When two components are mixed and two kinds of molecules approach each other, there occur induced dipole moments in both molecules by the mutual polarizing forces. They come nearer by the attraction between these dipoles. When they enter in the effective fields of π-electrons of the paired molecules to each other, there occurs overlapping of the π-electron clouds in the $\perp$-direction.

In other words, π–π attraction between benzene layers is induced by the close approach of the two components. As a result, the density distribution of π-electrons becomes larger in the $\perp$-direction than in the $\|$-direction. That is, π-electrons become more mobile in the $\perp$-direction rather than in the $\|$-direction. This result is in good accordance with the view of the charge-transfer spectrum,[6] which leads to the conclusion that the electric moment vibrates along the $\perp$-direction. Thus, the reversity of the dichroic property in molecular compounds is explained by the π–π attraction in the $\perp$-direction. The strength of this π–π attraction can be discussed semiquantitatively by the comparisons of $\Delta\lambda_{\max}$ and $\Delta \log \alpha_{\max}$. As shown above, these values are larger in quinhydrone than in *s*-trinitrobenzene–*p*-bromoaniline, which means the former is more stable than the latter. Similar results are obtained by the comparisons of the normal distance between benzene layers and the heat of sublimation[10] in both compounds.

If this π–π attraction becomes too strong, the molecule is highly polymerized even in the solution. Thus, Scheibe, *et al.*,[11] have found the "Z-band" in the solution of the cyanine type dyes.

From the measurements of dichroisms in the molecular compounds, the following conclusion has been reached: "The nature of the intermolecular force is the π–π attraction in the $\perp$-direction by the approach of both components due to mutual polarizing forces.

The author expresses sincere thanks to Prof. R. Tsuchida, Mr. S. Yamada, K. Osaki and H. Matsuda for their kind advices and encouragements throughout this work.

[10] I. Nitta, S. Seki, H. Chihara and K. Suzuki, Scientific Papers from the Osaka University, No. 29 (1951).

[11] G. Scheibe, *Kolloid Z.*, **82**, 2 (1938).

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Received September 24, 1951

[Contribution from the Department of Chemistry, Cornell University]

The Structure of B-Trichloroborazole[1,2]

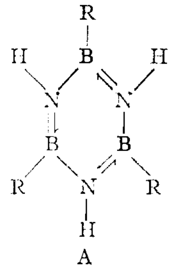
By D. L. Coursen[3] and J. L. Hoard

Analysis of the X-ray diffraction data obtained from single crystals of B-trichloroborazole has led to a complete determination of structure. Three-dimensional Fourier methods including corrections for finite termination of series were used to give accurate values of the atomic coördinates. The molecular configuration of B-trichloroborazole closely resembles that of *sym*-trichlorobenzene. Bond distances and interbond angles with estimated probable errors for the B-trichloroborazole molecule of symmetry D_{3h} are: B–N = 1.413 ± 0.010 A.; B–Cl = 1.760 ± 0.015 Å.; ∠NBN = 119 ± 1°; ∠BNB = 121 ± 1°. Some considerations which illuminate the nature of the reliability coefficient also are presented.

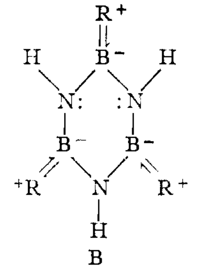
Introduction

The remarkable similarity in the physical properties of benzene and borazole ($B_3N_3H_6$) was pointed out by the discoverers[4] of the latter compound. Their assignment of an aromatic ring structure closely resembling that of benzene to the borazole molecule has received strong support from electron diffraction studies[5] and also from comparisons of spectra.[6]

There has seemed to be some uncertainty concerning the effect which is produced in the boron–nitrogen ring by replacing hydrogen atoms of borazole by other substituents. Wiberg[7] has suggested that B-substitution of groups with strong negative induction effects favors the aromatic structure A. The following substituents on boron are listed by Wiberg in the order of decreasing effectiveness in producing double bond character in the borazole ring: Cl > H > CH_3 > $N(CH_3)_2$. However, a study of the spectra of B-trichloroborazole, borazole and B-trimethylborazole has been interpreted[6] as indicating that both the methyl and the chlorine substituted compounds have less aromatic character than has borazole. It was suggested,[6] moreover, that this result for B-trichloroborazole would be expected if the contribution from structures of the type B were to become sufficiently important.



A



B

The results obtained in our study of B-trichloroborazole, while compatible with contributions to the structure of the molecule from both limiting formulations A and B, indicate that double bond

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[1] Supported in part by the Office of Naval Research, Contract No. N6ori-91, Task Order 4, Project No. NR052020, in part by the Atomic Energy Commission, Contract No. AT(30-1)-878.

[2] Preliminary account presented at the Spring (1950) Meeting of the American Crystallographic Association held at the Pennsylvania State College.

[3] Eastern Laboratory, E. I. du Pont de Nemours & Co., Gibbstown, New Jersey.

[4] A. Stock and E. Pohland, *Ber.*, **59B**, 2215 (1926).

[5] (a) A. Stock and R. Wierl, *Z. anorg. allgem. Chem.*, **203**, 228 (1931); (b) S. H. Bauer, This Journal, **60**, 524 (1938).

[6] C. W. Rector, G. W. Schaeffer and J. R. Platt, *J. Chem. Phys.*, **17**, 460 (1949).

[7] E. Wiberg, unpublished report obtained by the Office of Naval Research, EXOS:ONR:N425:RR:1h, Serial No. 12987, June 10, 1947.

resonance in the boron–nitrogen ring is at least as fully excited in the chlorine substituted derivative as in the parent borazole. Thus the negative induction effect of the chlorine as substituent would seem to be more important than the tendency of this atom to enter into multiple bond formation.

Experimental

B-Trichloroborazole, prepared by the method of Laubengayer and Brown,[8] was purified by sublimation within a vacuum chain having no ground glass joints. Since the material reacts rapidly with water to form boric acid and ammonium chloride, specimen crystals were grown inside cylindrical Pyrex glass capillaries of wall thickness too thin ($< 10^{-3}$ cm.) to show appreciable absorption or scattering of the CuKα radiation used in our study. Freely grown crystals were flattened needles subsequently shown to be orthorhombic. To prepare a specimen for X-ray study some of the material was distilled from the vacuum chain into one end of a capillary tube which was then sealed off. When the filled end of this tube was maintained at 50° and the other end at 48° over a period of several days, a single crystal of cylindrical cross-section and a centimeter or more in length would grow so as to fill completely the originally empty end. The specimen was then slowly cooled (about 2°/hr.) to room temperature in order to minimize the probability of cracking.

To record reliable and complete Weissenberg diffraction data it was desirable both that the axis of rotation, a rational direction in the crystal, be nearly parallel to the tube axis, and that photographs be obtained from rotation about all three crystal axes (or their equivalent). Excellent specimens for rotation about the c (needle) axis of the orthorhombic crystal were readily prepared. A satisfactory specimen with a second axis, b, inclined only 12° from the tube axis also was obtained. In about thirty trials, however, no crystal was grown having the a axis even approximately parallel to that of the capillary. A specimen suitable for rotation about a was cut under paraffin oil to approximately the desired shape and sealed within a thin-walled capillary in an atmosphere of dry nitrogen. Four crystals, three of which were cylindrical in cross-section, were used to give complete CuKα diffraction data. The a-axis specimen (designated T18) was 0.07 cm. long and had a rectangular cross-section 0.036×0.058 cm. Diameters of the cylindrical b-(T15) and two c-axis (T13 and T12) crystals were, respectively, 0.032, 0.032 and 0.006 cm. This last very thin needle (T12) when rotated about c gave Weissenberg data not requiring correction for variation of absorption with angle, and served as a standard during the elaborate procedure later used to reduce all intensities to a common basis.

Complete sets of Weissenberg equi-inclination photographs were obtained for rotation about the three principal axes. Three coaxial Type K films were used in each exposure and were developed under standardized conditions. The observed diffraction symmetry was D_{2h}-mmm; values obtained for the lattice constants, as determined from films on which NaCl pinacoidal reflections also were recorded, were $a = 14.00 \pm 0.02$, $b = 13.54 \pm 0.02$, $c = 3.95 \pm 0.01$ Å. (*not* kX). With four molecules in the unit cell the calculated density was 1.63 g./cc., to be compared with the pycnometrically measured value of 1.58 g./cc.

Intensities were estimated visually by comparison with a standard scale prepared with the greatest care. The densities of the spots on this scale, as measured with a Leeds and Northrup recording microphotometer, were nearly linear with exposure time. To obtain film factors the intensities of reflections appearing on one quadrant of all three films from each exposure were estimated using the scale, and the averaged intensity ratios of reflections appearing on the three coaxial films were obtained. These ratios varied somewhat for different exposures but had representative values of 11:3.3:1. Relative intensities were obtained for all reflections resulting from each exposure using the appropriate averaged film factors. These relative intensities were then corrected by the Lorentz, polarization and Tunell rotation factors to give relative squared structure amplitudes, $|F_{hkl}|^2$, still uncorrected for absorption, varying crystal size, Weissenberg extension or compaction, and relative exposure time.

Where extension and compaction, respectively, of two equivalent reflections on an n-layer Weissenberg film are evident, the averaged intensity of the pair should give the best common value. We found that in general it was easier to estimate accurately the intensities of spots exhibiting extension. It was feasible, however, to determine with precision the intensities of a dozen or more pairs of equivalent reflections appearing on both the extended and compacted sides of a film while covering the complete range of scattering angle. For all such pairs the values of

$$E = (I_c + I_e)/2I_e$$

where I_c and I_e, respectively, are the estimated intensities of the compacted and extended spots of a pair, were plotted as a function of distance of the spot from the center line of the film. The correction factors, E, were read from the curve thus obtained, and were applied to the intensity data obtained from the side of the film showing extension.

The linear absorption coefficient for CuKα radiation in crystalline B-trichloroborazole is 102 cm.$^{-1}$. For reflections from planes nearly or exactly parallel to the needle axis of the very thin reference crystal T12, the total change over the whole range of scattering angle in absorption by the specimen was negligible (2–3%). The diameters of all other crystals used were considerably greater than the "optimum" value, $1/\mu$–$2/\mu$. These larger specimens were used with especially long exposures so as to record a high proportion of the theoretically observable reflections despite the abnormally large effect of thermal vibrations in the crystal (it is shown later that the value of the thermal parameter, B, is greater than 6×10^{-16} cm.^{2}). A nearly ten-fold variation in absorption within the range of scattering angles, 0–180°, was required for equatorial reflections from either of the larger cylindrical specimens, T15 and T13. Absorption corrections were calculable with the aid of the rather accurately measured diameters of the crystals. We used the more accurate method of direct comparison of the data from corresponding exposures of T13 and the reference crystal, T12, (both c-axis specimens) to give the absorption corrections as a function of angle for T13. The function thus obtained could be carried over in good approximation to T15 since the diameters of T15 and T13 were equal.

Evaluation of correction factors arising from varying crystal size and exposure time depended, of course, on careful comparisons of relative $|F|^2$ values for reflections common to two or more exposures taken with different orientations of the specimen crystals. At an early state (before absorption corrections had been made for the thicker specimens) it was desirable to put the intensity data of the three Weissenberg exposures ($l = 0, 1, 2$) from the thin reference crystal, T12, on a common basis. The particular empirical method employed for this purpose utilized $|F|^2$ data uncorrected for absorption as obtained from the b-axis crystal, T15. The method is illustrated for the specific case of $|F_{h3l}|^2$ data from the third layer exposure of T15 but was also carried through with satisfactorily concordant results for $|F_{h0l}|^2$, $|F_{h1l}|^2$ and $|F_{h2l}|^2$ data.

A plot of the ratio of the corresponding $|F_{h3l}|^2$, $l = 0, 1, 2$ values from T12 and T15 against the distance of the reflection from the center line of the b-axis third layer film gave for each of the three values of l a practically straight line of negative slope. These three lines, moreover, approached closely to the axis of abscissas at large scattering angle and extrapolated to a common intercept on this axis. Multiplication of the $|F_{h31}|^2$ and $|F_{h32}|^2$ data from T12 by suitable constants, k_1 and k_2, so as to make the curves for $l = 0, 1, 2$ coincide gave the relative exposure factors, k_1 and k_2, needed to reduce all $|F^2|$ data from T12 to a common basis. It is evident that for each curve we were plotting a quantity proportional to the reciprocal of the absorption in the thick crystal, T15, against the angular variable (the absorption in T12 had trivial variation with angle). The slopes of the lines as first plotted differed only because the relative exposures, $l = 0, 1, 2$, from T12 were not identical. The large variation in absorption with angle for T15 caused it to give weaker intensities at small angle and larger intensities at large angle of scattering than T12.

Four independent pairs of values for k_1 and k_2 were obtained by applying this method in turn to the zero, first, second and third layer exposures from T15. It was concluded that the accuracy of the averaged results for k_1 and k_2 probably was about 5%, almost certainly within 10%.

The preceding discussion should make clear how the

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(8) C. A. Brown, Doctoral Thesis, Cornell University Library, 1948.

$|F|^2$ data from the *c*-axis crystals and, to a nearly comparable degree, that from the *b*-axis crystal could be reduced satisfactorily to a common relative basis. Some $|F|^2$ data, however, were obtainable only from the irregularly shaped *a*-axis crystal, T18, for which absorption corrections were large and varied strongly both with angle of scattering and with the relative orientation of the specimen. A majority of the reflections given by exposures with rotation about *a*, nevertheless, were also registered on films obtained with rotation about *b* or *c*. For such reflections it was possible to evaluate combined correction factors which took account of absorption, crystal size and relative exposure time. Using these points it was then feasible to sketch in on the film curves of constant correction factor. Since this process necessarily involved some extrapolation, it was desirable to use the $|F|^2$ data as fully as possible and, by applying all obvious tests for self-consistency, to attain the final curves by successive approximation. The graphical procedures developed in this process appeared to give such satisfactory results that they were applied to all of the data obtained from the thicker crystals, data from the thin crystal, T12, appearing always as the standard of reference.[9] (These procedures were, however, so inordinately time consuming that probably we shall not use them in future.)

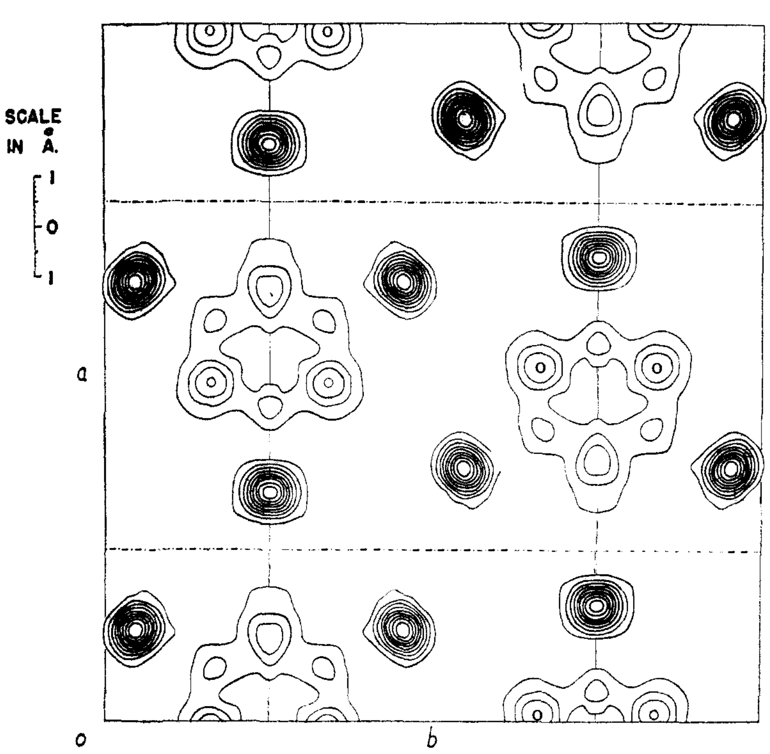

Fig. 1.—Fourier projection of electron density along the *c*-axis.

For most reflections values of $|F|^2$ were obtained from two or more specimens with rotation about different axes, and for a substantial proportion of all reflections estimates of $|F|^2$ were obtained from all four specimen crystals. In most cases the variations in the reduced $|F|^2$ values obtained from different crystals were not larger than one must expect from independently made intensity estimates for a spot on a given film. Despite the extraordinarily large effect of thermal vibrations in decreasing scattering power at larger angles, later simple calculations showed that our use of thicker specimens with adequate exposure time resulted in the recording of reduced $|F|^2$ of lower absolute value than has been usual in studies of this kind; 703 of a possible total (with CuKα radiation) of 879 forms were recorded. The values of $|F|^2$ were found to be quite generally small for reflections near the limit of observation, in part because of the large thermal decrease in scattering power, but also in part as a result of a low root mean square unitary structure factor from which there were few significantly large deviations. On this basis corrections for finite termination of series were expected and were later found to be small.

Chlorine atoms tend to dominate the scattering from the B-trichloroborazole unit, and it would require only a moderate average percentage error systematically applied to the reflection amplitudes to obliterate almost completely the contribution of boron atoms. Past experience seems to indicate that random errors of fair magnitude in the *F*-values would still permit of approximate determination of boron positions while giving rather poor electron density contours for these atoms on the Fourier maps. We believe that the satisfactory character of the contours for boron (and nitrogen) atoms in the section, $y = {}^1/_4$, of the three-dimensional Fourier synthesis (Fig. 4) constitutes indirect but rather convincing evidence that our experimental amplitude data were of high quality.

Determination of Structure

The observed systematic vanishings, (*hk*0) for *h* odd and (0*kl*) for $k + l$ odd, are characteristic for the space-groups C_{2v}^{9}–$Pn2_1a$ and D_{2h}^{16}–$Pnma$. A test for pyroelectricity was negative, in agreement with the subsequent successful analysis based upon *Pnma* as the true space-group.

In view of the short (3.95 Å.) *c* axis it seemed probable *a priori* that a Patterson projection along *c* should be relatively easy to interpret. Accordingly, the Patterson synthesis, $P(X,Y)$ of (*hk*0) squared amplitudes was calculated and found to show ten distinct non-equivalent peaks. While the majority of these peaks were composite, it proved feasible to interpret the pattern so as to give approximate *x* and *y* parameters for chlorine and, less accurately, for nitrogen and boron atoms. To aid in placing nitrogen and boron atoms it was assumed that the molecule has approximate threefold symmetry and is nearly planar. The asymmetric unit of the structure is half a molecule with one atom each of boron, nitrogen, chlorine (and hydrogen) lying in a mirror plane (perpendicular to the principal plane of the molecule) and with the remaining atoms occupying positions lacking any symmetry. Thus the special positions[10] 4(c), *x* 1/4 *z*, etc., of *Pnma* are used for one-third of each kind of chemically distinct atoms and the general positions 8(d), *xyz*, etc., for the remaining two-thirds.

The approximate *x* and *y* parameters as derived from $P(X, Y)$ were used to calculate structure factors for (*hk*0) reflections in order to assign phases to the corresponding experimental amplitudes. The resulting structure amplitudes, F_{hk0}, then were used to compute a Fourier projection $\rho(x, y)$, along *c* of relative electron density in the unit cell. This Fourier projection was refined by the usual method of successive approximation until no further changes in phase occurred. The final result for $\rho(x,z)$ is shown in Fig. 1 and the *x* and *y* parameters

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(9) Further details of this procedure and of other matters pertaining to the reduction of the intensity data are available in the Doctoral Thesis of D. L. Coursen, Cornell University Library, 1951.

(10) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder Borntraeger, Berlin, 1935, Vol. I, pp. 138–139.

read from the peak positions are given in Table I.

TABLE I

VALUES OF x AND y PARAMETERS FROM $\rho(x,y)$

Fourfold positions			Eightfold positions		
Atom	x	y	Atom	x	y
Cl	0.830	$^1/_4$	Cl	0.134	0.047
N	.1215	$^1/_4$	N	.988	.1605
B	.953	$^1/_4$	B	.0775	.168

If it be assumed that the molecules preserve approximate threefold symmetry, the departure on $\rho(x,z)$ of the three chlorine atoms of a molecule from an equilateral configuration indicate that the plane of these atoms is inclined about 28.7° from (001). The Fourier projection also is compatible with a nearly or exactly planar configuration of the molecule. Making use of these tentative conclusions it then proved feasible to delimit rather closely the range of z-parameters which would permit a satisfactory packing arrangement of the molecules. A set of z-parameters satisfying this criterion is the following. Fourfold positions: Cl, 0.779; N, 0.220; B, 0.546. Eightfold positions: Cl, 0.193; N, 0.472; B, 0.286.

In the next stage of refinement a Fourier projection along b of the relative electron density included in the range $y = 0$ to $y = {}^1/_2$ was computed. (By virtue of the mirror plane at $y = {}^1/_4$ this half-cell projection is just double the quarter-cell projection, $y = 0$ to $y = {}^1/_4$.) To compute this synthesis it was necessary first to use the complete set of parameter values as a basis for determining phases of all (hkl) structure amplitudes for which k is zero or odd. The half cell projection then was evaluated at intervals of $^1/_{60}$ along a and $^1/_{30}$ along c using the calculated phases and observed absolute values of these structure amplitudes. The usual process of recalculating phases, correcting the Fourier synthesis for phase reversals, etc., until all phases remained fixed led to the final half-cell projection shown in Fig. 2.

With the exception of the fourfold chlorine, there is a great deal of overlapping of peaks in this projection. Insofar as one can tell, however, the molecule appears to have the planar configuration. The only new values for x-parameters obtained from this projection are those for the fourfold and eightfold chlorine atoms, the latter being corrected for partial superposition of the fourfold nitrogen atom by subtracting a peak one-half the size of the eightfold nitrogen peak. The z-parameters of boron atoms and of fourfold nitrogen atoms were deduced using the x-parameters from $\rho(x,y)$ and assuming a planar molecule. The new z-parameters (Table II) are appreciably different from those obtained from packing considerations.

TABLE II

VALUES OF x AND z PARAMETERS FROM $\rho(x\ z)$, $y = 0 \rightarrow {}^1/_2$

Fourfold positions			Eightfold positions		
Atom	x	z	Atom	x	z
Cl	0.832	0.755	Cl	0.133	0.199
N	(.1215)	.220	N	(.988)	.465
B	(.953)	.532	B	(.0775)	.301

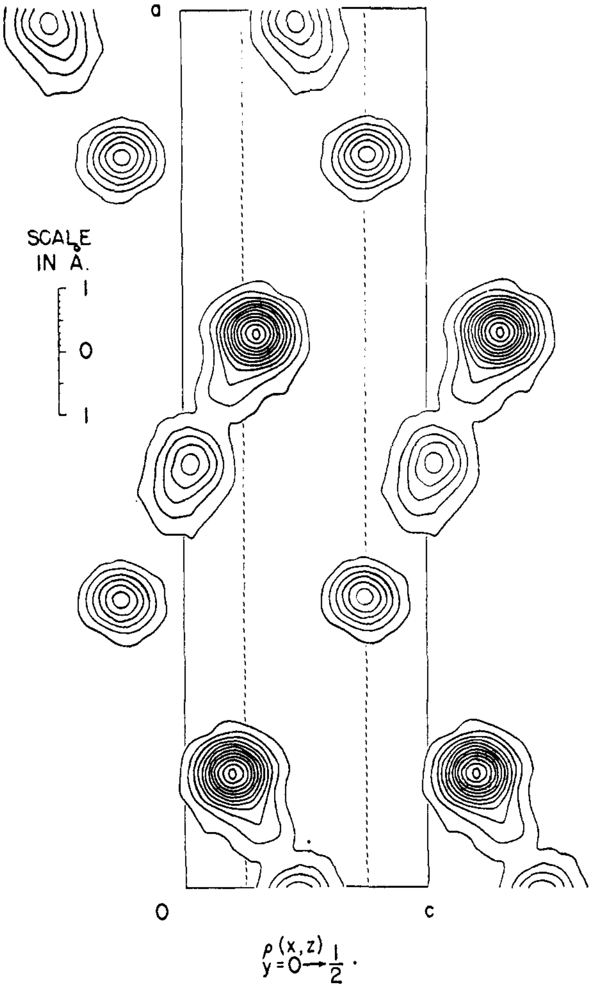

Fig. 2.—Half-cell Fourier projection along the b-axis.

Inspection of the plot (Fig. 1) of $\rho(x,y)$ shows that a projection along b of relative electron density in the range $y = 0$ to $^1/_8$ should effectively isolate two chlorine atoms occupying eightfold positions. This projection, moreover, utilizes all (hkl) structural amplitudes except those for which $k/4$ is integral and non-vanishing, and should provide highly accurate values for the x and z parameters of eightfold chlorine. A portion of the eighth-cell projection, $\rho(x,z)$ for $y = 0 \rightarrow {}^1/_8$ is shown in the insert of Fig. 3. The contours of the peak corresponding to a chlorine atom in the general position are satisfactorily concentric but are definitely elongated in a direction which proves to be accurately perpendicular to the principal plane of the molecule. The accurate final parameters for eightfold chlorine as derived from this synthesis are $x = 0.1355$; $z = 0.198$.

To obtain a correspondingly accurate value for the y-parameter of eightfold chlorine, the Fourier line synthesis $\rho(0.1355,\ y,\ 0.198)$, which uses all structural amplitudes, then was computed. A plot of this function against y is shown in Fig. 3. The precise position of the peak was evaluated by analytical methods leading to the final value $y = 0.0472$ for eightfold chlorine.

As one-third of all atoms lie in symmetry planes ($y = {}^1/_4, {}^3/_4$), the Fourier synthesis $\rho(x, {}^1/_4, z)$ requiring the use of all structural amplitudes was computed to give accurate x and z coördinates for atoms

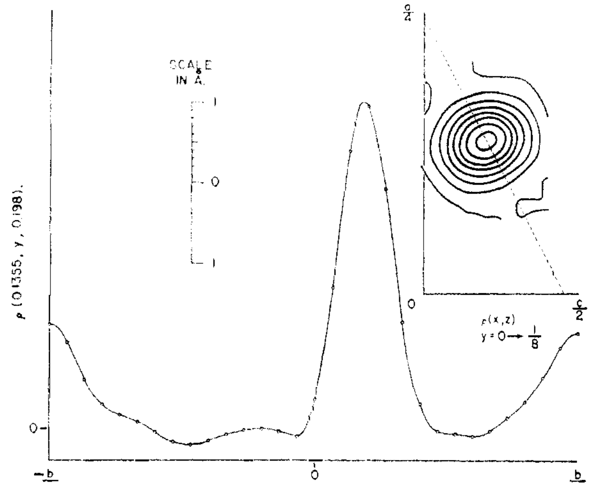

Fig. 3.—Fourier syntheses used to establish positions of eightfold chlorine atoms.

occupying fourfold positions. The resulting plot (Fig. 4) of $\rho(x,{}^1/_4,z)$ shows very satisfactory contours for chlorine, nitrogen, and even for boron atoms, a consequence, we believe, of the elaborate care taken with the recording and reduction of the intensity data. The data, however, are not good enough to place hydrogen atoms, although the character of the lowest contour in the vicinity of a nitrogen peak perhaps indicates a "near miss" in this respect.

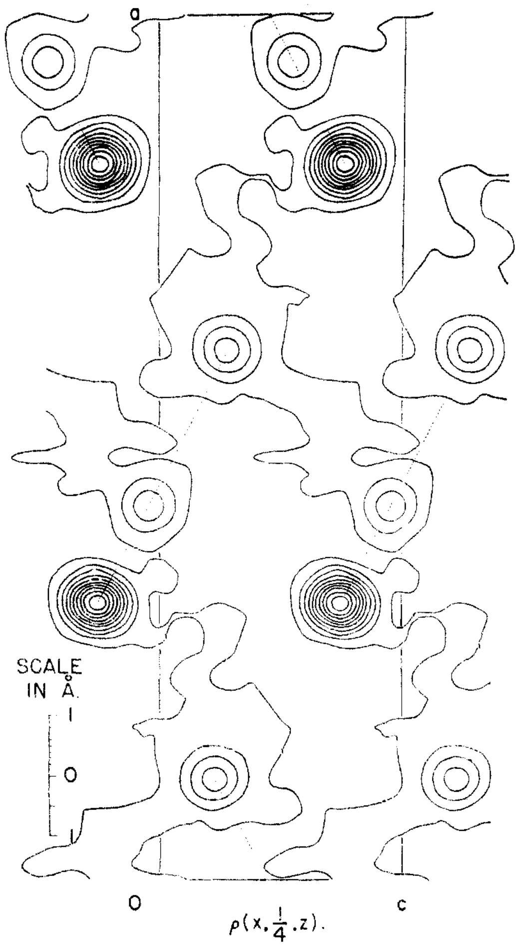

Fig. 4.—Section in mirror plane of triple Fourier synthesis.

Table III gives x and z coördinates of fourfold atoms (1), as read from $\rho(x,{}^1/_4,z)$, and (2), final values which include also small corrections for finite series termination. To obtain these corrections theoretical amplitudes were calculated (as discussed later) on the basis of the parameters given by the various Fourier syntheses of experimental amplitudes, and a Fourier section, $\rho_c(x,{}^1/_4,z)$, using these calculated amplitudes was constructed. The resulting small shifts in peak positions on ρ_c as compared with ρ were applied (with reversed signs) as corrections to the coördinates read from the Fourier synthesis of experimental amplitudes. The absolute values of these corrections for fourfold atoms were found to be: chlorine, 0.007 Å., nitrogen, 0.013 Å., boron, 0.037 Å.

Table III

Values of x and z Parameters for Fourfold Atoms

	x		z	
	$\rho(x,1/4,z)$	Final	$\rho(x,1/4,z)$	Final
Chlorine	0.832	0.832	0.758	0.7565
Nitrogen	.1225	.1225	.223	.220
Boron	.944	.9415	.548	.5515

It remained to find accurate coördinates for boron and nitrogen atoms in the general positions. For this purpose the three-dimensional differential analysis proposed by Booth[11] appeared to be particularly suitable. The accurately established positions of chlorine atoms and of those boron and nitrogen atoms lying in the mirror plane suggested that the molecule in the crystal conforms very nearly to the maximum symmetry of $D_{3h} - \bar{3}/m$. For the triangle of chlorine atoms is equilateral within about 0.5% and fourfold boron and nitrogen atoms lie within 0.01 Å. of the plane of the chlorine atoms. It seemed, therefore, that the amount of additional computations would be minimized if the differential syntheses were to use values of "trial" parameters for eightfold boron and nitrogen atoms deduced on the assumption of this highest possible symmetry. This hope proved to be extraordinarily well justified in application: only one set of calculations by the differential synthesis method was required in order to achieve convergence.

In order to make corrections for termination of finite series, a parallel set of differential syntheses based on the "trial" parameters but using calculated rather than observed amplitudes of reflection also was computed. If ϵ_0, ϵ_c represent, respectively, the shifts in an atomic coördinate as given by differential syntheses of observed and calculated amplitudes, then, according to the usual procedure, $\epsilon_0 - \epsilon_c$ should give the best estimate of the resultant correction to be applied to the "trial" parameter. The method should be most reliable when ϵ_0 and ϵ_c are both small and also are nearly identical both in magnitude and sign. These conditions are quite well satisfied by our data.

Table IV gives values for the "trial" parameters, ϵ_0, $-\epsilon_c$, and the final parameters for eightfold boron and nitrogen atoms. Although $\epsilon_0 - \epsilon_c$ is small for all coördinates the resulting shift in z-parameters is

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(11) A. D. Booth, *Trans. Faraday Soc.*, **42**, 444 (1946).

appreciable in consequence of the small value (3.95 Å.) of the *c*-axis.

TABLE IV

POSITIONS OF EIGHTFOLD BORON AND NITROGEN ATOMS

Boron				Nitrogen			
"Trial" parameter	ϵ_0, Å.	$-\epsilon_c$, Å.	Corrected parameter	"Trial" parameter	ϵ_0, Å.	$-\epsilon_c$, Å.	Corrected parameter
0.0780	0.0002	0.0012	0.0781	0.9890	−0.0066	0.0024	0.9887
.1600	.0230	−.0278	.1596	.1605	.0064	−.0124	.1601
.3040	.0148	−.0056	.3063	.4680	− .0190	.0082	.4653

Final values (to the nearest 0.0005) of all parameters are given in Table V.

TABLE V

FINAL PARAMETER DATA

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
B	0.9415	1/4	0.5515	B	0.0780	0.1595	0.3065
N	.1225	1/4	.2200	N	.9885	.1600	.4655
Cl	.8320	1/4	.7565	Cl	.1335	.0470	.1980

In order to make corrections for finite series termination and to carry out a general comparison of calculated with observed amplitudes of reflection the data were put on an approximately absolute basis through a procedure now to be described. If, for the reflection (*hkl*), F_c represent the calculated amplitude not including temperature factor, F_0 the experimental amplitude on the arbitrary scale used in estimating intensities, K the scale factor required to put experimental amplitudes on an absolute basis, and B the thermal parameter, then it was necessary to choose K and B so as to achieve a reasonably good fit on the average between $KF_0 \equiv F_0'$ and $F_c \exp[-B(\sin\theta/\lambda)^2] \equiv F_c'$, the values of the experimental and calculated amplitudes on the absolute scale.

In view of the markedly anisotropic contours of the peaks (Fig. 3) representing chlorine atoms in the general position it was obvious that the best matching of calculated and observed amplitudes could not be obtained with a single isotropic thermal parameter, B. It was equally obvious, however, that the very complete analysis by Fourier methods together with the nearly certain expectation that corrections for finite series termination would be small made it quite unnecessary to refine the model used in calculation beyond the point of achieving a fairly good fit on the average.

To determine K and B the averaged values $<F_0^2>$ and $<F_c^2>$ were computed for five separate ranges of $\sin\theta/\lambda$: 0.15–0.20, 0.25–0.30, 0.35–0.40, 0.45–0.50, 0.55–0.60 and a plot of $\log[<F_c^2>/<F_0^2>]$ against the corresponding mean values of $(\sin\theta/\lambda)^2$ was made. From the slope and intercept of the resulting straight line we found $2B = 12.2 \times 10^{-16}$ cm.^{2} and $K = 5.0$. Our decision to use the averaged squared amplitudes rather than $<|F_0|>$ and $<|F_c|>$ was quite arbitrary. Since the "reliability coefficient," $R = \Sigma|F_0' - F_c'|/\Sigma|F_0'|$, evidently is more closely related to a matching of amplitudes rather than of their squared values the alternative choice might have given a somewhat lower value for R.

The value $B = 6.1 \times 10^{-16}$ cm.^{2} thus obtained, though large, seems not incompatible with the properties of the crystal and the character of the structure. The detailed comparison of the final calculated and observed values of the reflection amplitudes indicates, indeed, that the value found for B is about the minimum acceptable.[12]

Accuracy of Results, Some Properties of the Reliability Coefficient

We gain a clearer idea of the probable accuracy of our work through a comparison with the elegant and complete determination of structure for naphthalene.[13] The two structures are of about the same complexity as will now be shown.

The molecular volumes of B-trichloroborazole and naphthalene differ by less than four per cent. in the crystals. In each case the asymmetric unit is half the molecule and fifteen parameters must be determined. The root mean square unitary structure factor, $\hat{\sigma}$, for all reflections in B-trichloroborazole as computed from the experimental data is approximately 0.20. Å. $\hat{\sigma}$ of 0.19 for general reflections not restricted by symmetry is estimated from the approximate statistical theory[14] with weighting of chemically distinct atoms in proportion to their scattering powers. The statistically expected value for all reflections is slightly larger, about 0.205, in substantial agreement with the experimental result. From the data cited by Hughes[14] we may expect the statistically calculated $\hat{\sigma}$ for general reflections in naphthalene, $1/\sqrt{20} = 0.222$, to be close to the experimental value. A slightly higher figure, say 0.23, is expected when all reflections are included.

The thermal parameter B is just enough larger for B-trichloroborazole than for naphthalene to make the ratio of the scattering power per molecule nearly a constant, 1.4, independent of angle. As the primitive unit in B-trichloroborazole contains four molecules as compared with two in naphthalene, the ratio of root mean square amplitudes (neglecting absorption) from specimens of equal volume should be about $\sqrt{2}$ (1.4) (0.20)/(0.23) = 1.7. This apparent advantage for purposes of recording experimental data from B-trichloroborazole is more than offset by its relatively large absorption for CuKα (μ = 102 cm.$^{-1}$ as compared with 6 cm.$^{-1}$ in naphthalene). Nevertheless the average magnitude of the experimental amplitude per unit volume at cut-off is but 50–60% larger in our data than in that from naphthalene. We were able to record a slightly larger percentage of all reflections theoretically obtainable with CuKα including a considerable group of lower unitary structure factor than was the case for naphthalene.

If any precise meaning is to be attached to relative values of the reliability coefficient for various structures, it should be required at least to calculate R-values by a standard method. One reasonably objective procedure is to include in the calculation of R terms for all reflections theoretically observable with CuKα, the experimental amplitude for each unobserved reflection being represented by half the minimum observable value *as determined by*

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(12) For a complete tabulation of calculated and observed amplitudes see reference 9.

(13) S. C. Abrahams, J. M. Robertson and J. G. White, *Acta Cryst.*, **2**, 233 (1949).

(14) E. W. Hughes, *ibid.*, **2**, 34 (1949).

the experimental technique. Applying this procedure we obtain from the B-trichloroborazole data $R = 0.22$, and from the published data for naphthalene[14] $R = 0.20$. If, however, the unobserved reflections are simply omitted from the calculation we find values of 0.20 and 0.185, respectively, for the two structures. (The published value of 0.168 for naphthalene doubtless was calculated by a quite reasonable but, nevertheless, more favorable procedure.)

The relatively small reductions in R obtained by ignoring unobserved reflections is a consequence of the care taken in both studies to record the largest practicable fraction of the possible reflections. The slightly larger value of R obtained for B-trichloroborazole is not unexpected. With no direct quantitative measurements of intensities and with large absorption corrections required we cannot expect our amplitude data to be as accurate as those for naphthalene. The model used in calculating amplitudes for the naphthalene structure, based as it was on a considerable experience with benzenoid structures, doubtless is superior to that for B-trichloroborazole. Given quantitatively measured experimental amplitudes, it would then be of great interest to carry through the laborious and thoroughgoing refinement of our model as an integral part of applying the $(F_0 - F_c)$-synthesis.[15] On the other hand so little can be expected from a modest improvement of our model beyond a correspondingly modest reduction in the value of R as, we believe, scarcely to justify the considerable additional labor which would be involved. We had rather present some further calculations which indicate in more detail how the value of the reliability coefficient depends upon the complexity of the structure and the manner of calculation.

Were we to use crystals of B-trichloroborazole of diameter in the "optimum" range, say one-half the diameter of the thicker crystals T13 and T15, and exposure times of more usual duration, we should record only about half instead of 80% of all reflections theoretically observable with CuKα. Through a combination of factors, of which the very steep thermal decrement is most important, the large majority of the missing reflections would lie in a band of $\sin \theta/\lambda$ adjacent to the theoretical maximum. It would not be unnatural in calculating R to ignore the missing reflections beyond the effective experimental limit (as is generally done when possible reflections beyond the CuKα limit are ignored). Going one step further and ignoring all reflections not recorded by our postulated "standard technique" (*but using calculated amplitudes based on the accurate parameters as determined*) we find $R = 0.17$. If, on the other hand, the calculation be made putting in for each unobserved experimental amplitude of this large group one-half the observable minimum on the "standard technique" photographs an R of about 0.32 is obtained. The values of R given by the various calculations are brought together in Table VI.

TABLE VI

DATA BEARING ON THE NATURE OF R

	$B_3N_3H_3Cl_3$	$C_{10}H_8$
A. Weakest 20% of reflections unobserved		
Suggested objective calculation	0.22	0.20
Unobserved reflections omitted	.20	.185
B. Weaker 50% of reflections unobserved		
Suggested objective calculation	0.32	
Unobserved reflections omitted	.17	

Comparison of the values 0.32 and 0.22 shows that a fairly crude model based on the parameters given by our Fourier syntheses does rather well in accounting for the amplitudes of the weakest group (comprising about 30% of the theoretical total) of reflections we were able to record. Comparison of the values 0.20 and 0.17 shows, however, that the quality of agreement attained is definitely poorer than for the stronger (50%) of reflections. Also, as mentioned earlier, comparison of the values 0.22 and 0.20 (or 0.20 and 0.185) shows that the weakest group (20%) comprising actually unobserved reflections were really so weak as to be relatively unimportant.

It is evident, moreover, that R is highly sensitive to and is adversely affected by the inclusion of an increasing number of weak reflections, *i.e.*, those of small unitary structure factor. The percentage accuracy in both experimental and calculated amplitudes decreases with decreasing unitary structure factor. The value of $\hat{\sigma}$ for a specialized class of reflections may be substantially larger than for general reflections within the same structure, leading to the familiar observation that R is commonly lower for the former. It follows that, other factors being equal, R increases with the complexity of the structure as measured by $\hat{\sigma}$.

In terms of Fourier analysis, which provides the most nearly objective method of quite general application (at least to centrosymmetric structures), it is wholly desirable to record the maximum proportion of theoretically observable reflections. If comparisons of R-values for various structure determinations are to be taken seriously the computations should be carried out for comparable circumstances, preferably by an objective method (such as that outlined earlier) which tends to penalize rather than to reward more or less in proportion to the unrecorded significant data. It should then be realized that the value of R is to a real degree a reflection of the complexity of the structure and is by no means an unambiguous criterion of accuracy. It cannot be expected, moreover, that values of R for structures determined by quite dissimilar methods should be strictly comparable. Minimization of a function closely related to R is required in the least squares[16] and related methods. Perhaps the most important advantage of such methods is that a careful analysis of special classes of reflections can lead to a quite accurate determination of structure.

A detailed examination of the structural results for naphthalene[13] and anthracene[17] raises the question whether the model used in minimization methods can be made entirely adequate without having a

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(15) W. Cochran, *Acta Cryst.*, **4**, 81 (1951). **4**, 405 (1951).

(16) E. W. Hughes, THIS JOURNAL, **63**, 1737 (1941); D. W. J. Cruickshank, *Acta Cryst.*, **2**, 154 (1949); **3**, 10 (1950); *etc.*

(17) V. C. Sinclair, J. M. Robertson and A. McL. Mathieson *ibid.* **3**, 251 (1950).

rather precise idea of the electron density function. Most important in this connection is the observation in naphthalene and anthracene of approximately 20% smaller peak values (with correspondingly more diffuse electron clouds) of the electron density for carbon atoms at the ends as compared with carbon atoms near the centers of the molecules. This effect, apparently indicative of molecular libration superimposed upon the translatory motions associated with the usual lattice vibrations, clearly is especially important for scattering at larger angles. The shapes of the electron density contours for chlorine atoms in B-trichloroborazole also seem to indicate libration of the molecule about the line of intersection of the molecular plane with the symmetry plane of the cell. It would appear that effects of this sort may be quite generally expected for structures of molecular type having especially larger thermal motions.

Insofar as we are aware, no one has attempted to construct a model for a structure which can be claimed to give intimate details (such as concentrations of electron density in bonds) comparable with those afforded by triple Fourier syntheses utilizing all recordable data. It seems to us that the one method which promises to go beyond the standard triple Fourier procedures is the very detailed form of the $(F_0 - F_c)$-synthesis.[15] In effect this method concentrates attention on an accurate fitting of high density contours for model and experimental structure, thus justifying claims of automatic correction for finite termination of series; also, to be sure, it makes a virtue of the fact that the model does not take into account those minor concentrations of electron density associated with bonds, hydrogen atoms, and the like. The interpretation of R-values, at least for reflections of not too small scattering angle, then becomes unambiguous.

On the basis of the σ-values alone, a larger value of R would be expected for B-trichloroborazole than for naphthalene. This conclusion doubtless is modified by the consideration that the chlorine atoms of the first structure have about 60% of the scattering power while their contributions to the resultant amplitudes depend upon but one-third of the variable parameters.

We conclude that our determination of chlorine positions in B-trichloroborazole is comparable in accuracy with the determination of carbon positions in naphthalene. The accuracy with which nitrogen and especially boron atoms are placed doubtless is smaller, and we have taken this into account in the estimates of probable errors in bond distances given in the following section.

Discussion of the Structure

The molecule of B-trichloroborazole as it exists in the crystal is planar within experimental error, for no boron or nitrogen atom departs from the plane of the chlorine atoms by more than 0.01 Å. The space-group requires the molecule to have a single mirror plane perpendicular to the plane of the molecule. The rather close approximation of the molecular configuration to the higher symmetry of the point-group D_{3h} is shown by the following tabulation of interatomic distances and interbond angles as calculated from the parameter data of Table V. The subscripts "4" and "8" identify atoms lying, respectively, in the fourfold (mirror plane) and eightfold (general) positions.

TABLE VII

Molecular Dimensions of B-Trichloroborazole

B_4–N_8 = 1.425 Å.
B_8–N_4 = 1.414
B_8–N_8 = 1.400
B_4–Cl_4 = 1.736
B_8–Cl_8 = 1.773
Cl_8–Cl_8 = 5.49
Cl_4–Cl_8 = 5.52

$\angle N_8B_4N_8$ = 117.3°
$\angle B_8N_4B_8$ = 119.9
$\angle B_4N_8B_8$ = 121.6
$\angle N_4B_8N_8$ = 119.7
B_8–B_8 = 2.448 Å.
B_4–B_8 = 2.467
N_8–N_8 = 2.434
N_4–N_8 = 2.432

Averaged Values with Maximum Deviations

B–N = 1.413 ± 0.013 Å.
Cl–Cl = 5.505 ± .015
B–B = 2.457 ± .011
N–N = 2.433 ± .001

B–Cl = 1.754 ± 0.019
∠NBN = 118.5 ± 1.2°
∠BNB = 120.8 ± 0.9°

It is immediately apparent that the molecular configuration approximates closely to the requirements of D_{3h}, and that we cannot decide whether the indicated deviations are real, at least in part, or are solely a consequence of experimental error. The only finite series correction to an atomic position which is large enough to affect significantly the molecular dimensions is that for B_4. This correction is responsible for the largest apparent fluctuations in distances and angles. Since, however, a careful recheck of all the calculations required in evaluating the position of B_4 (and other atoms in $y = {}^1/_4$) revealed no significant error, the result must be accepted in terms of the procedures used.

We may use the data of Table VII to assign a most probable configuration to an isolated molecule assumed to have the full symmetry of D_{3h}. The space-group requires certain distances and angles of Table VII to be repeated within the molecule and, in order to have the interior angles of the borazole ring add up to 720°, it is desirable to take a weighted average of the experimentally determined angles. It is not so clear that the weighted average is preferable in the case of interatomic distances, but the results of the differing procedures in every case agree within 0.005 Å. On this basis the predicted dimensions with estimated probable errors of the idealized molecule of symmetry D_{3h} are: B–N = 1.413 ± 0.010 Å., B–Cl = 1.760 ± 0.015 Å., ∠NBN = 119 ± 1°, ∠BNB = 121 ± 1°.

The picture we obtain is that of a typically aromatic molecule with the borazole ring just slightly larger than the carbon skeleton in benzene. Although the B–N bond distance is indicated as being slightly smaller than the value, 1.44 ± 0.02 Å., obtained in the electron diffraction study of unsubstituted borazole,[5b] it is seen that the combined experimental errors are not inconsistent with a common bond distance for both compounds. It does seem certain, however, that the B–N distance is not appreciably larger in B-trichloroborazole than in the parent molecule. The B–Cl bond distance, 1.76 Å., agrees within experimental error with the value, 1.74 ± 0.02 Å., obtained for BCl_3, and with the average, 1.76 ± 0.03 Å., observed for a number of compounds.[18]

As mentioned in the Introduction it has been suggested[6] that an unusually large amount of double bond character in the B–Cl bonds of B-trichloroborazole is accompanied by a smaller degree of double bond character in the B–N bonds than is characteristic of borazole. Far from supporting this suggestion, our data on bond lengths and on the molecular configuration would seem to exclude this possibility from further consideration.

The packing arrangement of the molecules is clear from a consideration of Figs. 1, 2 and 4. Mirror planes are shown as solid lines at $y = {}^1/_4$, $y = {}^3/_4$, diagonal glide planes with the glide $\frac{b}{2} + \frac{c}{2}$ are shown as alternately dotted and dashed lines at $x = {}^1/_4$, $x = {}^3/_4$, and axial glide planes with the glide $\frac{a}{2}$ are shown as dashed lines at $z = {}^1/_4$, $z = {}^3/_4$. The planes of the molecules are indicated in Fig. 4 by dotted lines.

Pairs of molecules (Fig. 1) straddle the mirror planes at $y = {}^1/_4$, ${}^3/_4$, occupy parallel planes which have a perpendicular separation of only 0.36 Å., and point in opposing directions along a. Successive molecules along a are tipped alternately +27.4° and −27.4° with respect to (001). The arrangement is such that every N–H bond is directed toward a chlorine atom of an adjacent molecule.

Along c the distance between the molecules is determined by contacts between equivalent chlorine atoms of neighboring cells. The corresponding Cl–Cl separation is c = 3.95 Å., or 0.35 Å. greater than the van der Waals separation expected from Pauling's tabulation.[19]

Perpendicular to c, the packing is determined by contacts between N–H groups and chlorine atoms. The closest approach along a, between N_4 and Cl_4, is 3.49 Å., along b, between N_8 and Cl_8, 3.56 Å. The electrostatic interactions N–H . . . . Cl implied by these distances are perhaps too weak to be called hydrogen bonding.

In terms of the loose packing of the molecules an averaged thermal parameter, $\bar{B}$ = 6.1 Å.^{2}, does not seem unduly large. The packing is especially free along the normal to the molecular plane and is tightest in the direction of the secondary molecular axis passing through fourfold atoms in the symmetry plane of the unit cell. These molecular axes are rotated about b by 27.4° from the positions of the c and a crystal axes, respectively.

All contours of eightfold chlorine peaks (Fig. 3) show a pronounced elongation normal to the molecular plane. The outer contours of fourfold chlorine peaks (Fig. 4) show a similarly oriented but much less pronounced elongation. This last seems to be true also for fourfold nitrogen peaks. It would appear that a libratory motion of the molecule about the secondary molecular axis lying in the mirror plane of the cell is superimposed upon and coupled with somewhat anisotropic lattice vibrations.

We are indebted to Mr. R. E. Hughes for computations of the differential syntheses leading to the accurate evaluation of parameters for eightfold nitrogen and boron atoms. We wish to thank Professor J. Monteath Robertson for encouraging and helpful discussions pertaining to accuracy and the nature of the reliability coefficient.

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(18) A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones and L. E. Sutton, *Trans. Faraday Soc.*, **33**, 852 (1937)

(19) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

ITHACA, N. Y. RECEIVED JULY 12, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Catalytic Activity of Supported Manganese Oxides for the Hydrogen Peroxide Decomposition[1]

BY JOHN MOOI AND P. W. SELWOOD[2]

The catalytic decomposition of hydrogen peroxide in dilute water solution on various supported manganese oxides has been studied. The activity of these catalysts as a function of the concentration of manganese on the support shows an increase with decreasing manganese concentration, followed by a sudden decrease for very low manganese concentrations. The influence of oxidation state, pH, support phase modification and temperature has also been studied. The data have been interpreted on the basis of a mechanism involving simultaneous oxidation and reduction of the catalyst by the hydrogen peroxide in which trivalent and tetravalent manganese take part. Low activities for samples of low manganese concentrations show the influence of the support in stabilizing one of these forms of the catalyst.

Information about the structure of supported oxides of manganese as obtained by the susceptibility isotherm method has been presented in two previous papers from this Laboratory.[1,3] The samples studied were several series of supported oxides and a few catalysts on various modifications of the support. The method of preparation of the samples was by impregnation with manganous nitrate solution followed by ignition to decompose the nitrate. By varying the concentration of the solution, series of samples of differing manganese content were prepared on high area so-called "γ"-alumina, on alumina containing sodium oxide, and on rutile. Ignition was generally at 200° with the exception of one series on "γ"-alumina, called the high-ignition series, for which the ignition

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(1) This is the eleventh paper from this Laboratory on the susceptibility isotherm. The tenth by Selwood and Lyon appeared in THIS JOURNAL, **74**, 1051 (1952). A Communication to the Editor in connection with the present paper appeared in THIS JOURNAL, **73**, 4333 (1950).

(2) Inquiries concerning this paper should be addressed to P. W. Selwood.

(3) P. W. Selwood, T. E. Moore, M. Ellis and K. Wethington, THIS JOURNAL, **71**, 693 (1949).