$\mathcal{E}_\mu^2 = E(\mu - x_o)^2 = \frac{\sum n_i w_i^2 \sigma_i^2}{(\sum_i w_i n_i)^2}$$

The problem is to determine the w_i for the various blocks such that $\mathcal{E}_\mu^2$ is minimized. In order to minimize $\mathcal{E}_\mu^2$, one finds that

$$w_i = \frac{\mathcal{E}_\mu^2 \sum w_i n_i}{\sigma_i^2} = \frac{K}{\sigma_i^2}$$

Now in practice, the σ_i^2 are not known, but are only estimated by $\frac{n_i s_i^2}{n_i - m}$. A point which is not commonly realized, and is to our knowledge not mentioned in even the advanced standard texts on statistical treatment of data, is that an unbiased estimate of the weight is not given by $\frac{n_i-m}{n_i}\,\frac{1}{s_i^2}$, but rather by a factor which differs markedly from this for small values of n. If it is assumed that the errors, $(x_{ij}-x_o)$, are normally distributed with mean 0 and second moment σ_i^2, then s_i has the following distribution where m is the number of degrees of freedom; the subscript i is dropped for convenience.

$$yds = Cs^{n-m-1}\exp(-ns^2/2\sigma^2)ds$$

where

$$C = \frac{n^{\frac{1}{2}(n-m)}}{\Gamma(\frac{n-m}{2})\;2^{\frac{1}{2}(n-m-2)}\;\sigma^{n-m}}$$

Then

$$E(1/s^2) = C\int_0^\infty \frac{1}{s^2}\,s^{n-m-1}\exp(-ns^2/2\sigma^2)ds$$

$$= \frac{n}{n-m-2}\;\frac{1}{\sigma^2}$$

Thus, an unbiased estimate for w_i is

$$w_i \approx \frac{n_i-m-2}{n_i}\cdot\frac{K}{s_i^2}$$

and <u>not</u>

$$\frac{n_i-m}{n_i}\cdot\frac{K}{s_i^2}$$

This gives us an unbiased estimate of w_i, but at first sight does not avoid the possibility of assigning infinite weight to a group if by chance s_i^2 is 0 for that group. Although this would be an extremely exceptional occurrence, in this exceptional case, one should be somewhat skeptical of the results[*].

We now wish to consider the proper weights to be assigned if the residuals from the grand mean of the unweighted values are to be used, i.e., S_i^2. It is easily shown that $S_i^2 = s_i^2 + (\mu - \mu_i)^2$. Therefore, we may substitute in the last equation on the previous page to obtain

$$w_i \approx \frac{n_i - m - 2}{n_i} \; \frac{K}{S_i^2 - (\mu - \mu_i)^2}$$

In general, however, we will not know $(\mu - \mu_i)^2$, nor its distribution, and therefore an unbiased estimate of w_i cannot be easily obtained by this method. However, for practical use we may disregard $(\mu - \mu_i)^2$, which will usually be considerably less than S_i^2, and arrive at reasonable, if not unbiased, estimates of weights.

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[*] This is essentially the same problem which always arises in statistical inference from small samples.

The error in adjustment of weights will always be one which gives less than the correct weight to a group with an initial low weight, but the correction will be in the right direction. If the weights arising from the first adjustment appear to be too far in error by the aforementioned w^2 test, an iteration of the process is in order.

In reporting the results of an investigation, we believe that the errors should be expressed merely by reporting the standard deviations and correlation matrix. However, it may be of interest to attempt an explanation, in terms of the standard deviations, of the limits of error commonly reported in investigations from these laboratories. It is common in statistical analyses to consider the 5% tolerance limit as the limit of acceptance of data, i.e., a is chosen such that $P\left\{(x-\bar{x}) > a\sigma\right\} = 0.05$; this corresponds to a = 1.96. Thus, on this basis a reasonable limit of error to be reported might be twice the standard deviation. Our experience in application of the method of least squares indicates that the limits commonly reported from this laboratory are, on the average, just about twice the standard deviation to be expected from a least squares treatment. Thus, plots of regions of acceptability have probably been approximately plots of the 5% error contour.

Since the errors expressed in the moment matrix represent only the errors arising from the least squares adjustment, it is necessary in reporting final estimated errors to include experimental errors which do not affect the observational equations as here derived. These are largely errors in the q-scale of the intensity curve, arising from errors in wave-length determination, camera length, film diameter and non-random errors in ring measurement. It has been estimated that these errors collectively correspond to a $\sigma_{\text{scale}} = 0.004$ for the apparatus which has been used in these laboratories. Consequently, to obtain the estimated total errors in distances, $\sigma^2_{\text{total}} = \sigma^2_{\text{least squares}} + r^2\sigma^2_{\text{scale}}$ must be calculated, the justification for this being based on the assumption that the covariance of the two errors is 0. It is to be noted, however, that this is to be done only for errors in distances, as the errors in angle are independent of scale. The probability mass for a parameter set involving both distances and angles may then be no longer represented as a quadratic form, and a quadratic correlation matrix can no longer be defined.

III. Some Structural Studies by the Electron Diffraction by Gas Molecules.

A. The Molecular Structure of Bicycloheptadiene

As an example of the use of the least squares method, bicycloheptadiene (C_7H_8, figure 12), a compound of interest as a highly-strained cyclic hydrocarbon, was chosen. The carbon skeleton has five independent shape parameters, ordinarily too many to permit ready analysis by the correlation procedure. It should thus provide a good test of the efficacy of the least squares method as applied to visual electron diffraction data.

The photographs were prepared, a visual intensity curve drawn, and a radial distribution curve calculated by the usual methods (20). The camera distance was 10.880 cm. and the electron wave length, 0.06056 Å. Visual intensity data extended to $q = 100$. The first three peaks in the radial distribution curve (figure 13) may be ascribed to bonded C-H, C=C, and C-C, respectively. The sharp peak at 2.30 Å must represent an average of terms similar to C_1-C_5, C_2-C_7, C_2-C_6, and C_1-C_4, all of which must be nearly equal due to the sharpness of the peak. A number of unbonded C-H terms account satisfactorily for the small shoulder on the inside of this peak, while longer

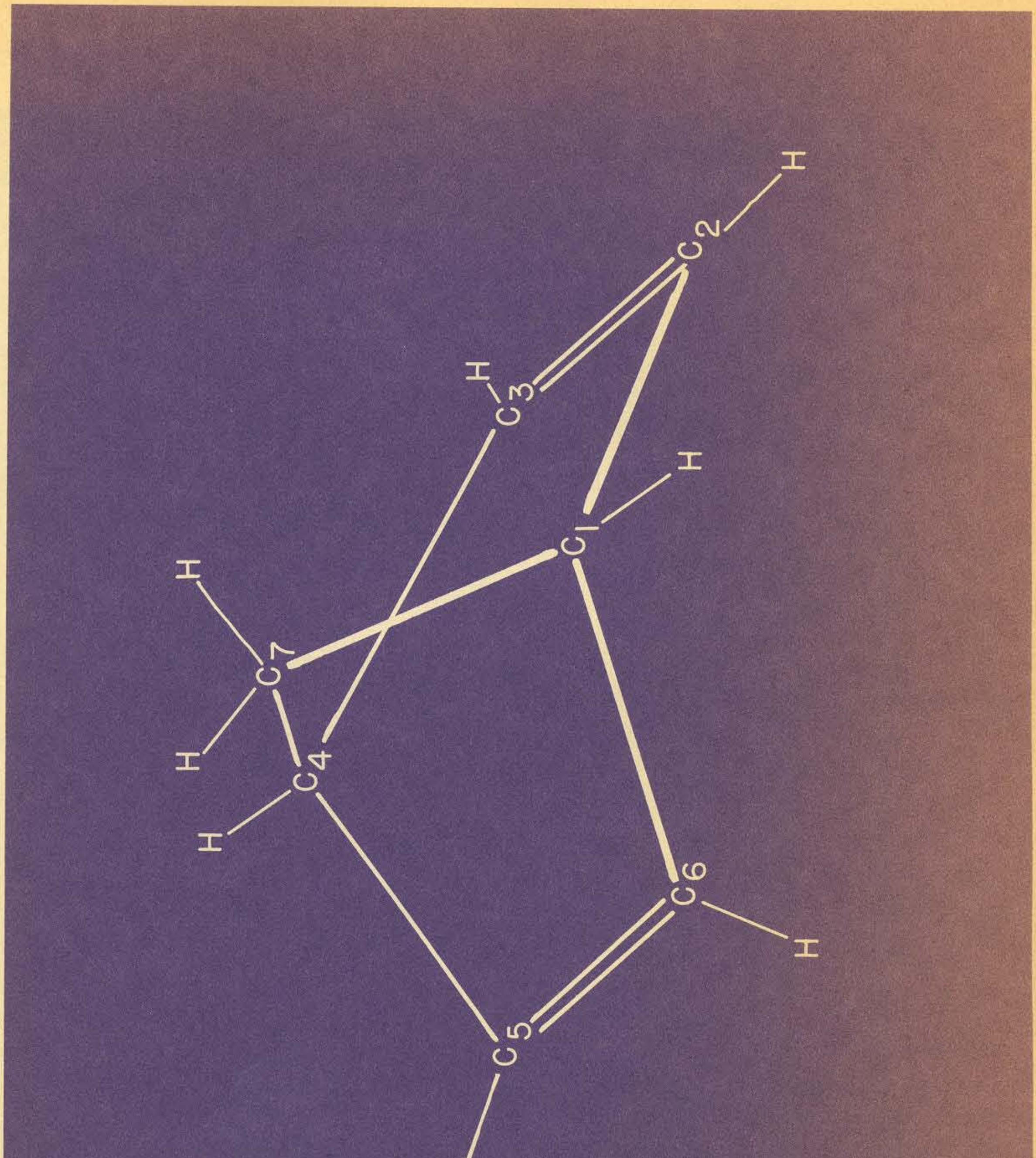

Figure 12

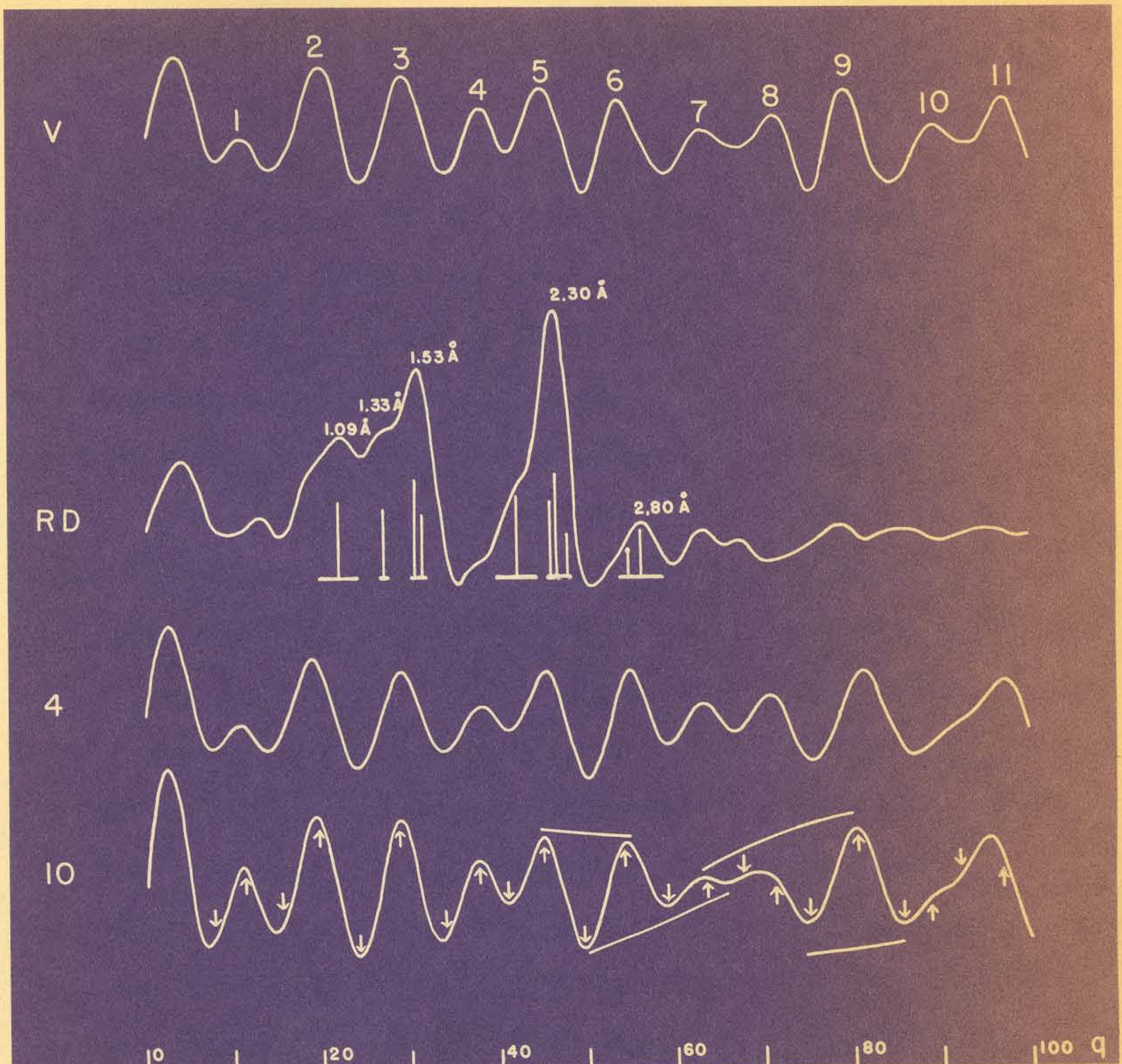
V
1
2
3
4
5
6
7
8
9
10
11
RD
1.09 Å
1.33 Å
1.53 Å
2.30 Å
2.80 Å
4
10
0
20
40
60
80
100
q

Figure 13

C-H terms and the long C_2-C_5 must fall under the smaller peak further out.

Because of the sharpness of the peak representing most of the cross-ring C-C distances, the choice of an initial model was greatly simplified. However, several theoretical curves were calculated in an attempt to obtain one as close to the visual as possible for the initial least squares adjustment. C_{2v} symmetry was assumed throughout. All C-H bond lengths were taken as 1.09 Å and H-C-H angles were chosen to minimize the angular strain about each carbon atom. Any errors in these assumptions on hydrogen positions are likely to be small, and any deviations from the assumed values should have little effect on the determined parameter values for the carbon skeleton. All models were calculated including the non-bonded C-H interactions, but no attempt was made to include these as parameters in the subsequent least squares adjustments. From past experience, it is known that, because of low weights and heavy temperature factors for the parameters fixing hydrogen positions, large variations in the choice of these parameters have but little effect on the choice of the best model. In calculation of the theoretical intensity curves, $\underline{a}$ in the factor $\exp(-aq^2)$

was taken as 0.00016 and 0.00030 for the C-H and C···H distances, respectively, in accord with past experience, and zero elsewhere.

Model 4 (see table IX) was chosen as the most satisfactory of the initial curves, and a preliminary least squares was carried out on it, omitting measurements of position. The increments in C_1-C_2, C_1-C_4, C_1-C_7, C_2-C_3 and C_2-C_7 were taken as the independent parameters. Details of this adjustment need not be given. The resulting model 10 was used as a basis for the final adjustment, some details of which will be given in order to illustrate by a concrete example some of the points brought out in the discussion of the least squares method.

A complete set of observations was made on the photographs, and the results of these observations and the calculated increments for parameter changes (in units of 0.01 Å) were translated into the mathematical language necessary for the adjustment. It should be pointed out that, although a visual curve was drawn (figure 13), it was used primarily as a reminder of the actual observations made on the photographs and as a guide in placing the Δ F's on somewhat of a relative scale. It is important that the observational equations represent as nearly as

Table IX

Distance	Model 4	Model 10	Final Model
C_1-C_2	1.50	1.53	1.522
C_1-C_3	2.31	2.34	2.328
C_1-C_4	2.35	2.34	2.329
C_1-C_7	1.54	1.55	1.558
C_2-C_3	1.32	1.34	1.333
C_2-C_6	2.32	2.41	2.370
C_2-C_5	2.67	2.76	2.719
C_2-C_7	2.24	2.28	2.296

possible the actual observations on the photographs rather than direct measurements on the visual curve, which contains many assumptions and inaccuracies.

All two-fold and three-fold qualitative observations were made and incorporated into the observational equations along with the position measurements for all features. There were a total of sixty such equations, thirty-eight qualitative and twenty-two positional. The actual numerical values entering the equations need not be recorded here. Their nature is indicated satisfactorily in figure 13[*], Weights assigned these equations ranged from 1 to 4[**]. The normal equations were derived, and the best parameter values and moment matrix were calculated as previously outlined. The increments, standard deviations, moment matrix, and inverse moment matrix are given in table X.

In a similar manner, a moment matrix and correlation matrix were derived for all bond distances

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[*] The critical marks on curve 10 have been proposed by Sheehan and Schomaker (21).

[**] An initial adjustment on this model showed positional features to be weighted too highly by the w^2 test, and an adjustment of these weights was made before the least squares adjustment here described.

Table X*

Parameter Increments and Moment Matrix

Number	Parameter	Increment	σ
1	C_1-C_2	-0.008 Å	0.009 Å
2	C_1-C_4	-0.011	0.028
3	C_1-C_7	0.008	0.015
4	C_2-C_3	-0.007	0.006
5	C_2-C_7	0.016	0.012

$M \times 10^4$

	1	2	3	4	5
1	0.806	0.876	-1.040	-0.159	-0.236
2		7.906	-1.854	-0.132	1.585
3			2.213	0.020	0.545
4				0.404	0.117
5					1.255

$M^{-1} \times 10^{-4}$

	1	2	3	4	5
1	4.256	0.300	2.407	-2.465	-0.816
2		0.459	-0.739	0.688	0.904
3			2.607	-2.200	-1.785
4				5.837	1.834
5					2.716

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*Both M and M^{-1} are symmetric about the main diagonal.

and angles. Final values for distances and angles, their standard deviations (corrected for scale error in the case of distances) and 5% limits of error are given in table XI along with the corresponding correlation matrix*. The correlation coefficients are seen to agree well with what is to be expected from the nature of the electron diffraction problem, as well as from the geometry of the molecule. Thus, there is a high negative correlation coefficient for the two single bond distances, so that the average must remain about the same with changes in either of them. The correlation coefficients for the double bond distance and the single bond distances are small. It must be remembered that there are certain geometrical correlations, as well as correlations introduced by the scattering formula, so that a completely naive discussion on the separation of distances in the radial distribution curve alone cannot be quantitatively accurate.

As an example of the use of the inverse error matrix B, it is interesting to calculate the probability contour on which a model, having all

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*As there are here more than the number of linearly independent quantities, the moment matrix is singular, and the quadratic form is degenerate. However, the correlation coefficients still have meaning.

Table XI

Final Parameters and Correlation Matrix

Number	Parameter	Best Value	σ	5% Limit
1	C_1-C_2	1.522 Å	0.011 Å	0.022 Å
2	C_1-C_7	1.558	0.016	0.032
3	$C_2=C_3$	1.333	0.008	0.016
4	$\measuredangle C_1-C_2=C_3$	109.1°	0.35°	0.70°
5	$\measuredangle C_2-C_1-C_7$	96.4	0.65	1.30
6	$\measuredangle C_1-C_7-C_4$	96.7	2.30	4.60
7	$\measuredangle C_6-C_1-C_2$	102.2	5.75	11.50

C

	1	2	3	4	5	6	7
1	1	-0.78	-0.28	-0.17	-0.08	0.62	-0.22
2		1	-0.23	-0.16	-0.16	-0.82	0.39
3			1	-0.69	0.30	0.03	-0.09
4				1	0.43	0.16	-0.36
5					1	0.54	-0.90
6						1	-0.81
7							1

parameters as in the best model but with the C-C bond distances equal at the average of the two, would lie. By the method previously described (using the matrix $B \equiv M^{-1}$ for the five parameters used in the adjustment), such a model was found to lie on the 35% contour. The interpretation is that such a model would be completely acceptable, as it lies within the 5% limit, but there is some indication of a split in these distances. Some justification for the belief that the 5% limit corresponds closely to limits estimated by the correlation method is found in the fact that model 10, which was judged to be a borderline case, lies on the 4% contour by the above calculation. Similar justification has been found in a least squares treatment of formyl fluoride by Jones (22).

The bond angles and distances found can be satisfactorily explained by a simple valence force potential expression. Assuming the bond distances to be those found experimentally, strain energies were calculated for a wide range of models with varying angles by the expression

$$U = \frac{1}{2}\sum_{i} k_i(\theta_i^o - \theta_i)^2$$

where θ_i^o is equal to the normal value for the bond angle, Θ_i is the value for a particular model, and k_i is the bending force constant for the angle. There are two principal uncertainties in such a calculation: The values to be used for the force constants and the value of the normal C-C=C angle. Calculations were carried out for the values of these constants given in table XII. The normal single bond angle was taken as tetrahedral for all models. Units of force for A, B and E are on no absolute scale, but represent only ratios of the various force constants. Values for model F are actual force constants in units of 10^{-11} dyne-cm-radians^{-2} for propane (23), isobutane (24), and propene (25). Ratios for model E were based on the assumption that $k_{123}/k_{174} = 1.5$ from the values for propane and propene, and that $k_{174}/k_{217} = 0.6$ as assumed by Heilbronner and Schomaker in a discussion of nor-tricyclane (26). Models A & B, calculated on the basis of the rather naive assumption that all force constants were equal, were initially studied to test the applicability of the method and to study the variation of the potential minimum with variation in the normal single-bond double-bond angle.

Potential energy values were plotted as equipotential contours as functions of two independent angles, C_1-C_2-C_3 and C_2-C_1-C_7. The contours

Table XII

Assumed Constants for Strain Energy Calculations

Model	k_{174}	$k_{217} = k_{612}$	k_{123}	θ_{123}°
A	1.00	1.00	1.00	125°
B	1.00	1.00	1.00	120
E	0.50	1.00	0.90	125
F	0.78	1.09	1.20	125

for model F, the most favorable, are shown in figure 14a. The contours are drawn at intervals of 0.0025 x 10^{-11} dyne-cm (0.36 kcal/mole). The position of the potential energy minimum for the different models varied over a range of about three degrees in C_2-C_1-C_7, but all values lay approximately on a straight line which also passed through the experimental point (figure 14b). In each case, the experimental point lay within the first contour line, and the minima of models A and F were well within the error ellipse for the experimental model. Thus, despite the uncertainties in the force constants, the agreement with experiment is gratifying. For the minimum in model F, which almost coincided with the experimental model, the strain energy due to angle deformation alone was calculated to be 0.335 x 10^{-11} dyne-cm or 48.3 kcal/mole.

Using the same force constants as in model F, but taking the single-bond C-C distance as 1.54 Å for both bonds, a calculation similar to the one above was carried out*. The minimum was found at

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*The C=C distance was kept at 1.333. As this is the normal value for this bond within experimental error, and since the force constant for C=C stretching is considerably greater than that for C-C, it is reasonable to assume that any lessening of strain will come about through changes in single-bond lengths.

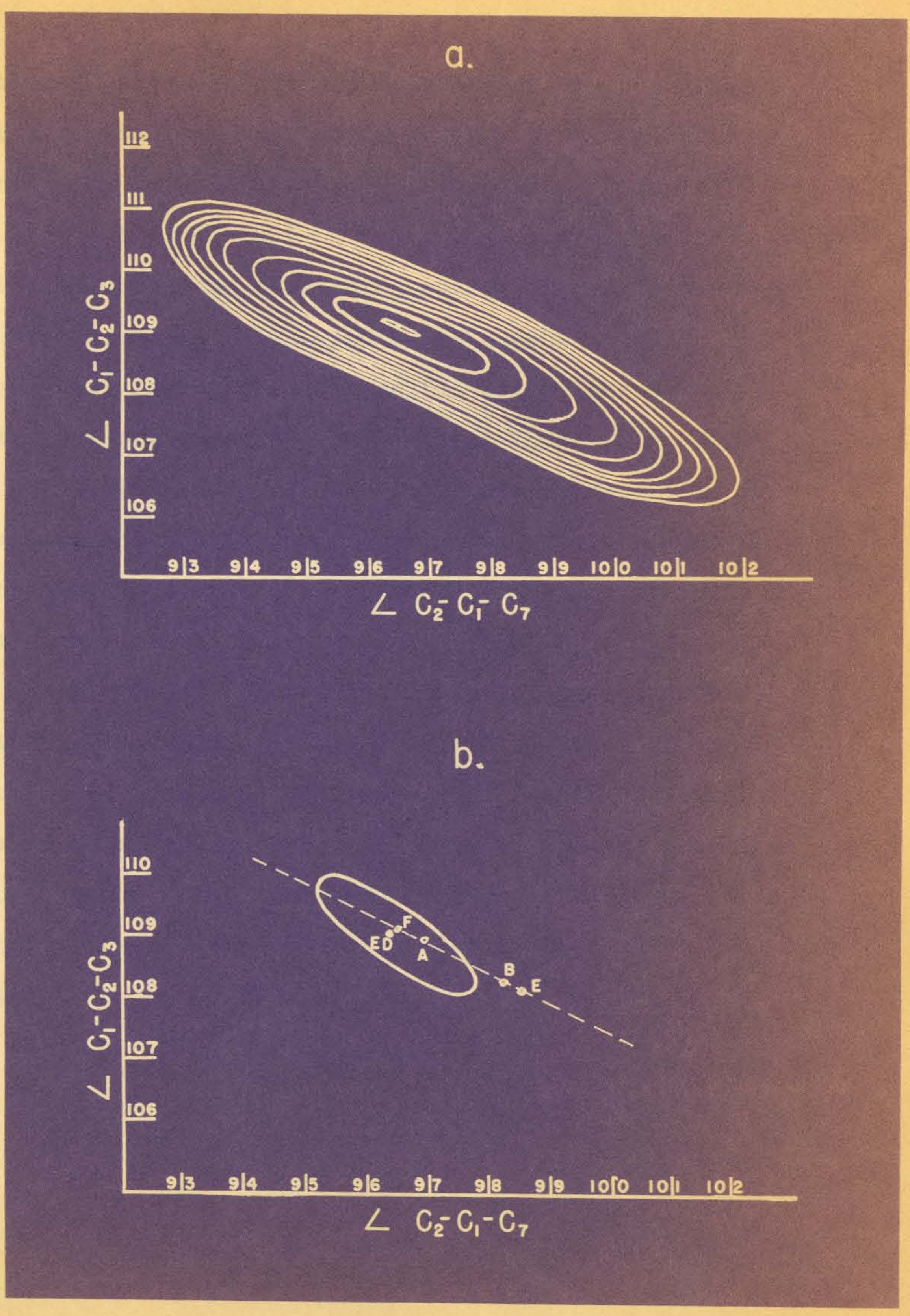
a.
112
111
110
109
108
107
106
∠ $C_1-C_2-C_3$
93
94
95
96
97
98
99
100
101
102
∠ $C_2-C_1-C_7$
b.
110
109
108
107
106
∠ $C_1-C_2-C_3$
F
E
D
A
B
E
93
94
95
96
97
98
99
100
101
102
∠ $C_2-C_1-C_7$

Figure 14

point G, which is not shown in the figure but lies midway between points A and F; the energy value at this minimum was 0.341 x 10^{-11} dyne-cm. Assuming a stretching constant of 4.5 x 10^{5} dyne/cm for the single bonds, the stretching energy for the experimental model is calculated to be 0.0045 x 10^{-11} dyne-cm. Making this correction brings the total strain energy for the experimental model up to 0.339 x 10^{-11} dyne-cm, a value which differs insignificantly from the value for the model with normal bond lengths, so that the experimental model is at least as stable as this.

In summary, the angles found in the molecule fit nicely those expected from minimization of the potential function, while the bond length splitting leads to a strain energy which is no greater than that for a model with equal bond lengths. The total strain energy for the experimental model is 0.34 x 10^{-11} dyne-cm or 49 kcal/mole.

B. The Molecular Structure of Bicyclo (2,2,2) octane

In connection with other work being done on cyclic hydrocarbons in these laboratories, it was felt that an investigation of the molecular structure of bicyclo (2,2,2) octane (figure 15) was in order, the amount of twist about the threefold axis being of particular interest. A recent interpretation (27) of the microwave spectra of the mono-bromide and chloride indicates that the angle of twist is 0 ± 4° and that the C-C bond length is 1.545 Å, all angles being approximately tetrahedral.

Electron diffraction photographs were prepared in 1950 by K. Hedberg and E. Heilbronner. Visual data extended to $q = 100$. The photographs were measured, a visual curve drawn, and a radial distribution curve calculated. The procedure was that commonly used in these laboratories (20). The radial distribution curve (figure 15) is approximately that predicted for a non-twisted model with a C-C bond distance of 1.52 Å and all angles tetrahedral. A theoretical intensity curve calculated for such a model gave quite good agreement with the visual. C-H was assumed to be 1.09 Å, and all non-bonded C-H interactions were included. In the

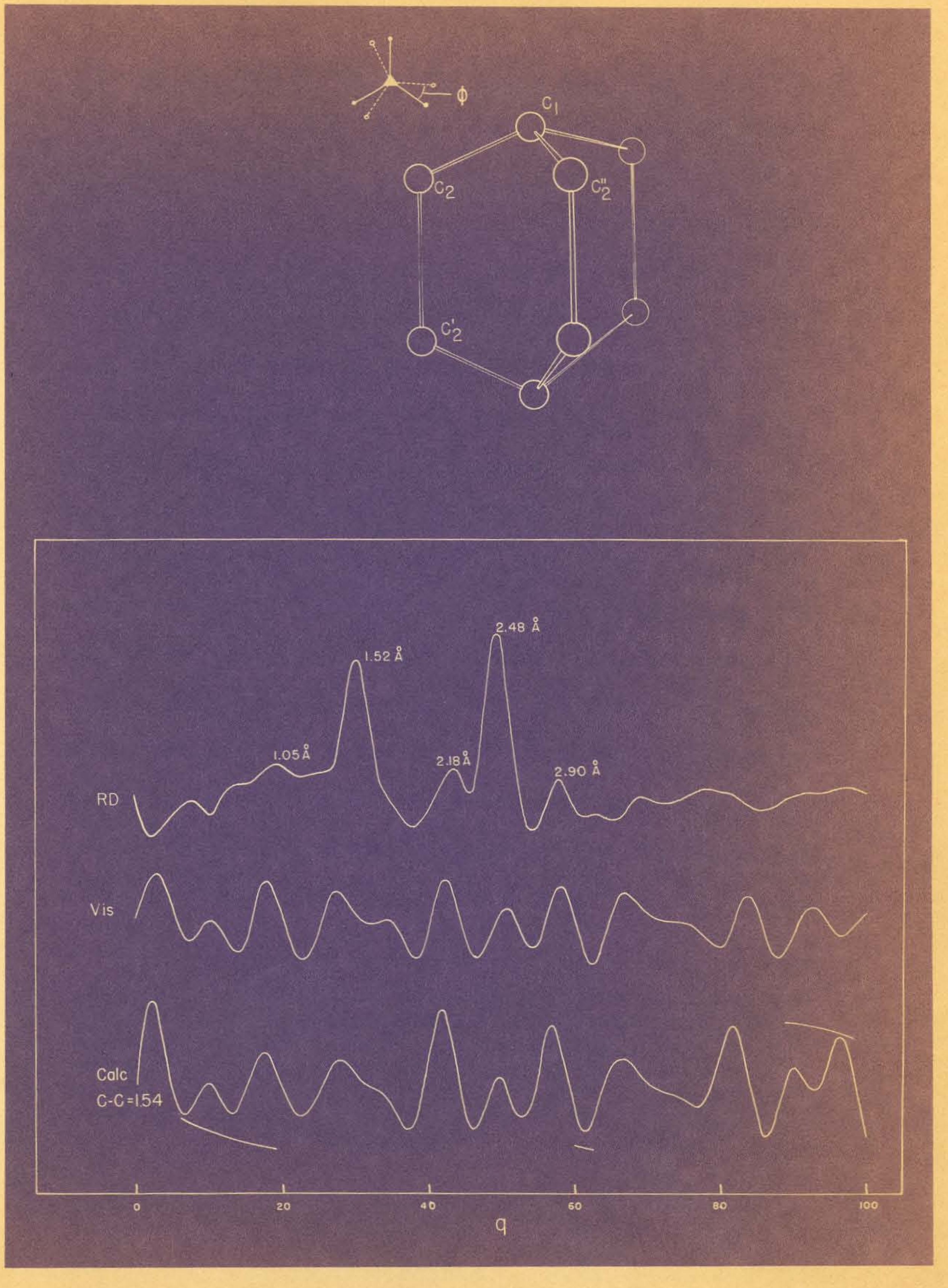
φ
C_1
C_2
C_2''
C_2'
2.48 Å
1.52 Å
1.05 Å
2.18 Å
2.90 Å
RD
Vis
Calc
C-C=1.54
0
20
40
60
80
100
q

Figure 15

expression $\exp(-aq^2)$, a was given the values 0.00016 for bonded C-H, 0.00030 for non-bonded C-H, and zero elsewhere.

In order to determine what changes in the model would improve the agreement, but principally to determine estimated errors, a least squares procedure was used. Parameters chosen for adjustment were $P_1 = C_1-C_2$, $P_2 = C_2-C_2'$, $P_3 = C_2-C_2''$, and $P_4 = \phi$. Initial values for these parameters were 1.51, 1.51, 2.47 and 0°. All two-fold and three-fold qualitative observations were entered into the adjustment, along with only those positional features which were not scale factor dependent alone. The increments in the distances were taken as 0.01 Å and the increment in the twist angle as 10°*. Forty qualitative and fifteen positional observational equations were used. The analysis was carried out in the usual way with the results given in table XIII. As the values

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*An initial adjustment was made with an increment of 1°, and a change of about 10° was indicated. The standard deviation was, however, also large. For this small increment, certain of the cross-ring terms which are twist-sensitive could not be accurately entered, so it is believed that the value given by the 10° increment has more meaning.

Table XIII

Parameter Increments

Parameter	Increment	σ	Adjusted Value
P_1	0.005 Å	0.007 Å	1.515 Å
P_2	-0.005	0.009	1.505
P_3	-0.003	0.007	2.467
P_4	1.6°	2.8°	1.6°

for the C-C bond lengths seemed to be abnormally short, it was decided that preparation of new diffraction photographs would be in order. These were prepared on the new apparatus recently built in these laboratories, using a wave length of about 0.062 Å and a camera distance of 9.628 cm. The photographs were identical with the older ones in all qualitative features, although they extended to a wider scattering angle ($q \approx 120$) and permitted more accurate analysis of the last two maxima shown in the curves in figure 15; these maxima bear more nearly the relationship found in the theoretical curve than previously assumed for the visual curve. A weighted average of q_{calc}/q_{obs} was found to be 1.020 ± 0.007, and the scale of the entire model was consequently changed by 2%. The best values for the bond lengths and angles together with a correlation matrix are given in table XIV; the standard deviations for the distances have been corrected for an estimated scale standard deviation of 0.004.

Since the changes in all the parameters are small, it is apparent that the original model (except for scale) must be regarded as acceptable. Indeed, the completely symmetric model with a C-C bond length of 1.540 Å lies on the 75% probability contour. The

Table XIV

Final Parameter Values

Number	Parameter	Value	σ
1	C_1-C_2	1.543 Å	0.009 Å
2	C_2-C_2'	1.533	0.011
3	$\measuredangle C_2''$-C_1-C_2	109.0°	1.2°
4	$\measuredangle C_1$-C_2-C_2'	109.7°	0.6°
5	ϕ	1.6°	2.8°

Correlation Matrix

	1	2	3	4	5
1	1	-0.95	-0.77	0.92	-0.21
2		1	0.67	-0.78	0.12
3			1	-0.50	-0.18
4				1	-0.71
5					1

model with no twist, but with the split in bond distances, lies on the 95% contour, and we may say with certainty that there is negligible probability of the twist being greater than 6°. There is slight indication that the molecule is stretched along the threefold axis, but, as noted above, the model with normal bond angles and equal distances lies well inside the 5% limit. The agreement with the microwave determination may be considered to be satisfactory.

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A Reinvestigation of the Structure of Difluoromethane by Electron Diffraction

By Walter C. Hamilton and Kenneth Hedberg

Received June 19, 1952

An early electron-diffraction investigation[1] of the structure of difluoromethane led to the parameter values C–F = 1.36 ± 0.02 Å., ∠ F–C–F = 110 ± 1°, C–H = 1.06 Å. (assumed) and ∠ H–C–H = 109° 28′ (assumed). Recently, an analysis of the infrared spectrum[2] of this substance, based upon the approximate symmetric top character of the molecule, led to two rotational constants and the parameter values C–F = 1.32 ± 0.01 Å., ∠ F–C–F = 107.0 ± 0.5°, C–H = 1.094 Å. (assumed) and ∠ H–C–H = 110° (assumed). Because of the serious discrepancies between the results of these two methods for the principal parameters (which cannot, of course, be explained by the difference between the assumed values for the remaining parameters), it seemed that a reinvestigation of the structure was in order.

The sample of difluoromethane, supplied by the Jackson Laboratory of the du Pont Co., contained 0.2–0.3% fluoroform and 0.05% chlorodifluoromethane. The camera distance was 10.91 cm. and the electron wave length 0.06056 Å. The methods used in the structure determination have been described elsewhere.[3]

Theoretical intensity curves were calculated over the shape parameter range C–F/F···F = 1.36/2.14 to 1.36/2.23, assuming C–H/C–F = 1.09/1.36 and ∠ H–C–H = 109°28′. All terms except H···H were included, and in the factor $\exp(-a_{ij}q^2)$, a was given the values 0.00016 and 0.00030 for the C–H and H···F distance, respectively, in accord with our experience, and zero elsewhere.[4]

It is our conclusion that the best agreement with the appearance of the photographs is given by a curve slightly closer to J than I (Fig. 1). The factors of particular importance for this decision are the characters of the doubled maxima 3–4, and 6–7, the position of maximum 9, and the relative depths of minima, 5, 6 and 8. Such qualitative considerations and comparisons of the observed and calculated positions of maxima and minima (see Table I for an example close to our final model) lead to the following values of the structural parameters: C–F/C–H = 1.36/1.09 (assumed), C–F = 1.35$_7$ ± 0.01$_7$ Å., ∠F–C–F = 107.5 ± 1.5°, ∠ H–C–H = 109.5° (assumed), symmetry C_{2v} (assumed). The effect of varying the H–C–H angle is small (compare curves I and L), and any possible error in the assumed value can have no significant effect upon the values of the determined parameters.

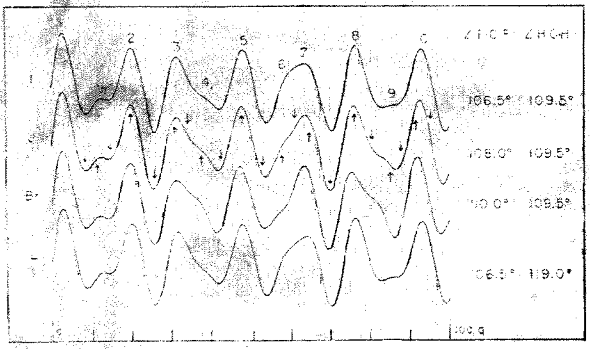

Fig. 1.—Difluoromethane: theoretical intensity curves.

TABLE I

COMPARISONS OF OBSERVED AND CALCULATED POSITIONS

Maxima and Minima (Curve J)

No.	Minima $Q_{\text{obsd.}}$[a]	Minima $Q_{\text{calcd.}}/Q_{\text{obsd.}}$	Maxima $Q_{\text{obsd.}}$	Maxima $Q_{\text{calcd.}}/Q_{\text{obsd.}}$
1	8.15	(1.067)	11.17	(1.083)
2	16.09	(0.928)	19.95	(0.995)
3	25.94	0.991*	31.02	1.017
4	34.26	1.036	37.69	1.008
5	42.67	0.980	47.84	0.997*
6	52.67	1.020	57.71	1.005
7	61.35	0.978	64.96	0.978
8	70.09	0.999*	76.19	.998*
9	80.46	1.007	85.05	.976
10	87.95	0.984	91.30	1.014
11	95.04	1.036		
Average 17 features		0.9990		
Average deviation		0.014		
Average 4 starred features		0.9963		
Average deviation		0.003		

Best model: C–F = 0.9980 × 1.36 = 1.35$_7$

[a] Average of W. H. and K.H. measurements.

Our results differ significantly from those of the early electron diffraction study in the value of the F–C–F angle, which we find to be more than 2° smaller. Our photographs, extending to a considerably larger scattering angle, presumably allow a more reliable interpretation of the difficult doublets 3–4 and 6–7 upon which the early angle determination was largely based as well as enabling us to see maximum 9, of which the position and degree of association with adjacent maxima are very F–C–F-angle sensitive. The C–F bond length result from the infrared investigation stands well outside our limit of error. It is to be noted, however, that the preliminary results of a recent microwave investigation[5] (which appeared during the course of our work) C–F = 1.36 Å., C–H = 1.09 Å., ∠ F–C–F = 108°, ∠ H–C–H = 112°, agree well with ours.

Acknowledgment.—We wish to thank Professor Verner Schomaker for his helpful comments regarding the interpretation of some of the more difficult features of the pattern.

Contribution No. 1702 from the
Gates and Crellin Laboratories of Chemistry
California Institute of Technology
Pasadena 4, California

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(1) L. O. Brockway, *J. Phys. Chem.*, **41**, 747 (1937).

(2) H. B. Stewart and H. H. Nielsen, *Phys. Rev.*, **75**, 640 (1949).

(3) K. Hedberg and A. J. Stosick, This Journal, **74**, 954 (1952).

(4) Some curves were calculated using values of $a_{F\cdots F}$ different from zero, however. It was concluded that $a_{F\cdots F}$ might be as large as about 0.00005 relative to a_{C-F} = 0, but that use of the value zero caused no error in the values of determined parameters.

(5) D. R. Lide, Jr., *Bull. Am. Phys. Soc.*, **27**, 51 (1952).

APPENDIX

Observed and Calculated Structure Factors for Dimethyl Phosphino-borine Trimer

A. Observed Reflections

Zone	k	l	$\|F\|_{obs}$	F_{calc}
0kl	0	2	49.00	52.70
	0	4	59.80	-75.01
	0	6	81.52	-83.70
	0	8	15.98	-11.75
	0	10	24.87	22.64
	1	1	4.24	- 2.42
	1	3	6.90	-13.59
	1	5	26.33	-23.02
	1	9	25.08	24.68
	1	11	14.68	14.47
	2	0	42.52	-57.68
	2	2	6.60	- 0.14
	2	4	22.60	25.79
	2	6	5.17	0.41
	2	8	23.37	-20.08
	2	10	6.43	- 2.61
	3	1	63.24	-96.19
	3	3	34.68	-51.60
	3	5	19.50	-18.08
	3	7	18.91	22.16
	3	9	18.26	14.85
	4	0	15.21	-23.84
	4	2	12.47	-23.18
	4	4	5.64	- 5.86
	4	6	35.99	41.76
	4	8	31.76	39.43
	4	10	6.21	- 7.06
	5	1	27.38	45.49
	5	3	36.00	49.11
	5	5	12.86	10.57
	5	7	21.57	-19.77
	5	9	11.89	-10.70

Zone	k	l	$\|F\|_{obs}$	F_{calc}
0kl	6	0	39.91	-49.59
	6	2	17.06	16.42
	6	4	9.90	12.10
	6	6	7.70	- 2.51
	6	8	14.10	-15.61
	7	1	1.73	- 3.89
	7	3	6.67	- 6.41
	7	5	16.80	12.32
	7	7	6.74	5.16
	7	9	11.38	-13.12
	8	0	82.84	104.81
	8	2	25.25	31.11
	8	4	33.61	-43.54
	8	6	45.21	-46.09
	8	8	5.97	- 5.11
	8	10	11.34	12.35
	9	3	24.10	-23.91
	9	5	17.38	-15.06
	9	9	15.56	15.53
	10	0	28.04	-27.06
	10	2	8.44	- 8.62
	10	4	18.35	19.29
	10	6	8.84	7.27
	10	8	9.85	- 8.64
	11	1	16.91	-22.51
	11	3	17.73	-22.08
	11	7	8.08	10.82
	12	0	15.09	-10.39
	12	2	15.41	-16.98
	12	6	19.65	19.51
	13	1	6.13	12.47
	13	3	17.68	21.48
1kl	0	1	59.80	56.61
	0	2	81.18	-96.17
	0	3	17.19	-14.37
	0	4	50.63	-53.06
	0	5	25.19	-21.27
	0	6	26.54	-17.01
	0	8	34.92	31.85
	0	9	12.89	8.93
	0	10	25.64	21.28

Zone	k	l	$\|F\|_{obs}$	F_{calc}
1kl	1	1	77.27	-101.57
	1	2	42.18	46.04
	1	3	32.73	25.05
	1	4	43.95	28.87
	1	5	55.94	55.69
	1	6	34.46	-29.47
	1	7	31.56	28.96
	1	9	10.18	- 7.49
	1	10	9.13	8.27
	1	11	12.21	-11.94
	2	1	44.83	-50.22
	2	2	26.21	-25.66
	2	3	12.97	1.56
	2	4	7.84	- 5.54
	2	5	37.14	33.57
	2	6	6.05	7.37
	2	7	11.69	-10.07
	2	8	4.45	7.53
	2	9	8.74	- 6.97
	3	1	52.50	-60.65
	3	2	33.35	-42.66
	3	3	4.33	- 9.26
	3	4	1.97	- 3.91
	3	5	16.02	17.35
	3	6	16.02	17.68
	3	7	41.87	43.16
	3	9	9.33	7.02
	3	10	10.10	-11.21
	3	11	14.89	-13.71
	4	1	6.52	2.07
	4	2	27.27	47.86
	4	3	7.46	0.31
	4	4	29.79	28.17
	4	5	19.14	-13.49
	4	7	24.19	23.63
	4	8	25.77	-25.09
	4	9	4.67	5.70
	4	10	13.65	-12.45
	5	1	31.58	34.87
	5	2	33.55	35.32
	5	3	15.32	16.12
	5	4	19.05	16.23
	5	5	21.26	-19.58
	5	6	21.98	-22.04
	5	7	33.37	-33.06

Zone	k	l	$\|F\|_{obs}$	F_{calc}
1kl	5	9	8.68	- 9.12
	5	10	8.25	7.93
	5	11	15.13	13.03
	6	1	25.20	-28.83
	6	2	16.68	-14.37
	6	3	11.98	10.97
	6	4	20.51	-15.69
	6	5	15.13	15.78
	6	6	12.54	11.16
	6	8	3.15	4.99
	6	9	6.37	- 7.85
	7	1	32.81	39.73
	7	2	13.58	-20.01
	7	3	11.07	-13.44
	7	4	9.60	-13.38
	7	5	22.32	-27.38
	7	6	18.88	20.41
	7	7	16.67	-15.44
	7	10	5.87	- 6.21
	8	1	18.69	24.44
	8	2	28.18	-31.71
	8	3	5.35	- 5.50
	8	4	31.44	-29.58
	8	5	16.98	-18.92
	8	6	9.69	- 6.50
	8	8	17.56	16.61
	8	9	2.98	4.88
	9	1	45.32	-45.39
	9	2	24.85	23.96
	9	4	3.15	7.04
	9	5	38.61	38.76
	9	6	13.28	-11.86
	9	7	19.56	16.58
	9	9	4.10	- 2.63
	10	1	8.84	-12.40
	10	4	6.60	6.92
	10	5	14.10	14.79
	10	7	6.44	- 6.61
	11	1	17.92	-16.20
	11	2	9.33	-12.22
	11	3	4.77	- 5.18
	11	5	9.32	8.71
	11	6	9.07	9.79
	11	7	19.10	16.57

Zone	k	l	$\|F\|_{obs}$	F_{calc}
1kl	12	2	18.83	19.90
	12	3	6.60	- 4.65
	12	4	19.28	17.44
	13	1	9.74	12.83
	13	2	6.44	10.38
	13	5	11.55	-10.38
2kl	0	0	85.84	-73.58
	0	1	24.83	18.56
	0	2	51.86	-58.38
	0	3	78.96	59.65
	0	4	37.07	30.32
	0	5	19.35	-18.29
	0	6	38.53	51.84
	0	7	28.05	-24.72
	0	8	30.77	28.74
	0	10	7.58	- 8.59
	0	11	5.54	4.97
	1	0	56.18	-64.70
	1	1	61.93	73.53
	1	2	28.29	12.03
	1	3	63.44	69.69
	1	4	25.94	24.08
	1	5	20.82	14.58
	1	6	14.99	18.45
	1	7	28.47	-24.93
	1	9	17.65	-15.27
	1	10	10.71	- 8.77
	2	0	59.96	-56.53
	2	1	27.59	-27.41
	2	3	13.09	2.68
	2	4	7.90	11.10
	2	5	26.19	22.01
	2	6	10.99	7.44
	2	7	15.13	14.93
	2	8	5.44	- 6.61
	2	9	6.37	- 6.72
	2	10	2.98	- 3.81
	2	11	9.89	- 9.24
	3	0	36.92	-25.21
	3	1	15.68	- 8.27
	3	2	6.21	1.82
	3	3	26.44	28.04
	3	4	24.27	-22.22

Zone	k	l	$\lvert F\rvert_{obs}$	F_{calc}
2kl	3	5	28.51	23.56
	3	6	6.97	6.12
	3	8	17.26	17.23
	3	9	23.33	-21.34
	3	11	15.41	-13.43
	4	0	85.89	106.45
	4	1	48.43	47.80
	4	2	32.23	31.68
	4	3	20.52	18.82
	4	4	32.06	-33.59
	4	5	8.55	-11.74
	4	6	43.45	-47.19
	4	7	16.30	-20.05
	4	8	12.21	-11.49
	4	10	12.47	12.21
	4	11	8.01	8.48
	5	0	19.25	11.77
	5	1	9.74	5.58
	5	2	20.82	19.57
	5	3	27.61	-23.75
	5	4	7.63	6.11
	5	5	23.95	-21.85
	5	6	15.35	-11.20
	5	8	13.19	-14.83
	5	9	22.33	20.90
	5	11	12.85	12.76
	6	0	35.20	-36.88
	6	1	5.36	- 4.80
	6	2	9.13	- 3.84
	6	3	15.13	-16.51
	6	4	16.05	11.65
	6	5	15.92	17.15
	6	6	13.54	10.24
	6	7	15.93	13.98
	6	9	7.84	- 6.07
	6	10	7.09	- 4.05
	7	0	42.24	45.09
	7	1	24.99	-31.73
	7	3	27.89	-33.93
	7	4	17.06	-17.74
	7	5	9.13	- 5.73
	7	6	15.47	-16.13
	7	7	13.70	14.99
	7	8	1.97	1.89
	7	9	9.38	7.96
	7	10	7.30	7.16

Zone	k	l	$\lvert F\rvert_{obs}$	F_{calc}
2kl	8	0	7.30	7.16
	8	1	13.16	15.90
	8	2	25.91	-25.79
	8	3	15.39	16.91
	8	4	13.93	13.69
	8	5	10.53	- 9.30
	8	6	31.28	30.42
	8	7	9.85	-12.58
	8	8	16.49	18.28
	9	0	11.26	-12.65
	9	1	31.54	31.30
	9	3	46.70	39.61
	9	4	14.06	15.09
	9	5	10.25	9.58
	9	6	7.38	7.79
	9	7	16.82	-16.07
	9	9	10.94	-11.59
	10	1	16.84	-15.19
	10	5	7.38	7.78
	10	7	5.80	7.82
	11	1	2.99	- 1.93
	11	3	8.48	8.47
	11	4	8.49	- 7.54
	11	5	12.58	9.73
	11	6	2.80	1.30
	12	0	35.67	36.35
	12	2	13.41	12.79
	12	3	8.44	8.38
	12	4	13.06	-14.96
	12	6	22.23	-20.32
	13	2	8.13	7.19
	13	3	11.30	-10.64
	13	5	7.23	- 9.40
	14	0	7.64	-11.44
	14	3	5.06	- 7.28
3kl	0	2	73.64	94.16
	0	3	7.10	2.86
	0	4	75.89	66.54
	0	5	15.54	-10.29
	0	6	38.22	-32.86
	0	7	20.52	26.29

Zone	k	l	$\lvert F \rvert_{obs}$	F_{calc}
3kl	0	8	31.01	-31.76
	0	10	14.58	-13.61
	0	11	3.58	- 5.66
	1	1	33.83	28.70
	1	2	10.58	0.65
	1	3	25.31	29.56
	1	4	7.58	3.15
	1	5	11.35	- 9.36
	1	7	29.43	-31.18
	1	9	16.04	-14.47
	1	11	11.81	11.82
	2	1	12.94	6.44
	2	2	35.17	-35.91
	2	3	7.70	6.04
	2	4	3.15	- 0.88
	2	6	26.39	25.84
	2	7	10.58	-11.55
	2	8	8.79	8.35
	2	9	5.54	- 2.65
	2	10	8.08	- 8.37
	2	11	4.23	2.76
	3	1	33.72	49.72
	3	2	4.87	5.66
	3	3	10.99	-13.43
	3	4	17.58	-15.07
	3	5	49.92	-54.65
	3	6	13.61	9.82
	3	7	6.90	- 5.33
	3	8	1.42	- 5.24
	3	9	8.39	8.66
	3	11	6.60	8.15
	4	1	59.57	55.40
	4	2	22.98	-25.52
	4	3	9.74	- 8.52
	4	4	45.50	-51.85
	4	5	32.64	-34.02
	4	6	39.52	-23.11
	4	7	17.40	-15.84
	4	8	19.49	18.10
	4	9	3.98	2.84
	4	10	26.96	28.01
	4	11	8.44	6.50
	5	1	49.84	-51.18
	5	2	12.86	-12.22

Zone	k	l	$\lvert F\rvert_{obs}$	F_{calc}
3kl	5	3	16.14	17.62
	5	4	3.72	- 3.39
	5	5	42.18	46.06
	5	7	15.51	12.09
	5	8	3.98	5.68
	5	9	8.84	- 9.50
	6	2	10.71	-14.70
	6	5	13.01	10.76
	6	6	22.60	25.23
	6	7	10.70	-10.75
	6	9	3.15	- 0.38
	6	10	9.06	- 8.12
	7	1	15.21	- 9.75
	7	2	14.42	- 8.99
	7	3	16.71	-18.19
	7	4	6.44	- 4.87
	7	5	5.07	4.50
	7	7	19.57	18.60
	7	8	4.87	3.73
	7	9	10.70	10.48
	8	1	9.66	- 9.26
	8	2	40.47	54.61
	8	3	0.99	- 3.33
	8	4	33.22	35.08
	8	5	3.86	2.59
	8	6	13.86	-15.90
	8	7	12.47	14.92
	8	8	18.13	-21.96
	9	1	19.77	16.13
	9	2	7.30	- 3.71
	9	3	7.50	9.31
	9	5	7.90	- 3.86
	9	7	21.51	-22.63
	9	9	5.71	- 6.95
	10	2	21.20	-21.06
	10	3	3.98	4.50
	10	4	3.98	- 3.74
	10	6	11.11	10.66
	10	8	5.96	6.81
	11	1	16.62	19.26
	11	3	1.97	- 6.93
	11	4	5.64	- 5.09
	11	5	16.35	-19.75

Zone	k	l	$\lvert F\rvert_{obs}$	F_{calc}
3kl	12	1	11.77	13.27
	12	2	11.21	-10.58
	12	4	16.04	-16.77
	12	5	13.05	-12.85
	12	6	8.62	-10.74
	13	1	20.91	-21.03
	13	2	1.97	- 3.20
	13	3	3.71	6.42
	13	4	3.59	- 3.17
	14	1	1.73	- 3.30
4kl	0	0	5.36	18.35
	0	1	17.73	21.69
	0	2	30.54	26.93
	0	3	13.13	13.49
	0	4	19.25	-14.31
	0	5	9.33	- 9.78
	0	6	34.15	-28.66
	0	7	18.18	-17.86
	0	8	15.80	-13.88
	0	9	2.63	- 2.24
	0	10	1.73	5.10
	0	11	4.54	5.16
	1	0	11.85	-14.80
	1	1	6.21	-13.31
	1	2	30.37	20.66
	1	3	64.85	-66.31
	1	4	28.35	24.03
	1	5	14.99	-16.71
	1	6	8.74	- 8.89
	1	7	14.24	14.82
	1	8	21.88	-23.89
	1	9	15.20	17.16
	1	10	5.64	- 2.75
	1	11	9.16	8.25
	2	0	23.31	-13.86
	2	1	28.67	-28.67
	2	2	13.39	9.83
	2	3	32.18	-23.78
	2	4	6.97	- 7.77
	2	5	10.71	8.52
	2	6	7.70	5.29
	2	7	18.34	18.85

Zone	k	l	$\lvert F\rvert_{obs}$	F_{calc}
4kl	2	8	7.90	5.95
	2	10	2.42	- 1.99
	2	11	6.12	- 6.31
	3	0	56.38	55.91
	3	2	2.80	2.29
	3	3	36.84	-40.12
	3	4	34.07	-37.01
	3	5	22.06	-17.60
	3	6	19.80	-17.93
	3	7	13.24	10.30
	3	8	10.70	11.10
	3	9	17.37	17.15
	3	10	9.99	7.88
	3	11	8.07	9.18
	4	0	54.41	-46.48
	4	1	6.13	4.91
	4	2	42.34	-42.10
	4	3	11.82	-11.35
	4	4	32.21	32.98
	4	5	21.02	-18.92
	4	6	25.25	32.05
	4	7	10.14	- 7.49
	4	8	9.69	7.32
	4	9	16.66	10.13
	4	10	6.97	- 5.95
	5	0	53.71	-59.41
	5	1	28.59	27.85
	5	2	5.87	- 8.29
	5	3	41.03	35.84
	5	4	35.25	36.88
	5	5	22.68	21.61
	5	6	22.02	21.68
	5	7	14.96	-10.92
	5	8	8.54	- 8.34
	5	9	22.55	-21.03
	5	10	9.79	- 8.35
	6	0	18.95	15.10
	6	1	21.81	-17.35
	6	2	6.30	- 0.18
	6	3	12.74	-12.24
	6	4	7.58	- 4.20
	6	5	9.22	8.54
	6	7	10.52	12.75

Zone	k	l	$\|F\|_{obs}$	F_{calc}
4kl	7	1	7.38	8.25
	7	2	8.08	-13.18
	7	3	35.22	42.85
	7	4	14.18	-13.62
	7	5	9.85	10.26
	7	6	8.07	8.38
	7	7	7.95	-10.70
	7	8	14.20	17.21
	7	9	8.44	-11.27
	8	0	23.42	24.23
	8	1	13.50	15.32
	8	2	15.48	10.76
	8	3	15.02	14.36
	8	4	9.22	- 6.51
	8	6	19.99	-19.47
	8	7	9.29	-12.17
	8	8	12.49	-10.46
	9	0	6.90	- 9.88
	9	1	14.53	-17.49
	9	2	19.35	7.57
	9	3	27.94	-28.58
	9	4	10.43	13.10
	9	5	9.17	-11.73
	9	6	3.72	- 4.08
	9	7	3.58	8.52
	9	8	11.73	-13.55
	10	0	8.95	- 9.11
	10	1	7.31	-10.92
	10	2	9.07	4.03
	10	3	10.53	- 9.96
	10	6	5.17	4.39
	10	7	4.87	8.64
	11	0	14.99	20.32
	11	3	10.58	-11.44
	11	4	11.11	-14.48
	11	5	7.17	- 7.48
	11	6	5.96	- 6.66
	12	0	16.62	-20.93
	12	4	8.61	9.94
	12	5	3.43	- 6.29
	13	0	19.28	-21.04
	13	1	9.95	11.87
	13	2	6.90	- 4.20

Zone	k	l	$\|F\|_{obs}$	F_{calc}
4kl	13	3	14.03	13.64
	13	4	10.09	12.99
	14	0	8.94	6.97
5kl	0	1	10.82	- 7.24
	0	2	13.97	-18.37
	0	3	23.80	20.04
	0	4	41.90	-45.18
	0	5	14.72	-10.34
	0	6	22.29	-20.27
	0	7	15.02	-12.44
	0	8	16.98	16.98
	0	9	11.20	-11.33
	0	10	25.17	26.69
	1	1	30.71	-32.35
	1	2	28.80	-32.35
	1	3	8.84	6.87
	1	4	23.51	-20.02
	1	5	39.97	36.94
	1	6	7.17	5.53
	1	7	9.01	4.76
	1	8	7.31	9.76
	1	9	3.59	- 5.30
	2	1	22.79	16.31
	2	2	8.26	-10.18
	2	3	9.17	-10.62
	2	5	7.38	- 7.51
	2	6	25.06	22.27
	2	7	11.30	6.90
	2	9	6.90	7.58
	2	10	8.83	- 8.17
	3	1	8.14	- 7.39
	3	2	7.24	8.09
	3	3	17.04	-15.25
	3	4	18.76	-14.20
	3	7	14.56	14.89
	3	9	10.13	8.39
	3	10	11.29	11.16
	4	1	39.13	-45.78
	4	2	70.62	74.31
	4	3	6.81	7.58
	4	4	49.23	55.19
	4	5	34.37	31.20

Zone	k	l	$\lvert F \rvert_{obs}$	F_{calc}
5kl	4	6	19.43	-20.41
	4	7	4.97	8.94
	4	8	28.73	-26.86
	4	9	3.43	- 6.01
	4	10	11.93	-13.61
	5	1	27.42	19.49
	5	3	5.87	8.21
	5	4	10.67	12.47
	5	5	7.46	- 6.98
	5	6	3.30	3.73
	5	7	21.93	21.35
	5	8	5.53	- 5.43
	5	9	5.26	- 5.78
	5	10	9.13	-10.44
	6	1	15.54	17.55
	6	2	21.94	-19.22
	6	3	13.82	-12.76
	6	5	3.30	- 4.62
	6	6	14.36	13.04
	6	8	10.29	4.57
	6	9	6.60	7.59
	7	1	23.90	23.52
	7	2	13.96	21.25
	7	4	14.32	14.60
	7	5	25.77	-27.26
	7	6	6.37	- 5.50
	7	9	8.26	4.05
	8	1	7.17	0.81
	8	2	15.67	-16.42
	8	3	7.90	8.89
	8	4	24.52	-26.47
	8	5	7.38	- 4.57
	8	6	12.94	-14.51
	8	7	12.58	-10.89
	8	8	11.12	13.95
	9	1	20.25	-20.25
	9	2	14.49	-18.97
	9	3	4.96	6.69
	9	4	7.10	- 7.45
	9	5	14.39	17.74
	9	7	6.74	6.38
	9	8	3.15	7.67

Zone	k	l	$\lvert F\rvert_{obs}$	F_{calc}
5kl	10	6	6.81	11.93
	10	7	5.53	4.87
	12	1	13.97	-15.86
	12	2	20.43	27.82
	12	4	13.00	18.38
	12	5	12.26	9.98
	13	1	7.89	8.12
6kl	0	0	37.82	-44.67
	0	1	8.44	7.32
	0	2	28.77	-22.43
	0	3	33.44	-34.33
	0	4	26.49	25.28
	0	5	17.46	-17.55
	0	6	20.05	21.13
	0	8	2.42	- 0.01
	0	9	9.73	14.52
	0	10	4.66	- 6.34
	1	0	30.05	-24.09
	1	2	15.07	- 9.75
	1	3	11.90	7.96
	1	4	19.02	15.58
	1	5	28.35	25.56
	1	6	17.77	13.33
	1	9	19.49	-21.46
	1	10	8.08	- 4.05
	2	0	32.94	32.20
	2	1	11.17	- 9.21
	2	2	16.66	14.41
	2	3	12.78	- 7.34
	2	4	20.03	-19.97
	2	5	4.24	5.74
	2	6	8.66	- 9.18
	2	7	9.73	6.93
	2	8	6.05	6.29
	2	10	2.21	3.19
	3	0	5.26	8.41
	3	1	31.34	30.81
	3	2	22.78	-18.68
	3	3	44.35	53.14
	3	4	5.64	4.32
	3	5	4.55	3.48
	3	6	8.55	6.77
	3	7	17.51	-18.89

Zone	k	l	$\|F\|_{obs}$	F_{calc}
6kl	3	8	5.87	6.48
	3	9	8.55	- 7.49
	3	10	6.12	1.14
	4	0	19.68	21.53
	4	1	18.78	20.47
	4	2	12.97	10.51
	4	3	36.33	38.72
	4	5	8.62	7.09
	4	6	25.83	-22.15
	4	7	14.56	-14.85
	4	8	19.15	-16.29
	4	9	10.71	-10.56
	5	0	3.59	5.17
	5	1	37.87	-33.18
	5	2	9.33	9.92
	5	3	53.30	-56.57
	5	5	7.10	- 6.46
	5	6	3.59	- 8.34
	5	7	21.50	19.97
	5	8	5.43	- 7.86
	5	9	9.85	10.40
	6	0	13.25	15.86
	6	1	17.12	-17.21
	6	2	8.26	6.80
	6	3	4.33	- 2.97
	6	4	14.42	-12.42
	6	7	4.87	5.65
	6	8	2.42	7.00
	7	0	11.07	12.61
	7	2	7.38	7.13
	7	3	11.12	- 8.14
	7	4	11.26	-10.66
	7	5	19.33	-18.19
	7	6	10.47	- 8.05
	8	0	28.96	-30.72
	8	2	11.20	-14.57
	8	3	14.46	-17.01
	8	4	14.83	17.95
	8	5	9.13	-11.91
	8	6	13.01	15.96
	9	0	21.08	-21.57
	9	3	7.31	5.31
	9	4	8.95	7.05

Zone	k	l	$\lvert F \rvert_{obs}$	F_{calc}
6kl	9	5	14.52	15.01
	9	6	9.95	9.38
	10	0	12.68	14.71
	10	4	8.84	- 9.93
	10	6	4.67	- 5.27
	11	1	10.25	12.19
	11	2	3.59	- 4.56
	11	3	14.17	19.83
	12	0	6.89	6.00
	12	1	6.89	11.59
	12	2	4.77	3.93
	12	3	11.39	13.43
7kl	0	1	45.39	-41.34
	0	2	30.88	24.36
	0	3	7.95	8.19
	0	4	31.14	24.13
	0	5	35.40	31.99
	0	6	8.14	6.08
	0	7	3.30	4.50
	0	8	19.40	-14.27
	0	9	7.78	- 7.58
	1	1	15.29	16.70
	1	2	2.63	- 2.87
	1	4	17.50	18.80
	1	5	2.80	- 7.50
	1	6	12.35	9.72
	1	7	17.20	-16.99
	1	8	6.67	- 6.61
	1	9	2.21	0.22
	2	1	20.21	19.17
	2	3	12.27	-12.68
	2	4	14.86	- 9.59
	2	5	12.31	- 9.15
	2	7	6.74	4.32
	2	8	2.42	- 0.02
	2	9	12.53	8.89
	3	1	17.61	20.47
	3	2	41.02	41.60
	3	4	31.14	26.86
	3	5	14.71	-12.94

Zone	k	l	$\lvert F\rvert_{obs}$	F_{calc}
7kl	3	6	16.14	-12.25
	3	7	13.08	- 8.98
	3	8	11.81	-12.20
	4	1	4.55	- 7.48
	4	2	40.21	-40.10
	4	3	12.64	13.41
	4	4	24.12	-24.04
	4	7	12.86	-10.73
	4	8	19.61	19.30
	4	9	12.46	- 9.07
	5	1	23.88	-23.87
	5	2	34.20	-39.00
	5	4	18.93	-19.77
	5	5	21.36	19.82
	5	6	9.89	7.88
	5	7	12.26	9.39
	5	8	12.85	12.99
	6	1	10.58	10.77
	6	2	2.99	2.18
	6	3	5.80	- 6.99
	6	5	9.37	- 9.03
	6	6	4.10	- 2.32
	6	7	8.33	7.57
	7	1	8.95	-13.00
	7	2	5.36	5.90
	7	4	9.13	-11.15
	7	5	3.98	5.65
	7	6	9.99	- 7.23
	7	7	10.63	12.19
	8	1	25.11	-24.27
	8	2	15.45	16.38
	8	3	4.67	7.40
	8	4	19.04	18.69
	8	5	18.61	17.95
	9	1	8.21	8.92
	9	2	6.74	2.95
	9	4	9.49	10.60
	9	5	4.66	- 7.50
	9	6	8.78	8.34
	10	1	9.54	12.45
	10	3	6.67	- 7.33
	10	4	7.90	- 5.60

Zone	k	l	$\lvert F \rvert_{obs}$	F_{calc}
7kl	10	5	6.12	- 6.75
	11	1	3.30	6.51
	11	2	12.86	18.54
	11	4	6.05	9.97
8kl	0	0	8.62	13.09
	0	1	20.41	20.68
	0	2	10.25	2.97
	0	3	34.16	32.21
	0	4	11.81	9.35
	0	5	22.71	21.68
	0	6	16.65	-16.65
	0	7	9.06	- 6.57
	0	8	19.88	-18.93
	0	9	19.98	-17.52
	1	0	20.68	19.47
	1	1	21.88	-21.51
	1	2	12.97	9.47
	1	3	31.23	-27.27
	1	4	18.59	-17.52
	1	5	7.24	- 3.57
	1	6	9.60	-11.26
	1	7	12.35	11.61
	1	9	10.75	6.11
	2	0	23.98	19.27
	2	3	7.78	9.16
	2	4	14.96	-14.09
	2	5	6.81	- 3.85
	2	8	8.33	9.61
	3	0	10.44	9.96
	3	1	5.79	- 5.61
	3	2	11.12	4.98
	3	5	14.56	-12.15
	3	6	11.51	- 8.71
	3	8	11.46	- 8.54
	4	0	50.59	-53.63
	4	1	12.49	-13.58
	4	2	14.03	-14.83
	4	3	23.78	-30.96
	4	4	22.70	25.29
	4	5	2.99	- 7.92
	4	6	20.85	22.54
	4	7	6.37	11.23

Zone	k	l	$\|F\|_{obs}$	F_{calc}
8kl	5	0	8.01	- 6.88
	5	2	5.17	- 3.86
	5	3	8.49	6.37
	5	4	7.95	- 4.58
	5	5	11.56	11.52
	5	6	9.85	7.44
	5	8	9.00	7.93
	6	0	19.02	13.30
	6	1	7.46	3.17
	6	2	9.96	7.31
	6	3	8.39	8.98
	6	4	17.14	-15.38
	6	5	3.15	- 1.97
	6	6	2.99	- 3.08
	6	7	1.97	- 4.71
	7	0	10.28	- 9.05
	7	1	14.80	16.06
	7	2	2.99	- 4.22
	7	3	17.20	17.97
	7	4	10.66	10.09
	7	6	3.71	4.90
	7	7	3.86	- 8.37
	8	1	11.02	11.46
	8	2	3.72	5.97
	8	3	19.19	18.39
	8	4	4.33	3.72
	8	5	13.50	13.17
	8	6	9.27	-11.26
	9	0	18.01	15.59
	9	1	12.73	- 8.88
	9	2	6.13	6.94
	9	3	19.19	-19.12
	9	4	11.81	-11.18
	9	5	3.98	- 1.50
	10	0	5.97	9.61
	10	2	2.80	- 1.55
9kl	0	1	15.48	16.90
	0	2	27.66	-26.58
	0	3	12.78	2.07
	0	4	12.63	- 8.13
	0	5	7.58	-10.22
	0	6	4.24	4.41

Zone	k	l	$\lvert F\rvert_{obs}$	F_{calc}
9kl	0	7	12.47	-16.21
	0	8	5.80	12.84
	1	1	8.62	- 8.59
	1	2	34.07	-32.58
	1	3	13.06	-10.31
	1	4	21.37	-16.87
	1	6	7.37	5.65
	1	7	11.84	14.28
	1	8	13.81	12.10
	2	1	11.52	9.80
	2	2	8.49	10.34
	2	5	8.21	- 5.76
	2	6	9.38	- 7.30
	3	1	22.61	-23.97
	3	2	4.97	- 6.43
	3	3	13.97	11.90
	3	4	10.90	-12.08
	3	5	16.04	15.86
	3	6	11.25	- 9.62
	3	7	5.16	8.25
	4	1	21.46	-20.04
	4	2	7.38	3.66
	4	4	14.61	10.59
	4	5	14.92	13.42
	4	6	9.16	7.65
	4	7	10.62	8.89
	5	1	21.49	22.48
	5	2	2.80	3.24
	5	3	9.07	- 8.55
	5	4	8.20	12.24
	5	5	18.13	-17.63
	5	6	8.00	7.21
	5	7	3.59	- 6.74
	6	1	10.25	8.68
	6	2	7.31	7.75
	6	4	6.67	- 4.08
	6	5	11.25	- 8.06
	7	2	17.39	19.51
	7	3	4.33	6.58
	7	4	10.63	8.63
	7	6	3.97	- 3.68

Zone	k	l	$\lvert F\rvert_{obs}$	F_{calc}
9kl	8	1	9.85	9.00
	8	2	12.73	-16.30
	8	4	7.24	- 7.07
	8	5	3.98	- 6.77
	9	1	4.33	- 5.20
	9	2	14.71	-20.28
	9	3	4.23	- 6.89
10kl	0	0	23.20	-26.34
	0	1	23.30	-24.77
	0	2	11.70	-11.87
	0	3	35.84	-33.64
	0	4	13.78	12.15
	0	6	18.43	16.46
	0	7	12.67	15.78
	1	0	11.16	-12.88
	1	1	4.33	1.99
	1	2	8.01	- 4.63
	1	3	6.73	4.53
	1	4	6.29	- 5.07
	1	5	5.64	4.76
	1	6	7.84	9.93
	2	0	2.41	0.88
	2	1	8.13	5.31
	2	2	2.99	- 0.15
	2	3	11.97	10.80
	2	5	10.06	- 9.10
	3	0	22.70	-25.39
	3	1	9.66	5.24
	3	2	3.30	- 6.16
	3	3	13.92	8.54
	3	4	16.25	15.12
	3	5	2.80	0.88
	3	6	10.82	12.36
	4	0	12.49	15.93
	4	1	4.97	5.01
	4	2	6.36	8.64
	4	3	10.52	5.48
	4	5	19.70	16.50
	4	6	9.70	-12.17
	5	0	18.71	19.39
	5	1	3.86	- 4.68

Zone	k	l	$\lvert F \rvert_{obs}$	F_{calc}
10kl	5	2	7.83	8.51
	5	3	12.42	- 7.93
	5	4	16.01	-14.81
	6	1	9.43	6.69
	6	5	7.90	- 7.35
	7	0	3.85	5.86
	7	1	1.97	- 0.31
	7	4	4.67	5.10
	8	0	11.29	-16.25
	8	1	13.27	-13.66
	8	2	4.78	- 7.39
	8	3	21.36	-22.32
11kl	0	1	21.35	-20.10
	0	3	11.97	1.21
	0	4	16.43	8.33
	1	1	15.09	17.25
	1	2	15.91	15.72
	1	3	7.10	- 7.17
	1	5	14.64	-14.32
	2	2	12.02	10.87
	3	2	8.39	6.56
	3	3	9.73	9.03
	3	4	10.28	6.54
	4	1	9.79	18.37
	4	2	6.12	-12.43
	5	1	5.87	- 0.87
	5	2	5.86	- 5.87
	5	3	10.67	- 7.14
	6	2	10.39	10.35
12kl	0	0	19.65	16.16
	0	1	5.26	4.42
	0	2	11.03	8.47
	0	3	7.51	7.42
	1	0	15.09	21.63
	1	2	5.87	8.96
	2	0	9.38	- 6.42

B. Unobserved Reflections[*]

Zone	k	l	$\lvert F\rvert_{obs}$	F_{calc}
0kl	1	7	6.80	- 0.45
	3	11	7.19	- 5.25
	5	11	6.66	1.99
	6	10	7.05	- 3.81
	9	1	2.70	4.01*
	9	7	6.67	2.65
	11	5	5.62	- 4.06
	12	4	4.90	2.32
	13	5	4.78	3.40
	14	0	3.22	-10.23*
	14	2	3.03	3.34*
1kl	0	7	6.80	0.08
	0	11	7.44	- 0.34
	1	8	7.56	2.00
	2	10	7.93	- 1.72
	2	11	7.31	0.76
	3	8	7.57	2.04
	4	6	6.38	- 1.43
	4	11	6.92	- 5.15
	5	8	7.57	- 1.07
	6	7	7.06	- 4.08
	6	10	7.05	2.15

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[*] In this section, $|F|_{obs}$ denotes the estimated minimum observable $|F|$. For starred reflections $|F|_{calc}$ is greater than $|F|_{obs}$.

Zone	k	l	|F| obs	F calc
1kl	7	8	7.31	- 2.46
	7	9	7.20	5.37
	8	7	6.93	1.66
	9	3	4.70	4.89*
	9	8	6.66	- 2.62
	10	2	3.84	- 0.77
	10	3	4.70	1.99
	10	6	6.23	2.05
	10	8	6.07	0.08
	11	4	5.25	- 1.87
	12	1	3.03	3.92*
	12	5	5.26	- 3.64
	12	6	5.25	- 3.33
	13	3	4.09	5.85*
	13	4	4.52	5.62*
	14	1	2.70	- 5.88*
	14	2	3.03	- 5.78*
	14	3	3.58	3.54
2kl	0	9	8.04	3.87
	1	8	7.57	- 3.71
	1	11	7.30	0.27
	2	2	3.84	- 0.73
	3	7	7.06	- 0.89
	3	10	7.81	0.67
	4	9	7.80	- 0.41
	5	7	7.20	0.94
	5	10	7.30	- 1.32
	6	8	7.44	- 3.38
	7	2	4.09	- 1.40
	8	9	6.66	2.33
	9	2	4.31	- 5.78*

Zone	k	l	$\lvert F\rvert_{obs}$	F_{calc}
2kl	9	8	6.51	- 4.00
	10	0	3.59	- 8.11*
	10	2	4.52	3.75
	10	3	5.09	- 2.96
	10	4	5.62	2.78
	10	6	6.22	- 1.82
	10	8	6.08	- 5.51
	11	0	3.59	2.45
	11	2	4.31	- 1.75
	11	7	5.79	0.42
	12	1	3.84	6.57*
	12	5	5.25	- 6.27*
	13	0	3.31	- 0.44
	13	1	3.58	- 1.09
	13	4	4.52	1.14
	14	1	3.03	- 5.11*
	14	2	3.31	- 2.05
3kl	0	1	3.84	- 8.29*
	0	9	8.04	2.49
	1	6	6.52	- 0.98
	1	8	7.71	- 1.54
	1	10	7.81	- 1.32
	2	5	5.93	1.37
	3	10	7.70	1.78
	5	6	6.80	- 2.58
	5	10	7.20	1.54
	6	1	4.31	- 0.07
	6	3	5.09	- 1.19
	6	4	5.62	- 1.78
	6	8	7.44	0.19
	7	6	6.80	0.45
	7	10	6.38	1.16
	8	9	6.52	2.70

Zone	k	l	$\|F\|_{obs}$	F_{calc}
3kl	9	4	5.92	4.49
	9	6	6.66	- 3.98
	9	8	6.52	1.77
	10	1	4.52	- 2.76
	10	5	6.07	1.49
	10	7	6.23	- 3.29
	11	2	4.90	- 1.92
	11	6	5.79	2.54
	11	7	5.62	- 2.61
	12	3	4.90	- 0.64
	14	2	3.58	- 3.38
4kl	2	9	7.93	1.24
	3	1	4.70	- 9.94*
	6	6	7.06	- 2.43
	6	8	7.44	0.65
	6	9	7.20	- 1.24
	6	10	6.52	1.66
	7	0	4.90	4.66
	8	5	6.67	- 4.28
	8	9	6.23	- 2.28
	10	4	6.08	- 3.77
	10	5	6.22	4.35
	11	1	5.08	- 6.18*
	11	2	5.26	1.44
	12	1	4.90	3.78
	12	2	4.89	- 9.49*
	12	3	5.08	- 0.30
5kl	1	10	7.43	0.96
	2	4	6.23	2.46
	2	8	7.94	- 1.46
	3	5	6.80	4.20
	3	6	7.31	0.46

Zone	k	l	$\lvert F\rvert_{obs}$	F_{calc}
5kl	3	8	7.93	0.81
	5	2	5.79	2.90
	6	4	6.52	0.69
	6	7	7.44	0.27
	7	3	7.19	- 4.35
	7	7	7.31	- 2.82
	7	8	7.05	- 6.81
	9	6	6.66	0.97
	10	1	5.79	6.07*
	10	2	5.93	- 4.77
	10	3	6.08	- 4.46
	10	4	6.22	0.33
	10	5	6.38	- 4.95
	11	1	5.62	- 0.03
	11	2	5.62	3.37
	11	3	5.79	- 5.02
	11	4	5.79	- 3.69
	11	5	5.78	- 1.65
	11	6	5.62	- 2.17
	12	3	5.26	4.96
	13	2	4.69	2.55
	13	3	4.70	2.24
6kl	0	7	7.93	2.93
	1	1	5.93	1.33
	1	7	7.94	2.11
	1	8	8.03	- 0.77
	2	9	7.71	- 2.53
	4	4	6.92	- 2.41
	5	4	6.93	- 0.82
	6	5	7.31	1.30
	6	6	7.44	- 2.22
	6	9	6.52	0.83

Zone	k	l	$\lvert F\rvert_{obs}$	F_{calc}
6kl	7	1	6.38	-2.13
	7	7	7.20	-1.24
	7	8	6.79	1.43
	8	1	6.38	-2.12
	8	7	6.79	1.50
	8	8	6.23	0.35
	9	1	6.37	0.76
	9	2	6.38	-1.45
	9	7	6.22	1.52
	10	1	6.07	-1.12
	10	2	6.23	6.08
	10	3	6.23	-3.03
	10	5	6.23	4.24
	11	0	5.78	1.47
	11	4	5.78	-0.11
	11	5	5.62	0.26
7kl	1	3	7.06	-1.75
	2	2	6.80	-0.71
	2	6	7.94	0.56
	3	3	7.06	-2.82
	3	9	7.05	0.53
	4	5	7.71	-1.72
	4	6	7.81	-2.11
	5	3	7.19	-0.25
	5	9	6.51	0.44
	6	4	7.31	0.36
	6	8	6.80	-0.65
	7	3	7.05	1.64
	7	8	6.38	2.78
	8	6	6.79	1.95
	8	7	6.38	3.98
	9	3	6.67	1.61
	10	2	6.38	-0.29

Zone	k	l	$\lvert F \rvert_{obs}$	F_{calc}
7kl	11	3	5.79	- 0.48
	12	1	5.09	- 0.37
8kl	1	8	7.44	1.39
	2	1	7.31	2.25
	2	2	7.44	0.99
	2	6	8.04	- 0.57
	2	7	7.81	- 5.22
	2	9	6.67	0.13
	3	3	7.56	2.07
	3	4	7.71	4.32
	3	7	7.71	- 2.67
	4	8	6.92	0.23
	5	1	7.30	2.20
	5	7	7.19	0.63
	7	5	7.20	2.09
	8	0	7.05	6.13
	10	1	6.23	- 0.53
	10	3	6.08	1.11
	10	4	5.79	- 6.29*
	11	0	5.62	3.16
	11	1	5.62	0.42
	11	2	5.45	1.84
9kl	1	5	8.03	3.61
	2	3	7.94	- 5.00
	2	4	7.94	- 0.17
	2	7	7.43	- 0.15
	2	8	6.80	- 3.77
	4	3	7.81	4.73
	6	3	7.43	- 2.14
	6	6	6.80	- 3.97
	7	1	7.31	4.52
	7	5	6.79	- 1.05

Zone	k	l	$\lvert F \rvert_{obs}$	F_{calc}
9kl	8	3	6.79	2.74
	10	1	5.79	1.70
10kl	0	5	7.81	- 2.84
	1	7	6.80	- 0.49
	2	4	7.81	- 2.26
	2	6	7.19	0.08
	4	4	7.56	- 4.42
	5	5	6.93	- 0.99
	6	0	7.30	- 0.38
	6	2	7.31	- 0.88
	6	3	7.19	4.48
	6	4	6.93	- 1.19
	7	2	6.93	1.16
	7	3	6.66	- 1.04
11kl	0	2	7.80	- 3.03
	0	5	7.06	14.00*
	1	4	7.86	9.91*
	1	6	6.37	- 1.69
	2	1	7.80	- 1.57
	2	3	7.57	0.10
	2	4	7.30	1.14
	2	5	6.93	0.09
	3	1	7.71	1.17
	3	5	6.66	- 1.80
	4	3	7.19	0.01
	4	4	6.79	- 4.60
	6	1	6.80	- 2.60
12kl	1	1	7.20	1.83
	1	3	6.80	- 1.07

Zone	k	l	$\lvert F \rvert_{obs}$	F_{calc}
12kl	2	1	7.05	2.16
	2	2	6.93	- 0.11
	3	0	6.92	7.30*
	3	1	6.79	- 3.21
	4	0	6.66	1.15

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Propositions

1. Yakel, in discussion of the shapes of Patterson peaks (P-1) gives a Gaussian approximation to the atomic form factor. This approximation is not the best one of this type for the calculation of electron density peak shapes when the data extends only to the practical copper limit.

2. Mulliken has proposed (P-2) a magic formula for use in calculation of dissociation and bond energies:

$$D_0 = \underbrace{\sum X_{ij}}_{\text{bonds}} - \underbrace{\tfrac{1}{2}\sum Y_{kl} + \tfrac{1}{2}\sum K_{mn}}_{\text{non-bonded electrons}} - P + RE$$

   where the X_{ij} and Y_{kl} are quantities depending on the overlap integrals, K is the exchange integral, and P and RE are promotion and resonance energies.

   a. It is proposed that the applicability of this formula to the prediction of bond distances in small-ring cyclic hydrocarbons be tested, particularly with respect to cross-ring interactions.

   b. I propose a simplification of this formula which lumps all non-bonded interactions into a single term, permitting a great saving of time in arriving at values which are fully as accurate as Mulliken's for most purposes.

3. Correlation of intensities between different sets of film in the collection of x-ray data for visual estimation may be most conveniently carried out by a statistical method. This procedure eliminates the necessity of collecting data around more than one axis, if this is done only for the purpose of correlating intensities. Certain anisotropies in temperature factor will, however, not be detected. When this information is not of importance, the method can be quite useful.

4. Cathodically charged aluminum electrodes immersed in a solution through which oxygen is bubbled at a constant rate do not develop a significant hydrogen overvoltage until a critical current density is reached. It is proposed that this fact may be of use in the study of the nature of oxide films on aluminum.

5. Longuet-Higgins and Coulson have given (P-3) a molecular-orbital and valence-bond-potential treatment to hydrindene in an investigation of the Mills-Nixon effect. It is proposed that an accurate x-ray diffraction investigation of this compound be carried out to check values for bond lengths, an earlier electron diffraction investigation (P-4) being inconclusive.

6. In connection with a recent investigation of the structure of dimethyl phosphino-borine trimer, the structures of the following compounds would be of interest:

   a. dimethyl phosphino-borine (monomer)

   b. dimethyl amino boron dichloride dimer

7. DuMond and Cohen, in their most recent adjustment of the universal physical constants (P-5), although careful in eliminating observational correlations, give too little attention to the proper weights for single observations. In particular, the standard deviation has in several cases been taken as half a quoted limit of error, and in others, the weights have been chosen inversely proportional to the <u>estimated</u> variances, a procedure which is not entirely correct. Such errors probably have negligible effects on the output quantities, but nevertheless should be discussed.

8. In the least squares adjustment of crystal structure parameters, unobserved reflections should be entered as approximately $0.55\ F_{min}$ and $0.7\ F_{min}$ for centrosymmetric and non-centrosymmetric space groups, respectively, the weights being approximately the same in both cases, viz., C/F_{min}^2. It is assumed that the least squares is carried out on mod F.

9. A tabulation for all space groups of general positions in Patterson space in terms of the positions of points in the fundamental set should be useful to crystallographers. A presentation which I feel to be the most useful is proposed.

10. The reaction between phosphine and formaldehyde in acid solution is reported (P-6) to produce the compound, tetrakis hydroxymethyl phosphonium chloride.

    a. Another possible formula for this compound is proposed.

    b. It is proposed that the addition of ammonia to this compound produces a a polymer similar to those produced by the action of ammonium chloride on PCl_5.

11. It is proposed that the application of the scientific method to ethics and esthetics is chiefly limited by the near impossibility of agreement on the fundamental definitions and axioms which are necessary in every science.

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