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# STRUCTURES OF SOME BRIDGE TYPE COMPOUNDS

by

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Major Subject: Physical Chemistry

Approved:

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In Charge of Major Work

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Head of Major Department

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# INTRODUCTION

If the tendency of metal atoms to use all their atomic orbitals is recognized (1, 2), the structural features of a large number of compound types may be understood. This rule holds even if there is an insufficient number of electrons in the valence shells of the constituent atoms to provide an electron-pair for every bond that is formed. The use by a metal of all its low-energy orbitals in bonding not only accounts for known 'electron-deficient' compounds, but predicts that metals with more low-energy orbitals than valence electrons should form 'electron-deficient' compounds when combined with elements or groups containing no unshared pairs. In the light of this rule the structures of trimethylaluminum and beryllium chloride described in this thesis can be understood.

At first 'electron-deficient' compounds were thought to be rare, to be confined to the boron hydrides and other third group hydrides and alkyls, but the realization that dimethylberyllium (3) and tetramethylplatinum (4) are 'electron-deficient' has extended the known range of occurrence. Even metals (5, 6) and interstitial compounds (7) may be understood better if regarded as 'electron-deficient'. The occurrence of 'electron-deficient' compounds can now be predicted using Rundle's rules (7):

1. One element, A, usually a metal, must have more stable bond orbitals than valence electrons.
2. Another element, B, must have relatively few bond orbitals. Consequently B will usually, but not always (metals), be a nonmetal and will be limited to hydrogen and the first row nonmetals.
3. The electronegativities of A and B must not differ so much that the bond is essentially ionic. The stability of 'electron-deficient' compounds is due to resonance stabilization, stability being a test when electronegativities are equal.

The first evidence of what effect 'electron-deficiency' would have on molecular shape, bond angles, and bond lengths in organometallic compounds is to be found in the X-ray study of tetramethylplatinum (4). This molecule is a tetramer in which platinum atoms and methyl groups occupy alternately the corners of a distorted cube, while three external methyl groups are bonded to each platinum. The main point to note here is that in order for the platinum metal atom to use all of its atomic orbitals a novel type bonding has occurred. To begin with, the platinum-platinum distance, 3.44Å, is much too long for bonding to take place (1.31Å is the octahedral radius for platinum (8)). Dismissing this and using the fundamental principle enunciated, the bonding may be understood. The following has been proposed: tetravalent platinum has six stable orbitals which may be used in octahedral-$d^2sp^3$ bonding, but three of these are engaged in normal bonding to methyls, leaving three unused orbitals and one electron. To make use of these three orbitals the carbon departs from its usual tetrahedral configuration and becomes octahedral, using the three orbitals. If the carbon to hydrogen bond in these bridge methyls were normally covalent, each carbon would contribute three orbitals and one electron for bonding the tetramer together. Noting that there are twelve bonds to be formed in the cube, the bond order of each would be one third. There exists the possibility that if the bond order of the carbon to hydrogen bonds for the bridge methyl were to be two thirds, then that of the bonds forming the edges of the cube would be one half. Which of these possibilities is correct is difficult to decide. The checking of whether the carbon-hydrogen stretching frequency in the bridge methyls is affected is precluded by the fact that a large number of normal carbon to hydrogen linkages exist in the molecule.

The methyl positions are not definitely located in this structure because of the low scattering factor of carbon in in contrast to that of platinum. These positions may be inferred from the location of the chlorine atoms in the analogous compound, trimethylplatinum chloride.

The structure of dimethylberyllium (3) confirms the expectation that beryllium would utilize its four low-energy orbitals in 'electron-deficient' bonding. The X-ray study of this compound revealed that it is isomorphous with silicon disulfide. The main structural characteristic of both compounds is the polymeric chain, the repeat unit being a four membered ring having metal and nonmetal at alternate corners -- the nonmetal acting as a bridge for bonding between the metal atoms. In dimethylberyllium, the striking feature of the ring is the bridge angle of but 66°. While this angle might be used to support the idea that beryllium-beryllium bonding occurs (the beryllium-beryllium distance is 2.09Å in comparison with the 2.12Å predicted by doubling the beryllium tetrahedral covalent radius), a more reasonable explanation is possible. Following Mulliken's suggestion (9), the bonding may be thought of as the symmetrical overlap of one tetrahedral orbital of the carbon over those of the two beryllium atoms to form a molecular orbital. The tetrahedral configuration about the beryllium remains almost unchanged (the C-Be-C angle is 114°), while the bridge angle becomes 66°. Thus the short beryllium-beryllium distance is a consequence of bridge bonding rather than the result of metal-to-metal bonding.

The equality of all the beryllium to carbon bond lengths is a notable feature, for this clearly violates the unsymmetrical bridge feature of both Pitzer's (10) and Longuet-Higgins' (11) proposals to be discussed later in connection with trimethylaluminum. The beryllium-carbon bond length, 1.92Å, is significantly different from that obtained by use of Pauling's rules and radii, 1.84Å, (12) and suggests that these rules are unreliable in unusual cases. The distance between the polymeric chains, 4.1Å, seems to confirm the covalent character of the bonding; ionic character of the methyl groups would require larger carbon-carbon distances between chains.

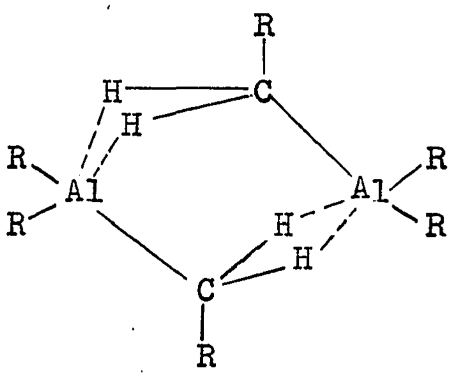
Diborane would seem to satisfy the specifications for 'electron-deficient' bonding. The compound is still, to an extent, a subject for dispute for accurate bond lengths and angles are not available. Convincing evidence in the form of spectrographic data favors the bridge type molecule described above. The observed infrared spectra (13) can be satisfactorily assigned on this basis. Fifteen out of seventeen active fundamentals are observed. These fifteen frequencies can be predicted with an average error of 2 per cent and a maximum error of 6 per cent by the insertion of six adjustable force constants in the theoretical equations. These force constants indicate the boron-hydrogen links external to the bridge are normal single bonds, while those forming the bridge are considerably weaker. To further distinguish the diborane structure from that of ethane, Price (14) has found that upon resolution of the perpendicular bands around 2600 and 970cm$^{-1}$, a well marked alternation of intensities is to be observed; in ethane every third line is but slightly accentuated. The configuration about the boron is tetrahedral, the boron bond angles in the ring being 100°

while those external to it, 120°. The boron-hydrogen distances are 1.18Å external to the ring, 1.41Å internal (15). More accurate data from a microwave spectral study is to be expected (16).

It would seem possible to explain the stability of the trimethylaluminum dimer in a way similar to that for dimethylberyllium. In order for the aluminum atom to make use of all four of its orbitals, only the bridge model need be considered logical in light of the fundamental principle of orbital utilization. This claim would be made in the face of other explanations for the molecule's stability, and indeed in the face of what others thought the molecule should look like. A review of all this follows.

That the molecule is a dimer is best substantiated by the cryoscopic study performed by Pitzer and Gutowsky (10). In this case the freezing point depression of trimethylaluminum in benzene was measured. Their work is subject to certain errors, namely, the failure of Raoult's law in dealing with actual solutions, and the impurity of the sample due to the reaction of trimethylaluminum with trace amounts of oxygen and water in the benzene. Nevertheless, the range in the polymerization factor, R, (which would be 2 if the molecule were a dimer) was from 1.997 to 2.023. The vapor study of Laubengayer and Gilliam (17) is less certain. These authors conclude that trimethylaluminum is a dimer at 70°C; however, their curve of apparent molecular weight versus temperature has an appreciably negative slope at this point. Since only one experimental point was observed at a temperature lower than 70°C, whether their curve becomes asymptotic to the molecular weight of the dimer, 144, is questionable.

Pitzer and Gutowsky also studied the higher alkyl homologs of trimethylaluminum. From the fact that the dimers seemed most stable to dissociation when two hydrogens were present on the α carbon, they concluded that the structure of trimethylaluminum was bridge-like with each bridge carbon being bonded to one aluminum with a normal covalent bond and to the other aluminum through two hydrogen atoms



The hydrogens were not participating in a "protonated" double bond suggested by Pitzer for diborane, but the bond was rather polar in nature, the highly positive aluminum attracting the negative carbon through two hydrogen atoms. The fact that the hydrogen-carbon dipole would be oriented with the positive end towards the aluminum did not seem to bother Pitzer and Gutowsky.

This structure satisfied the electron diffraction pattern, but the best evidence claimed for it was the Raman analysis. If the compound were to be like aluminum chloride, it would have to possess approximately the same number of polarized and depolarized lines in that spectra. But the halide possesses three definitely polarized, three definitely depolarized, and two doubtful lines, while the alkyl had five polarized, one definitely depolarized and three doubtful lines in the range below $700 \text{cm}^{-1}$. The trimethyl compound would seem to be of lower symmetry than aluminum chloride. It should be noted that while the carbon skeleton of this molecule may be $D_{2h}$ in symmetry, the symmetry of the molecule as a whole may not be so due to restricted rotation of the methyl groups. Deductions as to molecular symmetry through the use of Raman spectra have not always been reliable, especially in liquid state studies. To a degree, the confusion concerning the symmetry of benzene might be noted.

Of the electron diffraction study (18) it might be said that if it did not produce the answer, it did produce answers. Brockway and Davidson themselves suggested two models, one a bridge-type and the second akin to ethane. The dimensions for the first of these possibilities are as follows:

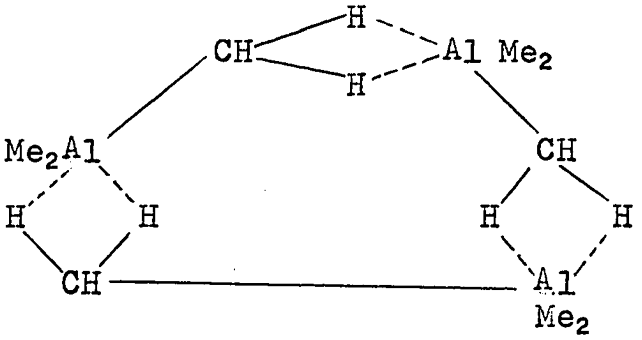
| | |
|---|---|
| Aluminum to bridge carbon | 2.10Å |
| Aluminum to nonbridge carbon | 1.90Å |

| | |
|---|---|
| Aluminum to aluminum | 1.90Å |
| Bridge angle | 54° |

for the second

| | |
|---|---|
| Aluminum to bonded carbon | 2.01Å |
| Aluminum to nonbonded carbon | 3.24Å |
| Aluminum to aluminum | 2.20Å |
| C - Al - Al | 100° |

They rejected the first of these possibilities as bringing the nonbonded aluminum atoms too close to one another. As was mentioned, Pitzer and Gutowsky felt that the electron diffraction data supported their concept of the trimethylaluminum dimer. Longuet-Higgins (11) found that the electron diffraction data would support a trimer of the form:



The bonding in the trimer would consist of "protonated" double bonds in contrast to Pitzer's idea of a polar bond between the aluminum and carbon through hydrogen atoms. Pitzer's objection (10) to this seems valid, for aluminum would be forced to violate the octet rule in this molecule.

In the same paper (11), Longuet-Higgins also proposed the "methylated" double bond for the dimer. This would be, in essence, the bridge model rejected by Brockway, the novelty lying in the explanation of the bonding. The aluminum atoms are joined by an ordinary $\sigma$ bond, while each bridge carbon is bonded by $\pi$ bonds to the aluminums, the $\pi$ orbitals overlapping the single remaining tetrahedral orbital of the carbon. Longuet-Higgins felt that the aluminum-aluminum distance should be between that of a single bond and a double bond. Seemingly this is a valid explanation. It is, however, singularly vague. Using this proposal, little can be said about the bond angles observed in this compound. A worse criticism is that the proposal is passive. If bridge bonding is found in a molecule, "methylated" double bonds would be an explanation. However, the proposal would be of little use in deciding between proposals for the molecular structure of a compound about which little or nothing is known, or in cases in which the evidence is not clear-cut.

In 1947 Rundle (1) predicted that:

1. Trimethylaluminum would be bridge-type in structure, in order to utilize all the metal's atomic orbitals.

2. The four aluminum-carbon distances in the ring would be between 2.1 and 2.3Å.

3. The four aluminum to carbon distances external to the ring would be 2.0Å.

4. The aluminum to aluminum distance would be between 3.0 and 3.5Å.

In the light of the dimethylberyllium structure, the latter prediction would be amended to a shorter metal to metal bond, so that the bridge angle would be about 66°.

It seemed interesting to check these various concepts by means of an X-ray diffraction study of trimethylaluminum hoping to come to a conclusion by an analysis of the bond angles and distances determined.

The function of chlorine as a bridge atom in trimethylplatinum chloride (4) in a way similar to carbon in tetramethylplatinum (4) excited interest as to whether or not the chlorine is participating in 'electron-deficient' bonding. The inability to locate the methyl groups except by inference prevented decision by a comparison of bond lengths or angles. It is to be noted that extra stability is obtained when the halogen acts as the bridge; the molecule has the opportunity to use either a methyl or a chlorine as a bridge, but uses the latter. The suggestion is that a bonding more stable than 'electron-deficient is being used, that it is coordinate-covalent.

This conclusion would seem confirmed in the case of the dialkyl gold bromide dimer (19). The bridging, in the same way, occurs through the two halogens. The four membered ring made by the two gold and the two bromine atoms has an 80° bond angle at the bromine bridge, the Br-Au-Br angle being 100°. The gold-bromine bond length is 2.64 Å, exactly what would be calculated using the covalent atomic radii. The bond angles are roughly what would be expected if the configuration about the gold were square-dsp, while the bromine is bonded through two p orbitals.

Another case in which covalent bonding seems correct is that of the palladous chloride polymer (20). This compound is an infinite chain made up of coplanar rings formed by the bonding of two palladium atoms through chlorine bridges. The palladium to chlorine distance is 2.31Å in comparison with 2.30Å calculated by use of the sum of the covalent radii of palladium and chlorine. The bond angles of almost 90° are extremely reasonable. Palladium uses the square $dsp^2$ orbital configuration while chlorine's two p-orbitals are at 90°.

It is to be noted that even in these cases, despite the fact the bonding is coordinate-covalent, the fundamental rule still is the full utilization of the metal's atomic orbitals, both the above compounds forming bridges to do so. This rule carries over to the aluminum halides, although here the nature of the bonding is a question. The electron diffraction study is notably poor. Both aluminum chloride and bromide (21) seem to be bridge-type. The bond angle in aluminum chloride, which should be tetrahedral, is but 80°. The aluminum-chlorine bond lengths are different, those internal to the ring are 2.21Å, while those external are 2.06Å. Whether or not these anomalies are due to the normal uncertainty associated with electron diffraction work is not made clear by the X-ray study (22), aluminum chloride is clearly ionic in the solid phase. If the bond length difference between the two types of aluminum-chlorine bond were to be valid, electron-deficient bonding might be assumed.

The X-ray study of aluminum bromide dimer (23) is uncertain. Since the aluminum-aluminum distance is too long for normal bonding, this compound must be bridge-type. However, the aluminum-bromine distances reported for the ring are not equal, 2.34 and 2.42Å. The bond lengths external to the ring are likewise inconsistent, 2.23 and 2.33Å. Bond lengths and angles would be of little help for decision.

To resolve the problem of whether halogen bridge bonds are covalent or not, more work could have been done on the aluminum bromide solid to resolve the ambiguity. Another way, perhaps a better one, suggested itself. Dimethylberyllium has been found to be isomorphous with silicon disulfide (3, 24). Both are type compounds, the former being electron-deficient, the latter coordinate-covalent. The two compounds are easily distinguishable by their bridge angles, that of dimethylberyllium being 66°, that of silicon disulfide, 80°. There existed the strong probability that if the compound beryllium chloride were to be at all covalent (in contrast to ionic) its bonding character could be identified by comparison of bond angles with these two compounds. In this way some light could be shed on halogen bridge bonds in general and the beryllium and aluminum halides in particular.

# THE STRUCTURE OF TRIMETHYLALUMINUM

## Experimental Procedure and Results

### Preparation and properties of trimethylaluminum

Most of the following is to be found in an article by Pitzer and Gutowsky (10). It is summarized here for the convenience of the reader. Trimethylaluminum is a clear, water-white liquid at room temperatures. It resembles water in viscosity. The reaction with water and air is explosive, the compound burning with the yellow and sooty flame typical of a hydrocarbon. The reactions of the compound with hydrocarbon greases and carbon tetrachloride are noteworthy.

The compound freezes at 15.0°C, has a specific gravity of 0.752 ($=d_4^{20}$). The magnetic susceptibility studies indicate the compound is diamagnetic; solutions in benzene are essentially nonconducting. The infrared absorption spectra, which the above authors obtained from the Spectroscopic Department of the Shell Development Company, follows in Table 1. The molar refraction of the monomer is 24.7 c.c.

The preparation of the material for our study was exactly the same as that described by Pitzer and Gutowsky (10). Again repeating: the type reaction is that described by Grosse and Mativity (25). A distilling column of ten to twenty plate efficiency was set up with fittings for nitrogen

Table 1. Infrared absorption spectra of trimethylaluminum.[1]

| 15 cm cell, P=12.6 mm | | |
|---|---|---|
| λ (μ) | (cm$^{-1}$) | Intensity |
| 3.380 | 2958 | 7 |
| 3.425 | 2919 | 0[a] |
| 3.49 | 2865 | 1[a] |
| 3.735 | 2677 | 0 (?) |
| 6.685 | 1496 | 0 (?) |
| 6.925 | 1444 | 1[b] |
| 7.67 | 1303 | 1 |
| 7.985 | 1252 | 7 |
| 8.295 | 1205 | 9 |
| 11.495 | 869 | 2 |
| 11.56 | 866 | |
| 12.875 | 779 | $10^+$ |
| 14.005 | 715 | $10^+$[b] |
| 14.35 | 696 | |

[a] Indicates a shoulder.

[b] A broad band.

[1] Quoted from reference (10).

at either 1 atm or reduced pressure. Methyl iodide was placed in the still with an excess of granular aluminum and mildly refluxed under 1 atm pressure of nitrogen for twelve or more hours until the reaction was complete. The trimethylaluminum, being more volatile than the general mixture of methylaluminum iodides also produced, was fractionated off slowly. Several fractions were taken, isolated in thin-walled glass capillaries, and checked for purity by means of the melting point. Samples containing even trace amounts of iodine showed large deviations from the true melting point.

### The low temperature X-ray study

Since trimethylaluminum is a liquid at room temperatures, it was necessary to resort to low temperature techniques in order to obtain X-ray single crystal data. Excellent articles exist in this field (26, 27, 28). To facilitate the introduction of the cold air leads into the camera, the Weissenberg camera, but not the precession camera, was modified in that the slit in the cylindrical camera in which the pinhole system normally rides was continued to the left edge of the camera. The Weissenberg screen and the beam catcher used for rotation or oscillation work were similarly slit. In this way the pinhole system, once adjusted to the X-ray source, was allowed to remain so; the camera and screens could be changed without disturbing the setup.

The sample was kept cold by means of an air stream which was pumped by a Cenco "Pressovac". To dry the air before it passed through a copper exchange coil immersed in dry ice, a novel drying system was devised. A pair of gallon cans were filled with copper turnings and the cans were furnished with copper inlet and outlet pipes. Copper screening was used to keep the turnings away from these tubes. The cans were placed in insulated chambers and surrounded by dry ice; the two systems were hooked together so that one could be removed while the other bore the load. This method of drying the air proved vastly superior to chemical drying. Leaks around the lids of the number 10 cans were easily stopped by freezing water in the lips before commencing operation. Although a test run of some 54 hours was made without stoppage due to icing in the leads, the system was depended upon for but 24 hours.

The plastic jet tube was mounted onto the pinhole system and directed normal to the sample. It was found that an orifice of a 1/4" was satisfactory. Smaller tubes permitted "frosting". The large dry air cone prevented this. Operation was at about -20°C for the Weissenberg work and 0°C for the precession. A longer uninsulated tube was necessary for the latter. For temperatures lower than this Fankuchen's modification (26) of the above is to be recommended.

Crystallizing the sample proved difficult, the technique used was to alternately freeze and thaw the liquid. Ten hours were often spent in obtaining a suitable crystal. These were checked as to suitability by means of the X-ray patterns obtained. It was a characteristic of the sample to crystallize with the c-axis almost parallel with the axis of rotation. Attempts to obtain other orientations proved futile except once when the b-axis was obtained parallel to the axis of rotation. This latter was fortuitous for it could not be repeated.

## Diffraction data

The X-ray diffraction data were obtained by means of the usual single crystal techniques except as described above. In order to obtain the complete sphere of reflection, the following photographs were taken:

Cu K α radiation - Weissenberg - (hk0) to (hk7)
- Oscillation - ($hk\ell$)
about both the c- and b-axes.
Mo K α radiation - Precession - ($h0\ell$)
Precession - ($h1\ell$)

The Weissenberg intensity data were entirely in the form of multiple films, while that of the precession were taken by means of timed exposures. Exposure time for each set of data taken on the Weissenberg was about 24 hours; the longest exposed picture in the ($h0\ell$) set was eight hours. The X-ray source unit in each case was that of the North American Phillips Company. The wave lengths used in calculations were $\lambda_{CuK\alpha} = 1.542\text{Å}$ and $\lambda_{MoK\alpha} = 0.7107$. The film used in all data taking was that of Eastman Kodak X-ray medical film with a film factor of 3.6 for CuKα.

The oscillation photographs taken about the c-axis revealed no horizontal planes, but a vertical one was located. Although the b-axis oscillation picture showed a horizontal mirror plane, no vertical mirror plane could be found. Thus the crystal belongs to the monoclinic crystal class. This was confirmed by the facts that the $(h0\ell)$ and $(h1\ell)$ reciprocal nets showed $C_2$ symmetry, the $(hk0)$ net $C_{2\ell}$ while the higher layers obtained while rotating about the c-axis, $C_\ell$ .

The lattice constants are: $a_0 = 13.0$, $b_0 = 6.96$, $c_0 = 14.7\text{Å}$, $\beta = 125°$. If the density of the liquid is assumed to be that of the solid some forty degrees colder, then there would be 6.8 trimethylaluminum monomers per unit cell. The assumption was made that the density increased on cooling and that there were really 8 monomers per unit cell. The density calculated on this basis is 0.887 gms/cm$^3$.

Indexing of the photographs obtained shows the occurrence of systematic absences which are as follows:

$(h0\ell)$ present only if h and $\ell$ are even

$(hk\ell)$ present only if $h + k = 2n$.

From this can be concluded that the space group is either

$C_{2h}^{6}$ - C2/c or $C_{s}^{4}$ - Cc. During the course of the investigation it was felt wise to eliminate the latter possibility. This was done by the method of Howells (29). This method works best when atoms are not in special positions and when there are a sufficient number of reflections to be statistical. The entire data in the form of $F^2$ were arranged in order of increasing $\sin^2\theta/\lambda^2$. Systematic absences were ignored, but accidental absences were retained in the list. All reflections having $\sin^2\theta/\lambda^2 \leqq \lambda^2/b_0^2$, $b_0$ being the shortest cell dimension, were omitted. The list was divided into several ranges according to the $\sin^2\theta/\lambda^2$ values and an average value $\langle F^2 \rangle$ obtained for each group. Needless to say, reflection multiplicities were considered. Each squared structure factor was divided by the appropriate $\langle F^2 \rangle$ and the quotient defined as z. N(z), the per cent of reflections having a z greater than or equal to z, was calculated for z from 10 to 90 per cent. The comparison of this plot of N(z) <u>versus</u> z for trimethylaluminum against the standard values of the centro-and noncentrosymmetric curves revealed the compound to possess a center of symmetry. A tabulation of results is in Table 2. From this can be said that the space group of trimethylaluminum is unambiguously $C_{2h}^{6}$ - C2/c (30).

The intensities of the observed reflections were estimated by eye and corrected for Lorentz and polarization factors. The corrections for the Weissenberg data were

Table 2. Data for the determination of the center of symmetry in trimethylaluminum.

| Number of terms | $\langle F^2 \rangle$ | Range $\sin^2\theta$ | z= | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 370 | 89 | 0.0206<br>0.084 | N(z)= | 25 | 34 | 42 | 45 | 49 | 51 | 59 | 63 | 67 |
| 528 | 43 | 0.084<br>0.17 | | 17 | 31 | 37 | 40 | 52 | 59 | 62 | 63 | 66 |
| 502 | 16 | 0.17<br>0.25 | | 26 | 30 | 30 | 35 | 45 | 49 | 53 | 56 | 60 |
| 438 | 7 | 0.25<br>0.34 | | 39 | 41 | 42 | 42 | 46 | 51 | 59 | 62 | 62 |
| average | - | - | | 27 | 34 | 38 | 41 | 48 | 53 | 58 | 61 | 64 |
| Theo. $\bar{1}$ | - | - | | 25 | 35 | 42 | 47 | 52 | 56 | 59 | 63 | 66 |
| Theo. 1 | | | | 9.5 | 18.1 | 25.9 | 33.0 | 39.4 | 45.1 | 50.3 | 55.1 | 59.3 |

obtained from a Lu chart (31), while those for the precession were obtained graphically from a plot constructed by use of Evans' equation (32),

$$\frac{1}{\text{L. P.}} = \frac{4\xi \cos\bar{\mu} \; (4 \sin^2\bar{\mu} - \xi^2)^{1/2}}{8 - 4\xi^2 + \xi^4}$$

The $\bar{\mu}$ used for all precession work was 25°.

To correlate the intensity data forthe eight levels obtained by means of the Weissenberg camera with each other and the $(h0\ell)$ data, an oscillation intensity set was taken by oscillating about the vertical mirror plane using the c-axis. These data were corrected for the Lorentz-polarization factor and for the velocity factor (33). The absorption correction was handled by means of the method of Albrecht (34). It was assumed that all reflections on a given layer line pass the same distance through the capillary. This distance X is easily calculated:

$$X = 2r/\sqrt{1 - (\ell\lambda/c)^2}$$

where r is the radius of the capillary, $\lambda$ the wave length and c the repeat distance. These distances were multiplied by the mass absorption coefficient calculated to be 18.0 $\text{cm}^{-1}$ and the absorption for each level was calculated from the exponential of the appropriate product. The diameter of the capillary was 0.106 cm. The indexing was performed exactly as described by Bunn (35).

The data so corrected and correlated was in the form used for the structure determination.

The structure determination

In the space group $C_{2h}^{6}$ -C2/c there are only four fold and eight fold parameter sets. Of these only the eight fold sets need be considered: one for the aluminum and one each for the three carbons of the asymmetric unit cell. The four fold sets may be rejected on the basis of either requiring special extinctions which are not observed, or [4(e)] possessing too high a point symmetry. The eight fold set is of the following form (30):

$$8(f) \quad 000,\ 1/2\ 1/2\ 0 \pm \left| xyz;\ x\bar{y}\ 1/2 + z \right| .$$

To obtain the values of the twelve parameters necessary for the structure determination, the zero level data, $(h0\ell)$, $(hk0)$, and $(0k\ell)$ were first used. Of these, the $(h0\ell)$ data seemed best suited for a start for the number of reflections was almost seventy in comparison with thirty odd for each of the other two sets. Furthermore, the b-axis is the shortest axis available for projection work. The Patterson function used in this case was:

$$P(xz) = \sum_{-\infty \atop h,}^{+\infty} \sum_{-\infty \atop \ell}^{+\infty} \left| F_{h0\ell} \right|^{2} \cos 2\pi\,(hx + \ell z),$$

offers a method conventionally used to discover trial structures. To adapt this formula for machine calculation the above was transformed to

$$P(xz) = \sum_{0}^{h} \sum_{0}^{\ell} \left\{ |F_{ho\bar{\ell}}|^2 + |F_{ho\ell}|^2 \right\} \cos 2\pi hx \cos 2\pi \ell z$$

$$+ \sum_{0}^{h} \sum_{0}^{\ell} \left\{ |F_{ho\bar{\ell}}|^2 - |F_{ho\ell}|^2 \right\} \sin 2\pi hx \sin 2\pi \ell z.$$

The actual calculation was made by means of an International Business Machine Tabulator with the aid of punched cards. This aid to calculation was applied to all projection work done. No adjustments of data for multiplicity were necessary in the above case.

Using the information obtained, several trial structures were devised. Their suitability was checked in several ways. First of all, any structure in which intermolecular carbon-carbon distances were less than the van der Waals distance of 4Å was rejected. Bragg-Lipson plots (36) for reflection planes having low order Miller indices offered an opportunity for quick calculation of structure factors to be compared with observed values.

Patterson projections were made onto the xy and yz planes:

$$P(xy) = \sum_{0}^{\infty} |F_{hoo}|^2 \cos 2\pi hx + \sum^{\infty} |F_{oko}|^2 \cos 2\pi ky$$

$$+ 2 \sum_{1}^{\infty} \sum_{1}^{\infty} |F_{hko}|^2 \cos 2\pi hx \cos 2\pi ky$$

$$P(yz) = \sum_{0}^{\infty} |F_{oko}|^{2} \cos 2\pi ky + \sum_{2}^{\infty} |F_{oo\ell}|^{2} \cos 2\pi \ell z$$

$$+ 2 \sum_{2}^{\infty} \sum_{1}^{\infty} |F_{ok\ell}|^{2} \cos 2\pi ky \cos 2\pi \ell z,$$

the above being suitable for machine calculation.

These projections, even in the case of $P_{xz}$, were extremely poor. No trial structure was found that would give complete agreement between observed and calculated structure factors, the most promising giving extremely poor agreement for the reflection (008).

Trial structure 1

| | x | y | z |
|---|---|---|---|
| Al | 0.067 | 0.067 | 0.067 |
| $C_1$ | 0.10 | 0.00 | -0.08 |
| $C_2$ | -0.017 | 0.28 | 0.08 |
| $C_3$ | 0.22 | -0.05 | 0.18 |

That this structure was correct seemed to be confirmed by a Harker-Patterson projection, $P_{xoz}$; the comparison of the signs and sign relationships obtained by means of Harker-Kasper inequalities and those determined from the calculated structure factors using the parameters of trial structure 1 was good. The Harker-Patterson was set up in the usual way (35). The Harker-Kasper analysis (37, 38) proceeded as follows: each structure factor was converted into a unitary structure factor, defined as :

$$U_{hk\ell} = F_{hk\ell} / \sum_{j=1}^{N} f_{j}.$$

In essence, one is "sharpening up" the structure factors, giving those which occur at large sin Θ values more weight. The observed structure factors are scaled, this being best done by Wilson's method (39), care being exercised to include multiplicities used for calculations. Of the general list of inequalities (38), the inequality

$$(U_H \pm U_{H'})^2 \leq (1 \pm U_{H+H'})\,(1 \pm U_{H-H'})$$

is most useful. Here $H = h,k,\ell$, $H+H = h+h', k+k', \ell+\ell'$. Grison's (40) tabulation of results for this inequality is convenient. That the phases determined turned out to be so consistent with those associated with a fallacious structure is hard to understand. The failure of the Harker-Patterson projection was less ignominious, reinterpretation in the light of the correct structure revealed at least the aluminum position was correct. Since the Fourier run with the phases determined only by the aluminum in its correct position revealed nothing correct as to the carbon compositions, $P_{xoz}$ was of little help.

At this stage two possibilities presented themselves, either trial structure 1 was correct and other factors were entering into the determination (libration, molecular rotation, or disorder were possible, see (41, 42, 43)), or it was wrong, the data being insufficient for the determination. Early in the structure determination a "sharpened" Patterson synthesis had been run with $(h0\ell)$ data. This projection was quite different from a normal Patterson, even the peaks to be ascribed to aluminum did not check. The "sharpened" Patterson was, therefore, rejected at that time. The failure of the normal Patterson suggested another look at the "sharpened" projection. A "sharpened" Patterson (44) is run in exactly the same fashion as the normal Patterson, but instead of the squared structure factors being used as coefficients, unitary structure factors, as described above, perform this function. No effort at scaling or temperature correction is made, however, in this case. The resulting projection, $P_{xz}$, (Figure 1) was easily interpreted by the use of the "head-to-tail" technique. Multiplicities checked nicely. "Sharpened" $P_{xy}$ (Figure 2) and $P_{yz}$ (Figure 3) were also run. The correlation of vectors with the proposed structure was not as good in the latter cases, as would be expected, but was more than adequate to suppose that a reasonable trial structure had been found.

Trial structure 2

| | x | y | z |
|---|---|---|---|
| Al | +0.02 | +0.083 | +0.083 |
| $C_1$ | +0.11 | +0.12 | 0.0 |
| $C_2$ | +0.17 | -0.083 | +0.22 |
| $C_3$ | -0.03 | +0.46 | +0.083 |

From this set of parameters structure factors for the three zero levels may be calculated. Suitable modifications of the following were used for each (30), noting f is the appropriate atomic scattering factor (45):

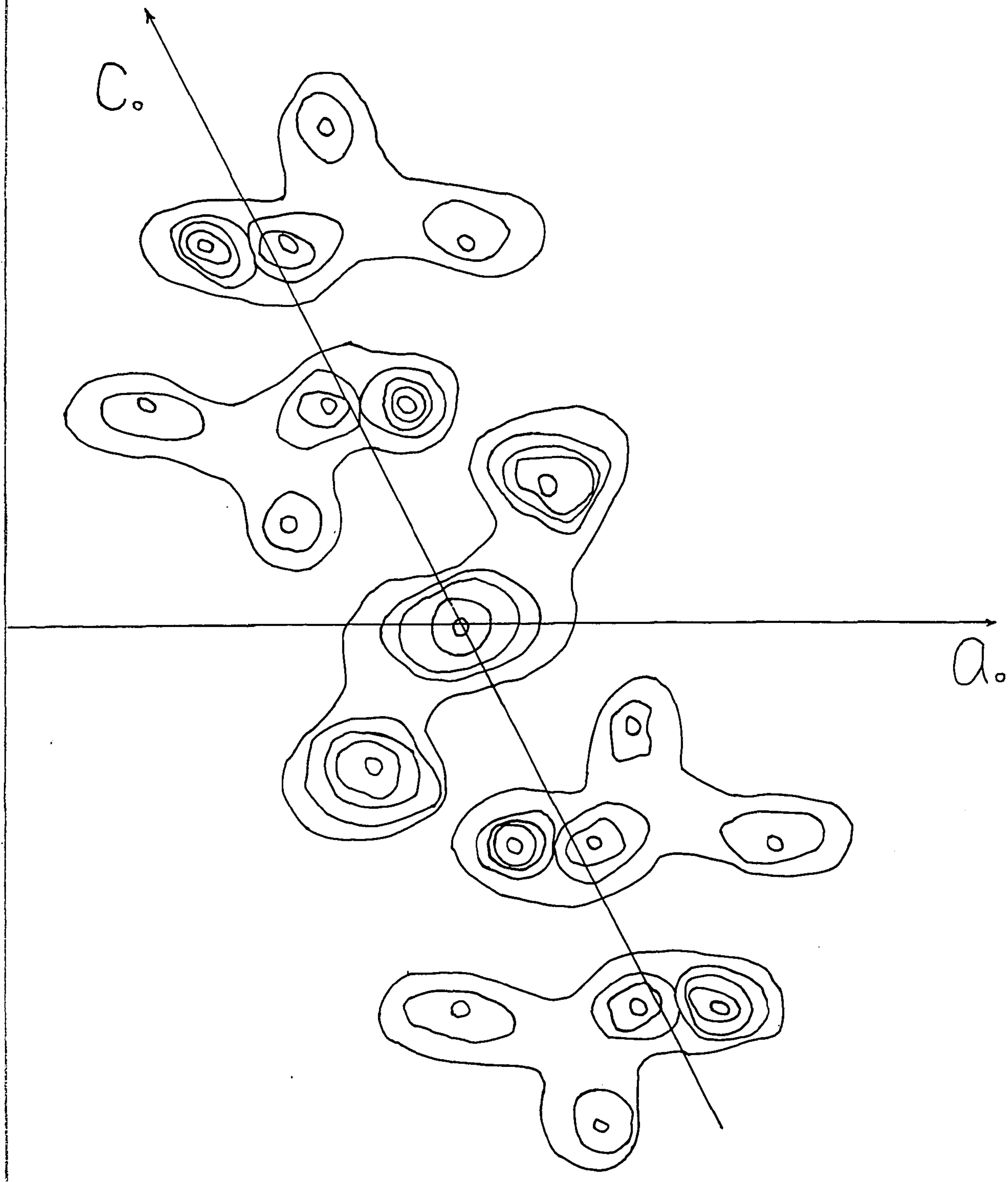


Fig. 1. Section of "sharpened" Patterson projection, $P_{xz}$, showing intramolecular vector peaks for the trimethylaluminum dimer.

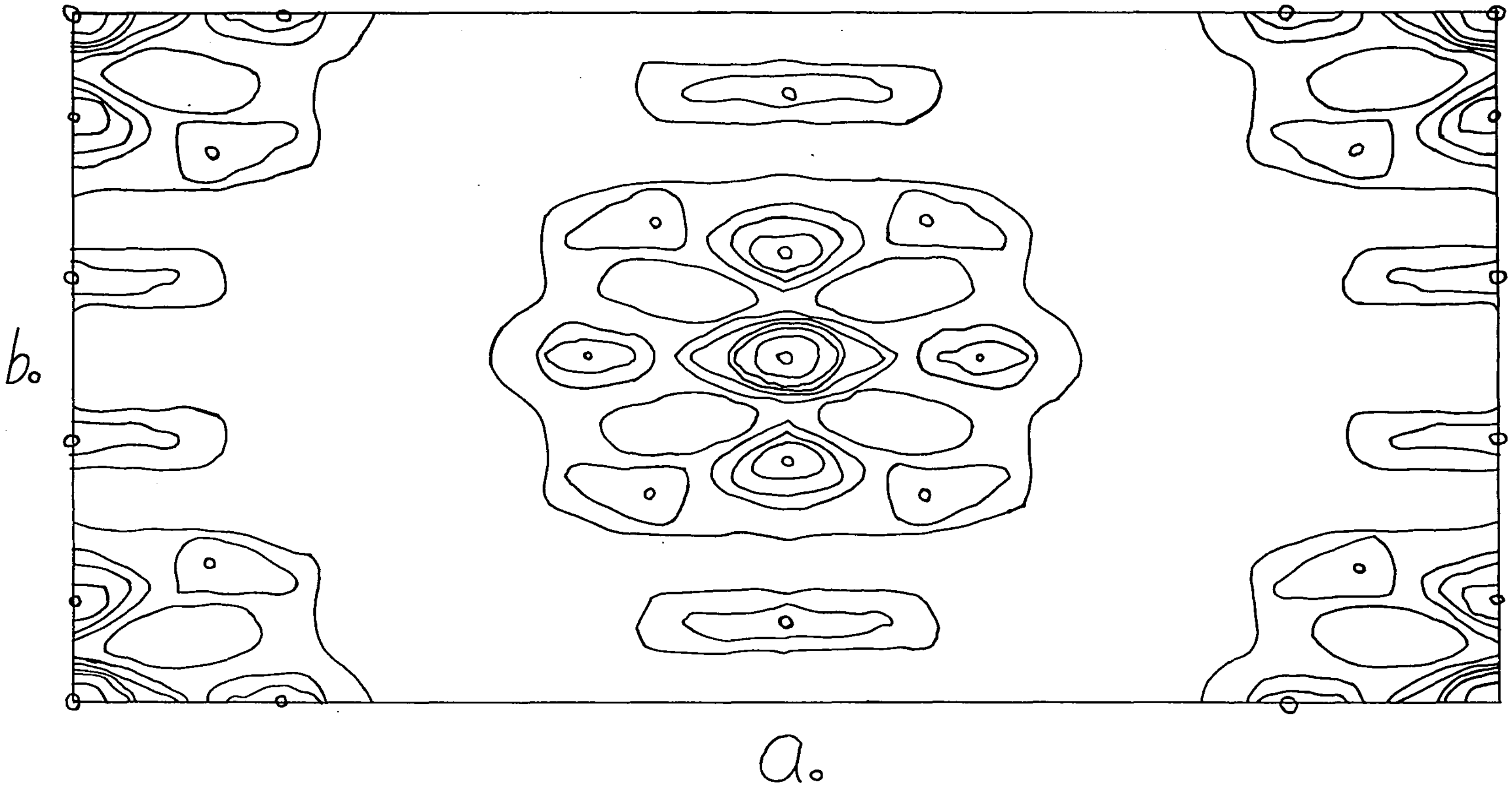


Fig. 2. The "sharpened" Patterson, $P_{xy}$, trimethylaluminum.

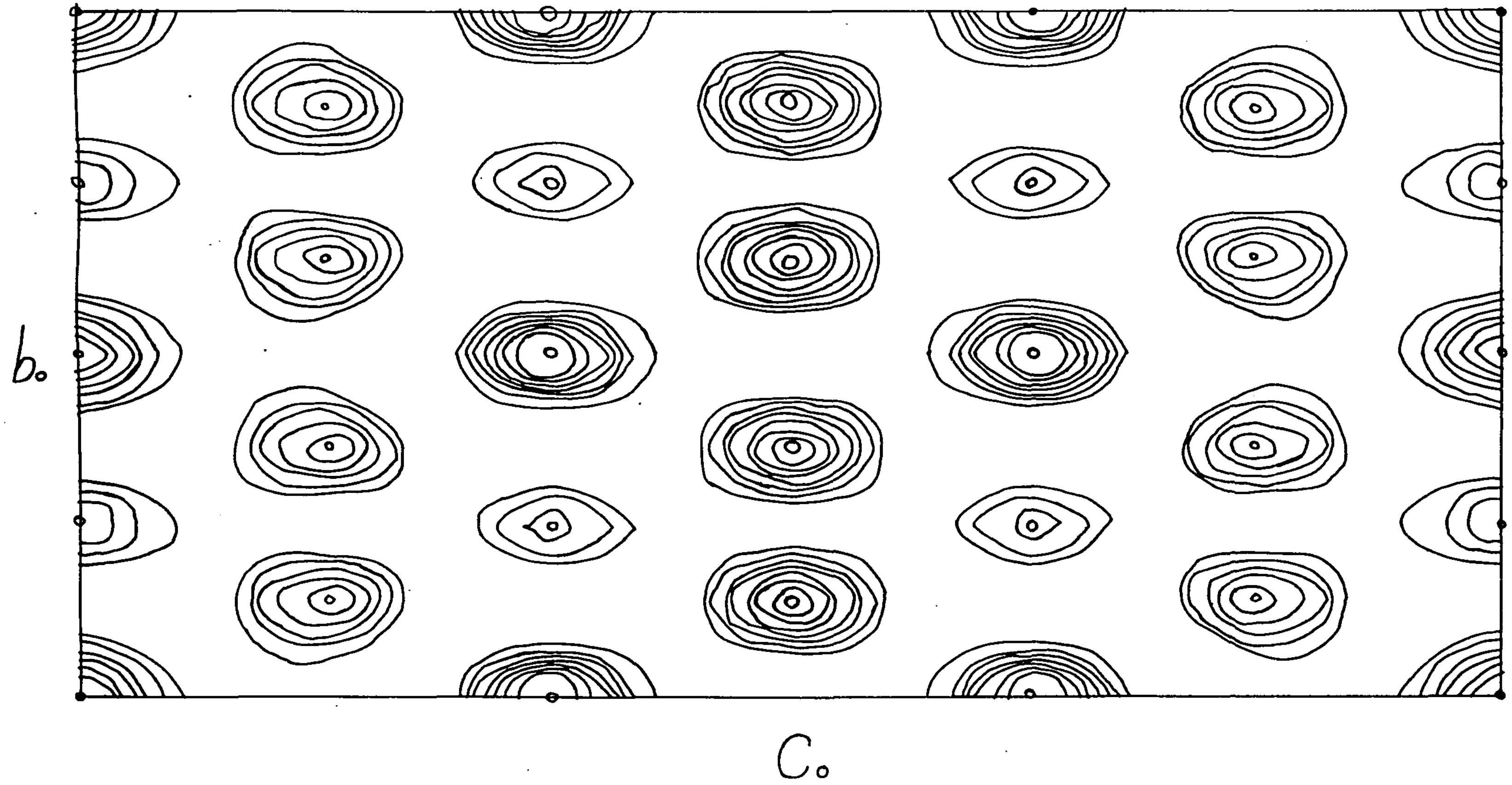


Fig. 3. The "sharpened" Patterson projection, $P_{yz}$, trimethylaluminum.

$$F_{hk} = 8f_{Al}\cos^2 2\pi \frac{h+k}{4} \cos 2\pi(hx_{Al} + z_{Al} + \ell/4)$$
$$\times \cos 2\pi(ky_{Al} - \ell/4)$$

$$+8f_c \cos^2 2\pi \frac{h+k}{4} \cos 2\pi(hx_{c_1} + z_{c_1} + \ell/4) \cos 2\pi(ky_{c_1} - \ell/4)$$

$$+8f_c \cos^2 2\pi \frac{h+k}{4} \cos 2\pi(hx_{c_2} + z_{c_2} + \ell/4) \cos 2\pi(ky_{c_2} - \ell/4)$$

$$+8f_c \cos^2 2\pi \frac{h+k}{4} \cos 2\pi(hx_{c_3} + z_{c_3} + \ell/4) \cos 2\pi(ky_{c_3} - \ell/4) \; .$$

The initial comparison of this calculated data with the observed indicated fair agreement. The worst disparities could be corrected by small shifts of the atoms. The measurement of agreement, the R factor ( $\equiv \sum||F_{obsd}| - |F_{calcd}|| / \sum|F_{obsd}|$ ), was quite high at this stage, above 0.40 for all three levels.

Refinement of the structure

The procedure most commonly used in the early stages of structure refinement is that of the Fourier technique. The two electron density projections best suited for this work were $\rho_{xz}$ (Figure 4) and $\rho_{yz}$ (Figure 5); $\rho_{xy}$ showed serious overlapping. $\rho_{xz}$ is equal to:

$$\rho_{xz} = \frac{4}{A} \sum_{0}^{\infty} \sum_{0}^{\infty} (F_{ho\bar{\ell}} + F_{ho\ell}) \cos 2\pi hx \cos 2\pi \ell z$$
$$+ (F_{ho} - F_{ho\ell}) \sin 2\pi hx \sin 2\pi \ell z$$

while

$$\rho_{yz} = \frac{8}{A} \sum_{0}^{\infty} \sum_{0}^{\overset{\ell=2n}{\infty}} F_{ok\ell} \cos 2\pi ky \cos 2\pi \ell z$$

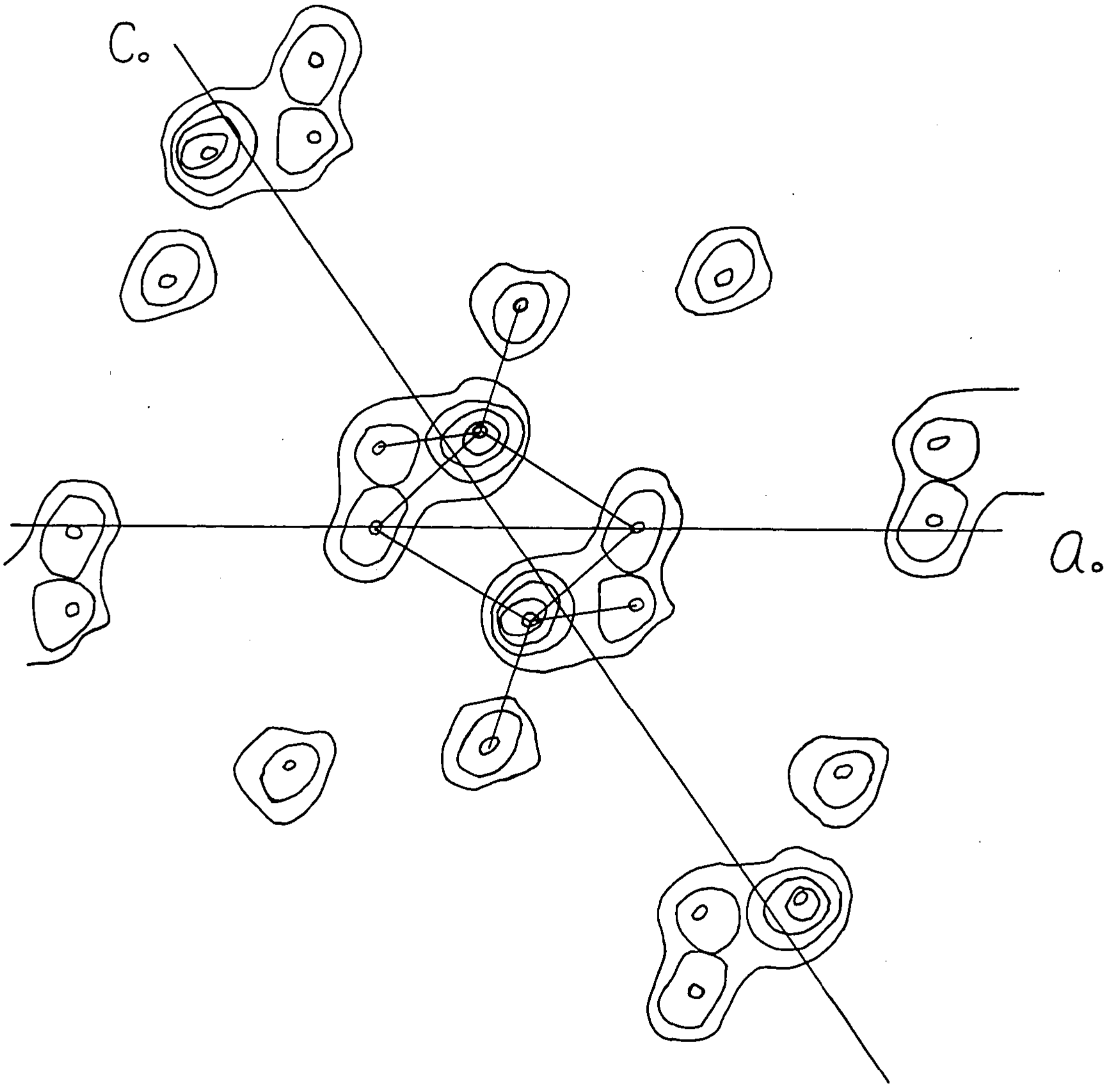


Fig. 4. Section of the Fourier projection onto the ac plane. Shows the trimethylaluminum dimer and environment.

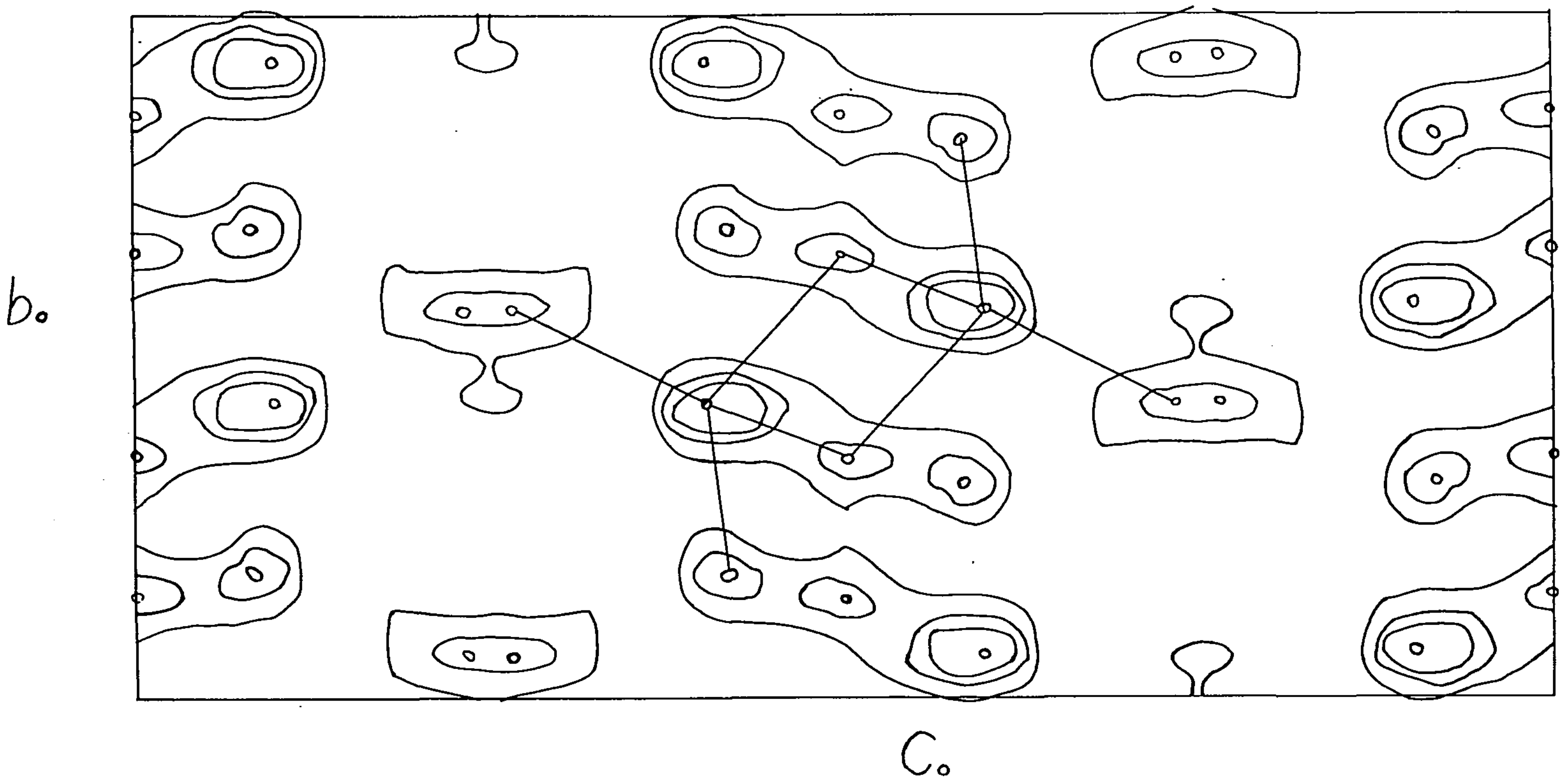


Fig. 5. The Fourier projection onto bc plane, trimethylaluminum.

$$-\frac{8}{A}\sum_{0}^{\ell=2n+1}\sum_{0} F_{0k\ell}\sin 2\pi ky \sin 2\pi\ell z.$$

In general, the usual techniques were followed in this refinement. A cycle consisted of determining the peak maxima by Booth's method (46), calculating the structure factors from these parameter values, running the next Fourier with observed structure factors and calculated phases (either + or -).

When no further changes in signs were indicated, i.e., the calculated phases obtained were identical with those with which the cycle began, a change in tactics was made. Several refinement techniques are available, varying in the amount of labor required to obtain convergence. One of the more rapid methods is the "back shift" (47). The calculated structure factors were put on the same scale as the observed, and temperature corrected. Both the scaling and temperature factor were obtained by applying the method of least squares to equations of the form

$$\log_{10} F_{obsd}/F_{calcd} = -\frac{B}{2.3}\frac{\sin^2\theta}{\lambda^2} + \frac{S}{2.3}$$

where B is the isotropic temperature factor and S, the scale factor. For the zero level data (hk0), (h0$\ell$), (0k$\ell$), B was equal to 3.9$\mathring{A}^2$. Then Fourier projections were run using calculated phases and calculated amplitudes (a synthetic Fourier), comparing peak positions with those obtained using observed amplitudes. If $x_1$ is the parameter value on the observed projection, $x_2$ on the calculated, and $x_3$ the new parameter value to be tried, then: $x_3 = x_1 - n(x_2 - x_1)$. The factor n is used to speed convergence. When the R factor was high, n was allowed to be 2, when low, 1. The $(0k\ell)$ projection converged rapidly, but the $(h0\ell)$ moved more slowly. The main trouble here was the partial overlap of the aluminum and one carbon. To secure delineation of these peaks, the h and $\ell$ indices were divided by two and the projection run in 1/120's. Using this technique, the projection was refined easily.

To confirm that the parameters determined from these projections were correct, the structure factors for the general $(hk\ell)$ data were calculated. This step was performed using International Business Machines equipment. Only the center of symmetry was utilized in this operation, F equaling for each atom $\sum_{i=1}^{8} f \cos 2\pi(hx_i + ky_i + \ell z_i)$. The essential steps were

1. Obtain the $hx_i$, $ky_i$, $\ell z_i$ products.
2. Summation of these products.
3. Formation of the cosine of this summation.
4. Multiplication by the atom form factors.
5. Final summation over the atoms in the unit cell and tabulation.

Several other techniques and this one are described in the current literature (48, 49).

Scale factors and temperature factors were evaluated for each higher layer in exactly the way described for the zero levels. A word might be said about the temperature factors for the higher layers. The reflections on these levels show a marked attenuation in width with increasing sin θ values. The attempt to integrate over the intensity by eye was not entirely successful. This trend, being a function of sin θ, has a marked effect on the temperature factor determined, but, since the effect is continuous, not on the accuracy of the calculated structure factors. Since this phenomenon did not occur on the precession data, the value of B determined from it is to be depended upon. This value was $3.9 \mathring{A}^2$. Each set of higher layer data was corrected by the "temperature factor" local to it. On this basis the following R factors were obtained:

Table 3. A list of R factors.

| Level | R(inclusion of non-observable reflections) | R(inclusion of only reflections observed) |
|---|---|---|
| $h0\ell$ | 0.27 | 0.25 |
| hk0 | 0.19 | 0.19 |
| hk1 | 0.32 | 0.31 |
| hk2 | 0.28 | 0.24 |
| hk3 | 0.21 | 0.21 |
| hk5 | 0.31 | 0.27 |
| hk6 | 0.22 | 0.21 |
| hk7 | 0.24 | 0.24 |
| average | 0.25 | 0.23 |

Either R factor may be accepted as being correct. Currently, the average of these two is regarded as the better indication of how well the structure has been done on the assumption that all "zero" reflections are not really zero. The R factor is comparable with many to be found in the literature; the fact that it is as high as it is, is due to the neglect of the hydrogen atoms which constitute roughly 25 per cent of the scattering matter of the unit cell. A comparison of observed <u>versus</u> calculated structure factors may be seen in Table 4.

Summary of results

The final parameter values determined are as follows:

| | x | y | z |
|---|---|---|---|
| Al | 0.028 | 0.073 | 0.091 |
| $C_1$ | 0.121 | 0.148 | 0.006 |
| $C_2$ | 0.148 | -0.072 | 0.230 |
| $C_3$ | -0.056 | 0.317 | 0.084 |

On this basis, the following bond angles and bond lengths were observed (Figure 6),

| | |
|---|---|
| $Al_1 - Al_2$ | 2.55Å |
| $Al_1 - C_{11}$ | 2.24Å |
| $Al_1 - C_{12}$ | 1.99Å |
| $Al_1 - C_{13}$ | 2.23Å |

1. $Al_1 - C_{13} \angle Al_1 - C_{21}$ 107°
2. $Al_1 - C_{12} \angle Al_1 - C_{11}$ 109°
3. $Al_1 - C_{11} \angle Al_1 - C_{13}$ 102°
4. $Al_1 - C_{12} \angle Al_1 - C_{21}$ 100°
5. $Al_1 - C_{12} \angle Al_1 - C_{13}$ 124°
6. $Al_1 - C_{11} \angle Al_2 - C_{11}$ 70°
7. Angle between "mirror" planes 94°

The error was calculated by Cruickshank's method (50).

Table 4. Comparison of observed and calculated structure factors for trimethylaluminum.

| Indices | $F_{obsd/4}$ | $F_{calcd/4}$ | Indices | $F_{obsd/4}$ | $F_{calcd/4}$ |
|---|---|---|---|---|---|
| 200 | 35 | +26 | $40\bar{6}$ | 27 | -20 |
| 400 | 1.7 | +4.0 | $60\bar{6}$ | 20 | -14 |
| 600 | 12 | +6.2 | $80\bar{6}$ | 0.0 | +1.4 |
| 800 | 4.0 | +2.8 | $10\cdot0\cdot\bar{6}$ | 2.7 | +4.0 |
| 10·0·0 | 4.0 | -3.4 | 008 | 0.0 | +1.8 |
| | | | 208 | | |
| 12·0·0 | 2.8 | -2.8 | 208 | 2.5 | +0.4 |
| 002 | 18 | +13 | 408 | 0.0 | -1.6 |
| 202 | 12 | +8.2 | 608 | 3.2 | +2.0 |
| 402 | 0.0 | +1.1 | $20\bar{8}$ | 5.2 | -6.2 |
| 602 | 6.8 | -6.2 | $40\bar{8}$ | 9.2 | -9.6 |
| 802 | 5.3 | -4.2 | $60\bar{8}$ | 9.5 | -6.6 |
| 10·0·2 | 3.0 | -3.0 | $80\bar{8}$ | 8.2 | -5.8 |
| $20\bar{2}$ | 27 | +22 | $10\cdot0\cdot\bar{8}$ | 6.8 | -7.4 |
| $40\bar{2}$ | 6.0 | +6.8 | $12\cdot0\cdot\bar{8}$ | 5.3 | -4.8 |
| $60\bar{2}$ | 5.8 | +4.6 | $14\cdot0\cdot\bar{8}$ | 3.2 | -2.8 |
| $80\bar{2}$ | 9.7 | +9.4 | 0·0·10 | 8.2 | +7.4 |
| $10\cdot0\cdot\bar{2}$ | 6.2 | +7.0 | 2·0·10 | 3.5 | +2.2 |
| 004 | 0.0 | -3.6 | 4·0·10 | 3.5 | +1.8 |
| 204 | 17 | -10 | $2\cdot0\cdot\overline{10}$ | 13 | +9.4 |
| 404 | 22 | -13 | $4\cdot0\cdot\overline{10}$ | 2.5 | +2.0 |
| 604 | 6.5 | -4.0 | $6\cdot0\cdot\overline{10}$ | 2.5 | -3.4 |
| 804 | 0.0 | -1.0 | $8\cdot0\cdot\overline{10}$ | 0.0 | +0.6 |
| $20\bar{4}$ | 27 | -17 | $10\cdot0\cdot\overline{10}$ | 3.3 | -4.6 |
| $40\bar{4}$ | 28 | -17 | $12\cdot0\cdot\overline{10}$ | 7.0 | -8.2 |
| $60\bar{4}$ | 5.8 | +4.8 | $14\cdot0\cdot\overline{10}$ | 4.5 | -4.0 |
| $80\bar{4}$ | 8.7 | +10 | 0·0·12 | 4.7 | +5.4 |
| $10\cdot0\cdot\bar{4}$ | 6.8 | +6.8 | 2·0·12 | 2.5 | +2.8 |
| $12\cdot0\cdot\bar{4}$ | 3.7 | +5.2 | $2\cdot0\cdot\overline{12}$ | 5.0 | +5.2 |
| 006 | 23 | -16 | $4\cdot0\cdot\overline{12}$ | 6.7 | +5.0 |
| 206 | 17 | -12 | $6\cdot0\cdot\overline{12}$ | 4.7 | +4.6 |
| 406 | 4.8 | -4.6 | $8\cdot0\cdot\overline{12}$ | 3.8 | +2.6 |
| $20\bar{6}$ | 14 | -13 | $10\cdot0\cdot\overline{12}$ | 2.3 | +1.0 |

Table 4 (Continued).

| Indices | $F_{obsd}/4$ | $F_{calcd}/4$ | Indices | $F_{obsd}/4$ | $F_{calcd}/4$ |
|---|---|---|---|---|---|
| $8\cdot0\cdot\overline{14}$ | 5.8 | +6.4 | 311 | 8.6 | -11 |
| $10\cdot0\cdot\overline{14}$ | 5.5 | +5.0 | 111 | 7.2 | -10 |
| $12\cdot0\cdot\overline{14}$ | 3.0 | +2.0 | $11\bar{1}$ | - - | - - |
| $4\cdot0\cdot\overline{16}$ | 1.8 | -2.2 | $31\bar{1}$ | 5.3 | -6.5 |
| $10\cdot0\cdot\overline{16}$ | 2.5 | +3.4 | $51\bar{1}$ | 3.0 | -2.3 |
| 110 | 19 | +26 | $71\bar{1}$ | 1.4 | -1.9 |
| 310 | 2.3 | +4.4 | $91\bar{1}$ | 2.8 | +4.4 |
| 510 | 5.7 | +4.6 | $11\cdot1\cdot\bar{1}$ | 2.2 | +3.8 |
| 710 | 7.1 | +7.2 | 621 | 5.1 | -6.8 |
| 11·1·0 | 1.9 | -2.0 | 421 | 12 | -11 |
| 020 | 10 | +7.4 | 221 | 13 | -14 |
| 220 | 3.9 | +5.0 | 021 | 2.2 | +0.3 |
| 420 | 5.0 | +4.2 | $22\bar{1}$ | 7.2 | +6.7 |
| 620 | 5.4 | +5.0 | $42\bar{1}$ | 2.9 | +2.9 |
| 820 | 2.6 | +1.8 | $62\bar{1}$ | 3.6 | +4.7 |
| 130 | 5.9 | +4.6 | $82\bar{1}$ | 4.6 | +4.4 |
| 330 | 4.6 | +5.8 | $10\cdot2\cdot\bar{1}$ | 3.9 | +3.8 |
| 530 | 3.5 | +2.6 | $12\cdot2\cdot\bar{1}$ | 1.9 | +2.6 |
| 040 | 7.1 | -7.2 | 731 | 4.9 | -5.5 |
| 240 | 3.9 | -3.6 | 531 | 15 | -11 |
| 150 | 9.0 | -9.0 | 331 | 13 | -16 |
| 350 | 3.7 | -4.0 | 131 | 7.9 | -7.8 |
| 11·5·0 | 0.6 | +1.2 | $13\bar{1}$ | 0.9 | -1.0 |
| 060 | 5.7 | -4.4 | $33\bar{1}$ | 0.0 | -2.4 |
| 260 | 4.6 | -2.8 | $53\bar{1}$ | 1.9 | +3.9 |
| 460 | 3.0 | -2.8 | $73\bar{1}$ | 4.5 | +8.0 |
| 660 | 2.8 | -3.2 | $93\bar{1}$ | 4.1 | +4.7 |
| 170 | 4.3 | -3.8 | $11\cdot3\cdot\bar{1}$ | 2.9 | +2.3 |
| 370 | 2.9 | -3.2 | $13\cdot3\cdot\bar{1}$ | 1.4 | +2.9 |
| 570 | 2.9 | -2.4 | 841 | 3.6 | -3.2 |
| 770 | 1.6 | -1.0 | 641 | 4.3 | -4.8 |
| 080 | 2.8 | -4.0 | 441 | 7.2 | -9.0 |
| 280 | 2.6 | -2.4 | 241 | 7.2 | -7.0 |
| 480 | 1.8 | -1.2 | 041 | 5.2 | -4.8 |
| 511 | 1.8 | -0.3 | $24\bar{1}$ | 4.7 | -8.5 |

Table 4 (Continued).

| Indices | $F_{obsd}/4$ | $F_{calcd}/4$ | Indices | $F_{obsd}/4$ | $F_{calcd}/4$ |
|---|---|---|---|---|---|
| $44\bar{1}$ | 2.2 | -4.2 | 222 | 3.1 | -2.5 |
| $64\bar{1}$ | 3.1 | +6.0 | 022 | 3.8 | -3.7 |
| $84\bar{1}$ | 3.9 | +5.5 | $22\bar{2}$ | 11 | -11 |
| $10{\cdot}4{\cdot}\bar{1}$ | 3.0 | +3.0 | $42\bar{2}$ | 14 | +15 |
| $12{\cdot}4{\cdot}\bar{1}$ | 1.6 | +3.8 | $62\bar{2}$ | 7.7 | +9.0 |
| | | | $82\bar{2}$ | 6.7 | +6.5 |
| 751 | 3.8 | -4.5 | $10{\cdot}2{\cdot}\bar{2}$ | 5.1 | +5.5 |
| 551 | 5.0 | -7.5 | 532 | 2.6 | +3.7 |
| 351 | 6.0 | -6.0 | 332 | 6.7 | +6.3 |
| 151 | 2.5 | -1.5 | 132 | 2.0 | +0.4 |
| $15\bar{1}$ | 1.8 | -2.5 | | | |
| $35\bar{1}$ | 1.3 | -2.7 | $13\bar{2}$ | 1.4 | -1.6 |
| $55\bar{1}$ | 2.6 | +3.9 | $33\bar{2}$ | 2.5 | +3.7 |
| $75\bar{1}$ | 3.9 | +6.5 | $53\bar{2}$ | 1.0 | +2.0 |
| $95\bar{1}$ | 2.3 | +1.1 | $73\bar{2}$ | 1.4 | -2.5 |
| 861 | 1.6 | -1.6 | $93\bar{2}$ | 0.0 | -1.0 |
| 661 | 2.4 | -2.9 | 442 | 3.5 | +2.0 |
| 461 | 2.4 | -3.4 | 242 | 0.0 | -0.7 |
| 261 | 0.0 | -1.3 | 042 | 4.6 | -4.3 |
| 061 | 0.0 | -0.1 | $24\bar{2}$ | 3.6 | -3.0 |
| $26\bar{1}$ | 1.4 | -1.2 | $44\bar{2}$ | 0.0 | -0.5 |
| $46\bar{1}$ | 1.1 | -0.6 | $64\bar{2}$ | 2.5 | -1.4 |
| $66\bar{1}$ | 1.8 | +2.9 | $84\bar{2}$ | 3.1 | -3.7 |
| $86\bar{1}$ | 0.0 | +1.4 | 552 | 2.3 | +0.6 |
| $37\bar{1}$ | 2.3 | -1.2 | 352 | 0.0 | -2.7 |
| 481 | 1.6 | +1.6 | 152 | 4.3 | -2.0 |
| 281 | 1.6 | +0.3 | $15\bar{2}$ | 6.5 | -3.9 |
| 312 | 2.6 | -2.0 | $35\bar{2}$ | 4.3 | -6.0 |
| 112 | 3.5 | -0.3 | $55\bar{2}$ | 3.0 | -3.7 |
| $11\bar{2}$ | 11 | +11 | $75\bar{2}$ | 4.6 | -2.3 |
| $31\bar{2}$ | 16 | +20 | $95\bar{2}$ | 3.6 | -3.8 |
| $51\bar{2}$ | 12 | +12 | 462 | 2.7 | -0.1 |
| $71\bar{2}$ | 11 | +11 | 262 | 1.0 | +1.0 |
| $91\bar{2}$ | 11 | +11 | 062 | 2.4 | +1.5 |
| $11{\cdot}1{\cdot}\bar{2}$ | 3.1 | +4.8 | $26\bar{2}$ | 7.4 | -6.5 |
| 422 | 3.5 | -1.4 | $46\bar{2}$ | 7.4 | -11 |

Table 4 (Continued).

| Indices | $F_{obsd}/4$ | $F_{calcd}/4$ | Indices | $F_{obsd}/4$ | $F_{calcd}/4$ |
|---|---|---|---|---|---|
| $66\bar{2}$ | 5.8 | -7.0 | $13\bar{3}$ | 15 | -14 |
| $86\bar{2}$ | 5.3 | -4.5 | $33\bar{3}$ | 8.9 | -7.0 |
| $10{\cdot}6{\cdot}\bar{2}$ | 3.0 | -4.4 | $53\bar{3}$ | 15 | -12 |
| 372 | 2.5 | -1.4 | $73\bar{3}$ | 8.9 | -9.5 |
| 172 | 5.7 | +0.9 | $93\bar{3}$ | 0.0 | +0.4 |
| $17\bar{2}$ | 5.7 | -1.0 | $11{\cdot}3{\cdot}\bar{3}$ | 2.6 | +2.5 |
| $37\bar{2}$ | 4.5 | -5.0 | 643 | 2.3 | -3.8 |
| $57\bar{2}$ | 3.5 | -4.1 | 443 | 4.2 | -4.4 |
| $77\bar{2}$ | 2.4 | -1.9 | 243 | 11 | -11 |
| $97\bar{2}$ | 1.7 | -2.4 | 043 | 18 | -19 |
| $28\bar{2}$ | 2.5 | -2.0 | $24\bar{3}$ | 10 | -15 |
| $48\bar{2}$ | 0.0 | -2.5 | $44\bar{3}$ | 8.1 | -9.0 |
| 713 | 0.0 | +1.3 | $64\bar{3}$ | 6.2 | -6.5 |
| 513 | 1.0 | +0.1 | $84\bar{3}$ | 0.0 | 0.0 |
| 313 | 6.1 | -8.0 | $10{\cdot}4{\cdot}\bar{3}$ | 2.6 | +3.2 |
| 113 | 23 | -18 | 753 | 2.7 | -4.4 |
| $11\bar{3}$ | 13 | -13 | 553 | 2.7 | -4.0 |
| $31\bar{3}$ | - - | - - | 353 | 2.7 | -1.9 |
| $51\bar{3}$ | 7.7 | -7.5 | 153 | 6.6 | -5.5 |
| $71\bar{3}$ | 4.8 | -4.2 | $15\bar{3}$ | 6.2 | -9.0 |
| $91\bar{3}$ | 2.5 | +4.1 | $35\bar{3}$ | 5.2 | -7.0 |
| $11{\cdot}1{\cdot}\bar{3}$ | 3.6 | +4.3 | $55\bar{3}$ | 5.8 | -5.0 |
| 423 | 2.3 | -3.6 | $75\bar{3}$ | 3.5 | -3.2 |
| 223 | 14 | -13 | $66\bar{3}$ | 1.6 | -2.7 |
| 023 | 13 | -15 | 463 | 0.0 | -0.8 |
| $22\bar{3}$ | 3.3 | -1.0 | 263 | 0.0 | -0.3 |
| $42\bar{3}$ | 6.5 | -7.0 | 063 | 2.3 | -2.5 |
| $62\bar{3}$ | 11 | -15 | $26\bar{3}$ | 3.5 | -2.9 |
| $82\bar{3}$ | 4.6 | -6.0 | $46\bar{3}$ | 2.8 | -2.2 |
| $10{\cdot}2{\cdot}\bar{3}$ | 2.7 | +2.7 | $66\bar{3}$ | 2.3 | -0.3 |
| $12{\cdot}2{\cdot}\bar{3}$ | 1.9 | +1.3 | 573 | 2.3 | +0.7 |
| 733 | 1.1 | -5.5 | 283 | 1.9 | +2.0 |
| 533 | 2.3 | -3.6 | 083 | 2.3 | +3.2 |
| 333 | 6.9 | -8.5 | $28\bar{3}$ | 2.5 | +3.8 |
| 133 | 17 | -17 | 483 | 1.9 | +2.0 |

Table 4 (Continued).

| Indices | $F_{obsd}/4$ | $F_{calcd}/4$ | Indices | $F_{obsd}/4$ | $F_{calcd}/4$ |
|---|---|---|---|---|---|
| 68$\bar{3}$ | 0.9 | +0.5 | 84$\bar{4}$ | 3.9 | -2.7 |
| 13·1·$\bar{4}$ | 2.6 | +3.7 | 64$\bar{4}$ | 0.0 | -0.6 |
| 11·1·$\bar{4}$ | 4.1 | +4.0 | 44$\bar{4}$ | 4.1 | +3.0 |
| 91$\bar{4}$ | 5.6 | +5.5 | 24$\bar{4}$ | 0.9 | +1.3 |
| 71$\bar{4}$ | 8.7 | +9.5 | 044 | 0.0 | -0.9 |
| 51$\bar{4}$ | 2.7 | +3.4 | 244 | 2.6 | +2.2 |
| 31$\bar{4}$ | 8.1 | -8.5 | 444 | 4.1 | +3.7 |
| 11$\bar{4}$ | 2.2 | -2.0 | 11·5·$\bar{4}$ | 2.0 | -3.0 |
| 114 | 3.0 | -4.4 | 95$\bar{4}$ | 3.2 | -2.5 |
| 314 | 12 | -15 | 75$\bar{4}$ | 3.3 | -3.0 |
| 514 | 8.7 | -11 | 55$\bar{4}$ | 0.0 | 0.0 |
| 714 | 3.2 | -3.5 | 35$\bar{4}$ | 4.5 | +4.4 |
| 14·2·$\bar{4}$ | 1.8 | +1.8 | 15$\bar{4}$ | 3.9 | +4.1 |
| 12·2·$\bar{4}$ | 3.9 | +2.9 | 154 | 5.5 | +2.9 |
| 10·2·$\bar{4}$ | 2.9 | +0.9 | 354 | 4.2 | +4.0 |
| 82$\bar{4}$ | 4.2 | +2.8 | 554 | 3.7 | +2.5 |
| 62$\bar{4}$ | 5.5 | +7.0 | 10·6·$\bar{4}$ | 1.5 | -0.7 |
| 42$\bar{4}$ | 0.0 | +2.9 | 86$\bar{4}$ | 2.7 | -1.3 |
| 22$\bar{4}$ | 2.5 | -3.1 | 66$\bar{4}$ | 2.6 | -4.1 |
| 024 | 0.0 | -3.0 | 46$\bar{4}$ | 0.0 | -1.8 |
| 224 | - - | - - | 26$\bar{4}$ | 1.8 | +2.2 |
| 424 | 7.7 | -6.0 | 064 | 2.5 | +3.0 |
| 624 | 4.7 | -3.3 | 264 | 4.3 | +3.8 |
| 824 | 2.3 | +3.2 | 464 | 4.7 | +4.7 |
| 13·3·$\bar{4}$ | 1.6 | +2.7 | 664 | 2.6 | +3.3 |
| 11·3·$\bar{4}$ | 1.0 | +2.6 | 97$\bar{4}$ | 1.3 | -0.7 |
| 93$\bar{4}$ | 0.0 | +0.1 | 77$\bar{4}$ | 1.5 | -2.2 |
| 73$\bar{4}$ | 0.0 | 0.0 | 57$\bar{4}$ | 0.9 | -2.5 |
| 53$\bar{4}$ | 0.0 | +1.1 | 37$\bar{4}$ | 0.9 | +1.2 |
| 33$\bar{4}$ | 5.3 | -3.2 | 17$\bar{4}$ | 2.3 | +3.0 |
| 13$\bar{4}$ | 7.2 | -7.5 | 174 | - - | - - |
| 134 | 3.5 | -3.6 | 28$\bar{4}$ | 1.8 | +2.7 |
| 334 | 0.0 | +1.2 | 915 | 2.3 | +1.8 |
| 534 | 0.0 | +1.4 | 715 | 3.2 | +3.8 |
| 10·4·$\bar{4}$ | 1.5 | -1.6 | 515 | 1.6 | -1.3 |

Table 4 (Continued).

| Indices | $F_{obsd}/4$ | $F_{calcd}/4$ | Indices | $F_{obsd}/4$ | $F_{calcd}/4$ |
|---|---|---|---|---|---|
| 315 | 2.9 | -3.8 | $44\bar{5}$ | 7.5 | -6.0 |
| 115 | 2.6 | -4.8 | $64\bar{5}$ | 6.4 | -3.2 |
| $11\bar{5}$ | 2.0 | -1.7 | $84\bar{5}$ | 6.8 | -7.0 |
| $31\bar{5}$ | 1.6 | -0.9 | $10\cdot4\cdot\bar{5}$ | 5.8 | -8.5 |
| $51\bar{5}$ | 3.2 | -2.9 | $12\cdot4\cdot\bar{5}$ | 2.6 | -3.0 |
| $71\bar{5}$ | 5.0 | -5.5 | 755 | 3.1 | +2.4 |
| $91\bar{5}$ | 3.8 | -3.7 | 555 | 2.3 | +0.9 |
| 825 | 4.4 | +6.0 | 355 | 0.0 | +2.5 |
| 625 | 7.1 | +7.0 | 155 | 1.6 | +3.7 |
| 425 | 5.3 | +2.7 | $15\bar{5}$ | 4.5 | -4.2 |
| 225 | 2.3 | +0.7 | $35\bar{5}$ | 7.8 | -9.5 |
| 025 | 0.0 | +0.5 | $55\bar{5}$ | 5.7 | -5.0 |
| $22\bar{5}$ | 6.7 | -6.5 | $75\bar{5}$ | 7.0 | -3.8 |
| $42\bar{5}$ | 8.9 | -13 | $95\bar{5}$ | 5.7 | -7.0 |
| $62\bar{5}$ | 9.9 | -15 | $11\cdot5\cdot\bar{5}$ | 3.1 | -4.3 |
| $82\bar{5}$ | 9.9 | -12 | 665 | 0.0 | +0.6 |
| $10\cdot2\cdot\bar{5}$ | 4.9 | -6.0 | 465 | 0.0 | +0.9 |
| $12\cdot2\cdot\bar{5}$ | 2.9 | -0.8 | 265 | 0.0 | +2.5 |
| 935 | 2.6 | +3.1 | 065 | 0.0 | +0.7 |
| 735 | 5.9 | +6.0 | $26\bar{5}$ | 3.1 | -3.8 |
| 535 | 7.0 | +3.7 | $46\bar{5}$ | 3.1 | -4.0 |
| 335 | 3.4 | +1.2 | $66\bar{5}$ | 1.6 | -1.6 |
| 135 | 0.0 | +1.5 | $86\bar{5}$ | 1.6 | -2.7 |
| $13\bar{5}$ | 6.4 | -4.6 | $57\bar{5}$ | 2.3 | +1.7 |
| $33\bar{5}$ | 11 | -13 | $77\bar{5}$ | 2.3 | +1.3 |
| $53\bar{5}$ | 11 | -12 | 316 | 6.1 | -5.5 |
| $73\bar{5}$ | 11 | -11 | 116 | 8.9 | -11 |
| $93\bar{5}$ | 7.8 | -12 | $11\bar{6}$ | 6.7 | -8.5 |
| $11\cdot3\cdot\bar{5}$ | 3.4 | -4.8 | $31\bar{6}$ | 8.1 | -10 |
| 845 | 4.4 | +4.6 | $51\bar{6}$ | 14 | -16 |
| 645 | 3.6 | +2.4 | $71\bar{6}$ | 6.4 | -8.5 |
| 445 | 0.0 | -1.1 | 226 | 4.7 | -4.2 |
| 245 | 0.0 | +0.4 | 026 | 6.3 | -7.5 |
| 045 | 2.6 | -1.7 | $22\bar{6}$ | 4.2 | -4.5 |
| $24\bar{5}$ | 7.7 | -10 | $42\bar{6}$ | 7.3 | -5.5 |

Table 4 (Continued).

| Indices | $F_{obsd}/4$ | $F_{calcd}/4$ | Indices | $F_{obsd}/4$ | $F_{calcd}/4$ |
|---|---|---|---|---|---|
| 62$\bar{6}$ | 7.4 | -9.0 | 51$\bar{7}$ | 0.9 | +0.1 |
| 82$\bar{6}$ | 4.0 | -4.7 | 71$\bar{7}$ | 3.0 | -4.9 |
| 136 | 5.6 | -6.0 | 627 | 4.0 | +4.7 |
| 13$\bar{6}$ | 6.9 | -7.0 | 427 | 5.9 | +6.5 |
| 33$\bar{6}$ | 2.1 | -1.6 | 227 | 3.4 | +3.2 |
| | | | | | |
| 53$\bar{6}$ | 0.0 | +1.0 | 027 | 3.3 | +3.0 |
| 73$\bar{6}$ | 0.0 | -0.4 | 22$\bar{7}$ | 7.7 | +8.0 |
| 246 | 2.9 | +2.3 | 42$\bar{7}$ | 1.2 | +0.6 |
| 046 | 0.0 | +1.0 | 62$\bar{7}$ | 4.3 | +8.5 |
| 24$\bar{6}$ | 2.1 | +1.7 | 82$\bar{7}$ | 3.6 | -3.7 |
| | | | | | |
| 44$\bar{6}$ | 5.0 | +4.2 | 737 | 1.9 | +2.0 |
| 64$\bar{6}$ | 3.1 | +2.7 | 537 | 4.6 | +5.5 |
| 356 | 3.6 | +2.6 | 337 | 5.8 | +6.5 |
| 156 | 5.6 | +6.0 | 137 | 3.9 | -3.8 |
| 15$\bar{6}$ | 4.5 | +6.0 | 13$\bar{7}$ | 5.8 | -6.5 |
| | | | 33$\bar{7}$ | 4.6 | +6.0 |
| 35$\bar{6}$ | 5.4 | +4.8 | 53$\bar{7}$ | 1.7 | -3.3 |
| 55$\bar{6}$ | 4.4 | +4.8 | 73$\bar{7}$ | 3.3 | -5.5 |
| 266 | 2.7 | +2.7 | 93$\bar{7}$ | 1.8 | -2.5 |
| 066 | 3.6 | +5.5 | 647 | 1.3 | +1.2 |
| 26$\bar{6}$ | 3.3 | +3.5 | | | |
| | | | | | |
| 46$\bar{6}$ | 4.6 | +3.4 | 447 | 4.5 | +3.9 |
| 66$\bar{6}$ | 3.6 | +5.5 | 247 | 4.2 | +4.8 |
| 376 | 1.5 | +0.8 | 047 | 4.6 | +5.0 |
| 176 | 3.0 | +4.7 | 24$\bar{7}$ | 5.7 | +6.5 |
| 17$\bar{6}$ | 3.3 | +4.9 | 44$\bar{7}$ | 2.4 | +3.0 |
| | | | | | |
| 37$\bar{6}$ | 3.0 | +2.3 | 64$\bar{7}$ | 1.8 | -1.6 |
| 57$\bar{6}$ | 2.9 | +3.2 | 84$\bar{7}$ | 1.8 | -2.5 |
| 77$\bar{6}$ | 2.4 | +3.4 | 557 | 2.4 | +2.2 |
| 086 | 2.4 | +4.2 | 357 | 3.5 | +4.0 |
| 28$\bar{6}$ | 2.4 | +2.7 | 157 | 2.5 | +3.1 |
| | | | | | |
| 517 | 2.5 | +2.4 | 15$\bar{7}$ | 2.2 | +1.8 |
| 317 | 2.8 | +1.7 | 35$\bar{7}$ | 0.9 | +0.3 |
| 117 | 2.5 | +1.5 | 467 | 1.4 | +1.5 |
| 11$\bar{7}$ | 7.0 | +7.5 | 267 | 1.7 | +1.6 |
| 31$\bar{7}$ | 6.0 | +10 | | | |

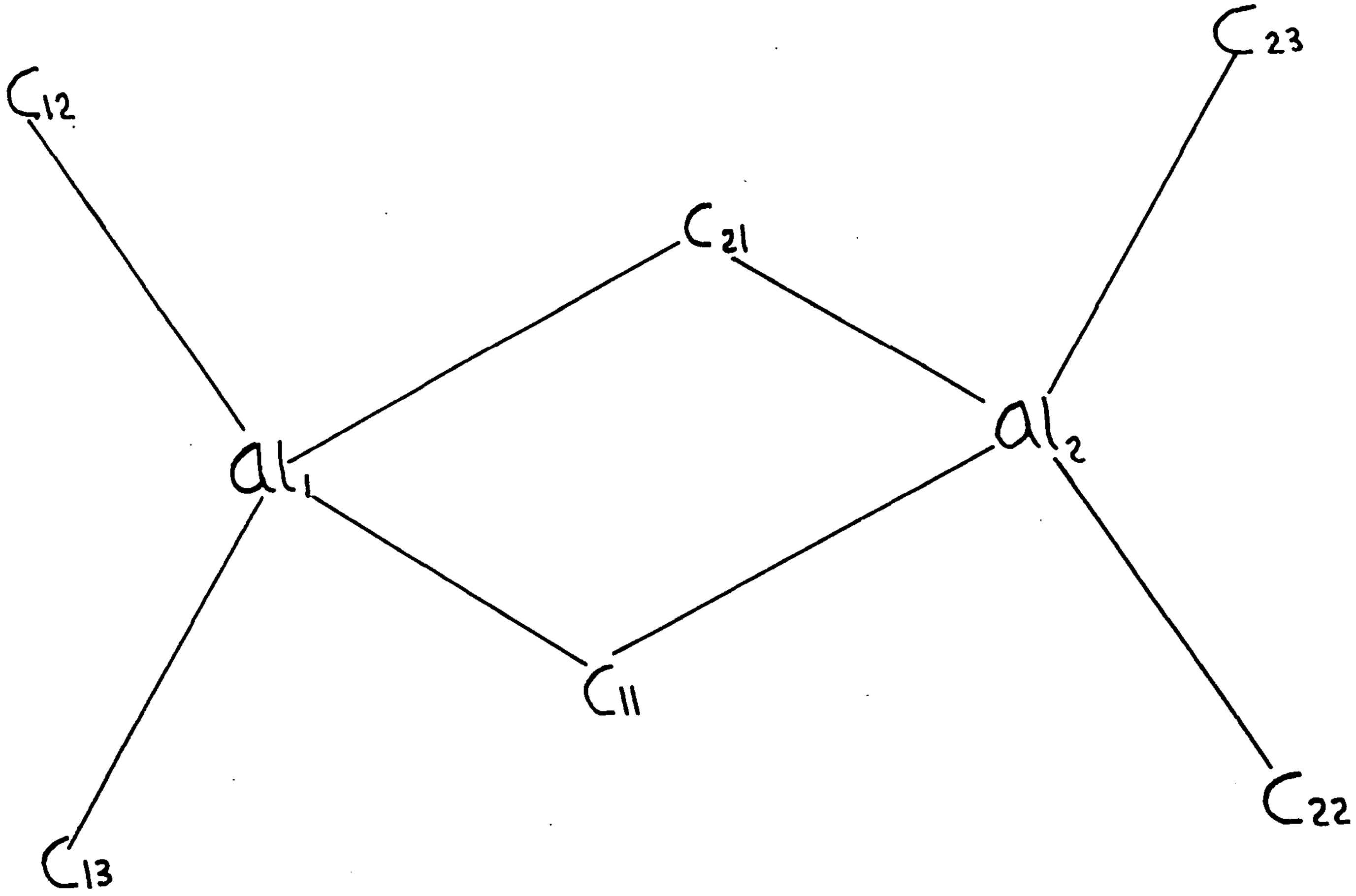


Fig. 6. The nomenclature for the trimethylaluminum dimer.

For a monoclinic crystal these errors are

$$\sigma(x) = \frac{\{\sigma^2(A_h) - \cos^2\beta\,\sigma^2(A_\ell)\}^{1/2}}{A_{hh}\sin^2\beta}$$

$$\sigma(y) = \frac{\sigma(A_k)}{A_{hh}}$$

$$\sigma(z) = \frac{\{\sigma^2(A_\ell) - \cos^2\beta\,\sigma^2(A_h)\}^{1/2}}{A_{hh}\sin^2\beta},$$

where $A_{hh} = -2pN(p/\pi)^{3/2}$, and

$$\sigma(A_h) = \frac{2\pi}{aV}\left\{\sum_3 h^2\,\Delta F^2\right\}^{1/2},$$

and $\sigma(A_k)$ and $\sigma(A_\ell)$ are analogous to $\sigma(A_h)$. The value of p, 4.69, was found to be sufficiently good for this work. $\Delta F$ in the above expressions is the difference between the observed and calculated structure factors. The errors determined are as follows:

| | (x) | (y) | (z) |
|---|---|---|---|
| Al | 0.008Å | 0.002Å | 0.004Å |
| C | 0.02 Å | 0.004Å | 0.008Å |

The method is known to underestimate errors and no correction was made for series termination error. An estimated error of ± 0.02 would seem reasonable. This may be checked by the comparison of the $Al_1$-$C_{11}$ distance with that of $Al_2$-$C_{11}$, and the $Al_1$-$C_{13}$ distance with that of $Al_1$-$C_{12}$. The members of each pair differ by 0.01Å or less from each other. Assuming the three dimensional error to be $\sqrt{3}$x 0.02Å, then each angle calculated would be uncertain to about 0.017 radians or 1°. Therefore, the difference between angles, equal to 2°, is just within the experimental error. In the light of this, the 94° angle between the planes which would be the mirror planes in the ideal molecule having $D_{2h}$ symmetry is not unreasonably far from 90°.

## Discussion

The prediction that the trimethylaluminum molecule is a bridge-type dimer in order for the aluminum to make use of all its low-energy orbitals is confirmed by the experimental evidence. There is no evidence of further polymerization; the trimer proposed by Longuet-Higgins (11), and the ethane-type molecule suggested by the electron diffraction study (18) are incorrect. The fact that all bond lengths within the bridge ring are equal, plus the confirmation of the Raman evidence that at least the aluminum and carbon skeleton is $D_{2h}$ in point symmetry discredits Pitzer's suggestion (10) discussed earlier. The molecular shape is, however, in excellent agreement with Rundle's predictions, comparison of the summarized bond angles and lengths (p 40) with those predicted (p 10) reveals no discrepancies.

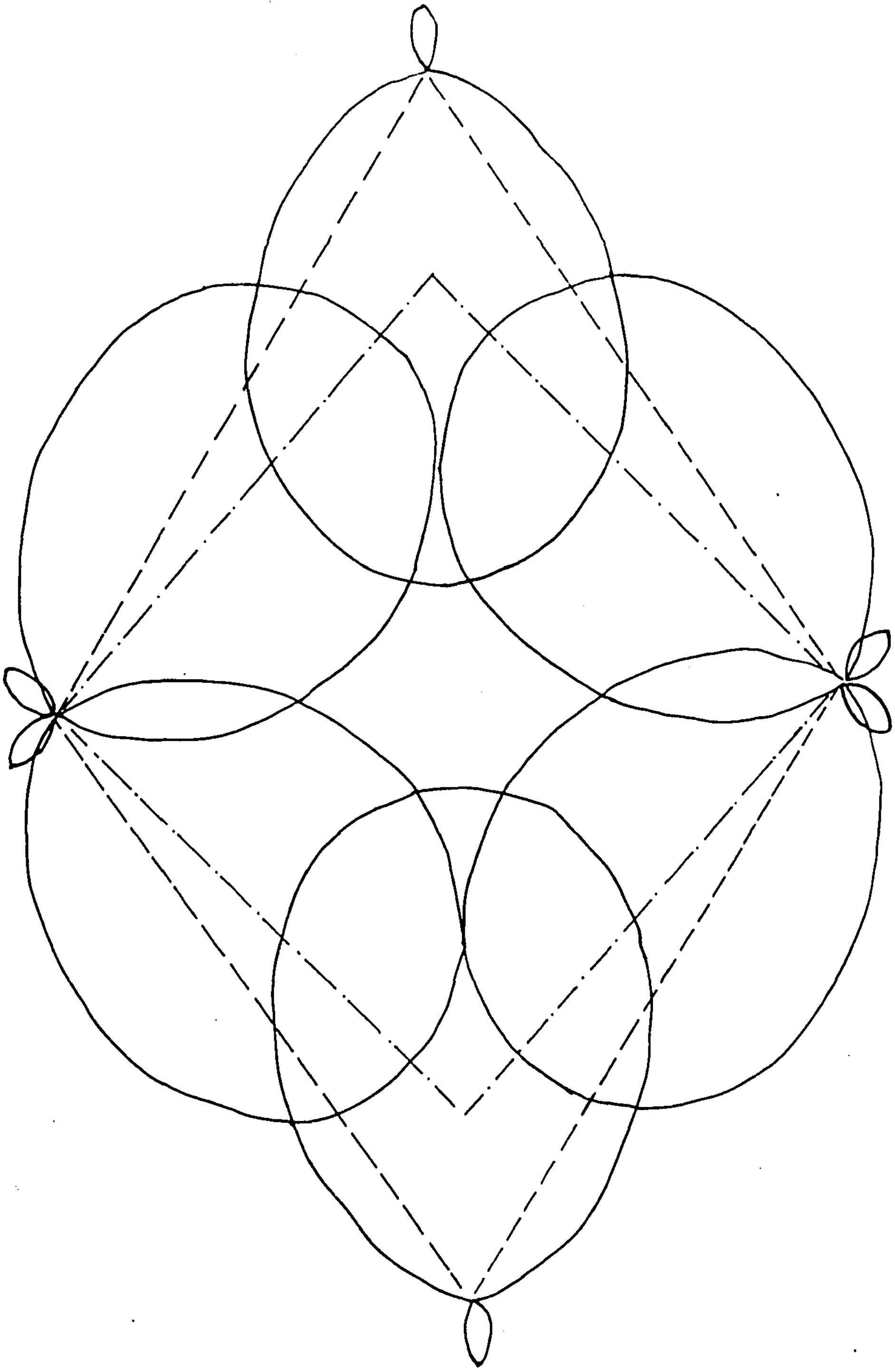
It is to be noted that the aluminum-carbon distances external to the ring, all 1.99Å compare well with the 2.03Å calculated using the tetrahedral radii of aluminum and carbon (8). Furthermore, using these radii and Pauling's rule (12):

$$R(1) - R(n) = 0.300 \log n,$$

where R(1) is the single bond radius, R(n) the radius of the atom participating in a bond of order n, the aluminum-carbon distance internal to the ring is calculated to be 2.21Å, in excellent agreement with the observed distance. The bond order used in the calculation was one half. This analysis of the bond lengths confirms the nature of the bonding in the bridge as 'electron-deficient'.

The configuration about the aluminum is, to a degree, distressing. The bond angle internal to the ring is entirely normal, 110°. One could suppose the aluminum is using its tetrahedral orbitals, however, the bond angle external to the four-membered ring is 124°. Since a similarly large external angle is observed in diborane (15), it must be real. Any explanation of the bonding must also explain the bond angle at the bridge carbon of 70°. It is to be noted that Kimball (51) claims that if bond and orbital directions are coincident, then only an appreciable amount of p and d character in the bridge carbon's orbital would permit this atom to form bonds at an angle of 70°. In line with this, Gillespie (52) has recently published a paper explaining the stability of trimethylaluminum, dimethylberyllium, and tetramethylplatinum. Gillespie first points out that the utilization of 3d orbitals by first row elements is not to be supposed unreasonable, that the promotional energy necessary for carbon to make use of these orbitals is about 11 e.v. The suggestion runs that the bridge carbon uses three $sp^3$-tetrahedral orbitals for bonding to hydrogen, and two spd hybrids for bonding to the aluminum. On this basis, the carbon-hydrogen bond is viewed as a two thirds bond, while the aluminum-carbon bond is normally covalent. Several pieces of experimental evidence make this proposal seem incorrect. To begin with, the promotional energy is far too high, 253 kcals/mole/carbon, this is to be compared with the normal aluminum-carbon bond energy of about 70 kcals. The carbon-hydrogen stretching frequency as reported by Pitzer (10) is entirely normal, and no evidence of a weakened bond is to be seen. The carbon-hydrogen stretching frequency was also checked in dimethylberyllium with similar results (53). Gillespie's prediction that the aluminum-carbon bond in the bridge ring will be normally covalent is also incorrect, the experimentally determined distance is far greater than that found for the bonds external to the ring.

In contrast to this, the following explanation is offered. The configuration about the aluminum cannot be considered tetrahedral since, although the internal bond angle (within the ring) is 110°, the external angle is 124°. Therefore, it must be assumed that the orbitals external to the ring are richer in s-character than tetrahedral, while those within the ring have more p. If this were so, the external angle can be understood since s-character increases orbital angles (p orbitals are at 90°, $sp^3$ are at 109°, $sp^2$, at 120°, etc.), but the internal angle remains a problem since the orbital angle might well be as low as 90°. The bond angle is reasonable only if it does not coincide with the orbital angle. The p-rich orbitals are to be viewed as being directed towards the lower, thicker portion of the single tetrahedral bridge carbon orbital, while the bond is directed from the aluminum to the origin of the bridge orbital, the site of the carbon atom. So while the orbital angle is 90°, the bond angle is 110° (Figure 7). The acute bridge angle of 70° is caused by the aluminum atoms moving together so as to secure maximum overlap of orbitals, and to obey the directional properties of the single carbon tetrahedral orbital. All orbitals forming the bridge are, of course, hybridized to form a molecular orbital. This explanation is made more reasonable by comparison of the bond angles with those of diborane. In diborane, the bridge hydrogen's s-orbital does not have directional properties, the bond and orbital directions are coincident. Here the external angle is again 124° and the angle at the boron, internal to the bridge, is 90°. The inference is that diborane is demonstrating the orbital configuration that is present in trimethylaluminum. The external angles are



- - - Bond direction, - . - . - Orbital direction.

Fig. 7. Orbital configuration in the dimer.

exactly the same; the internal bridge angles would be the same if the bond and orbital directions in trimethylaluminum were coincident, which they cannot be because of the above consideration of the directional properties of the carbon's tetrahedral orbital and maximum orbital overlap.

Two other suggestions for the bonding should be considered. There is no evidence of ionic character in the solid. The Van der Waals distances between methyl groups are all about 4.0Å, which is normal for these groups when engaged in covalent bonding. Methyl ions would require greater intermolecular distances. If metal to metal bonding is considered, as it should be since the aluminum-aluminum distance is 2.55Å *versus* 2.52Å predicted by doubling the tetrahedral radius (8), a possible qualitative picture may be seen. The alumimum-aluminum bond and all the aluminum-carbon bonds would be regarded as fractional, perhaps of bond order 0.4. Quantitatively one runs into trouble; on the basis of a 0.4 bond order aluminum-aluminum bond, one would calculate a bond length of 2.63Å, significantly different from the 2.55 Å observed. If the bond order of one is ascribed to the aluminum-aluminum bond, then the aluminum-carbon bonds would have to be of order 0.25. This value is considerably lower than the 0.50 calculated for them. Considerations of metal-metal bonding therefore incurs difficulties which are not easily resolved. It is to be recalled, moreover, that in tetramethylplatinum the stabilization of the molecule occurred exclusively through platinum-alkyl bonding, these bonds being sufficiently long to separate the platinum atoms far enough apart so that the bonding could be unambiguously described.

Recently (54), a molecular orbital treatment has been applied to the trimethylaluminum dimer. The purpose of this calculation was to compare the heat of dimerization for the case where the dimer has no aluminum-aluminum interaction with that in which there is. The assumption is made (55) that the coulombic integral for carbon,

$$q_c = q_{Al} + n\beta$$

where β is the exchange integral for a normal bond,

$$\beta = \int \psi_{C_{tetra}} H \psi_{Al_{tetra}} \, d\tau .$$

This exchange integral is modified for the bent bridge bond for its deviation from ideal. The β is multiplied by a factor X which is determined by the angle deviation, in this case 35°. X equals the ratio between the f for the bent bond and that for a normal bond, . Since

$$f = 1/2 + 3/2 \cos 35°,$$

X is equal to 0.863. The secular equation for a normal molecular orbital treatment is:

$$\begin{vmatrix} q_{Al} - w & 0.863\ B & 0 \\ 0.863\ \beta & q_{Al} + n\beta - w & 0.863\ \beta \\ 0 & 0.863\ \beta & q_{Al} - w \end{vmatrix} = 0.$$

The secular equation was solved for three cases, n=0, 1, 2.

This solution for the energy was compared with that of a normal aluminum-carbon bond, obtained from

$$\begin{vmatrix} q_{Al} - w & \beta \\ \beta & q_{Al} + 2\beta - w \end{vmatrix} = 0.$$

The difference between these two is the resonance energy, or the heat of reaction. The results are in Table 5.

Table 5. Results of the molecular orbital treatment, neglecting aluminum-aluminum interation.

| n | 0 | 1 | 2 | |
|---|---|---|---|---|
| Resonance energy/bond | $0.44\beta$ | $0.40\beta$ | $0.32\beta$ | |
| Per cent of bond energy/molecule | 44% | 36% | 23% | |
| Bond energy, basis $E_{Al-c}$ = 67.4 kcals. | 29.6 | 24.0 | 15.4 | kcals/mole |

The case where aluminum-aluminum bonding is considered will now be set up. For the bent bond, f is equal to 1/2 + 3/2 cos 55°, or 1.36. This is squared and divided by 4, the value of f for the normal bond. The ratio of the normal $\beta_{Al-Al}$ to $\beta_{Al-c}$ is about one half, this estimation being made by comparison of bond energies. Therefore,

$$\beta_{Al-Al} = 1/2.\ 1.85/4 \cdot \beta_{Al-c} = 0.23\ \beta.$$

The secular equation is:

$$\begin{vmatrix} q - w & 0.86\beta & 0.23\beta \\ 0.86\beta & q + n\beta - w & 0.86\beta \\ 0.23\beta & 0.86\beta & q - w \end{vmatrix} = 0 .$$

For the normal bond, $w = 2q + 3.24\beta$. The difference between the w for the bent bond and that for the normal bond again gives the resonance energy. The results are in Table 6.

Table 6. Heat of reaction results for the case where aluminum-aluminum interaction is considered.

| n = | 0 | 1 | 2 |
|---|---|---|---|
| ΔH dimerization | 43.0 | 33.7 | 19.6 kcals/mole |
| per cent of bond | 64% | 50% | 29% |

If n is about 2, and this seems most reasonable, there is little difference in resonance energy between the two cases. One concludes that aluminum-aluminum bonding is, at best a secondary effect.

Although the structure of Pitzer and Gutowsky (10) is wrong, it did explain the stability of the homologs of the trimethylaluminum dimer which possess α hydrogens. Thus trimethylaluminum, triethylaluminum, and tri-n-propylaluminum all exist as dimers, but triisopropylaluminum is a monomer. One would like to explain the instability of the triisopropylaluminum dimer in terms of methyl replusions. This would seem more than reasonable since the methyl groups on the bridge carbon come within 1.8Å of those on the external isopropyl groups. This is to be compared with the 2.5Å distance between methyls in tetramethylmethane. The stabilizing effects of dimerization would not be sufficient to overcome not only this steric strain, but also the decrease in entropy incurred in dimerization.

# THE STRUCTURE OF BERYLLIUM CHLORIDE

## Experimental Procedures

### Preparation and properties of beryllium chloride

Beryllium chloride is a colorless solid which crystallizes in long needles. The anhydrous compound was prepared for us by the metallurgy group of the Ames Laboratory of the Atomic Energy Commission. This was done by passing dry hydrogen chloride over beryllium oxide. Beryllium chloride is highly hygroscopic so crystals suitable for the X-ray work were mounted in glass capillaries. A convenient technique for handling the crystals in the open air without recourse to a dry box was to manipulate them under mineral oil previously dried by sodium. This film of oil made microscopic examination of the crystals impossible so no optical properties can be reported. No face development was apparent.

### X-ray data

The beryllium chloride needles were mounted so that the needle axis was coincident with the axis of rotation on the X-ray cameras. Weissenberg data, (hk0), (hk1), (hk2), were obtained by rotating about this needle axis. The X-ray source in this case was that of the North American Phillips Company, the radiation Cu K $\alpha$, = 1.542Å. All intensity work for these levels was done by taking pictures with multiple films. The ($h0\ell$) data were examined by use of the precession camera, the X-ray source being a General Electric XRD-3 unit with stabilized voltage and current. Molybdenum radiation, Mo Kα, was used with a wave length of 0.7107Å; the precession angle was 25°; the factor, F, was set permanently at 6.00. Unfortunately, reflections with $\ell$ greater than six could not be observed by this method. To obtain suitable ($00\ell$) data for determining the z parameter, the capillary was mounted perpendicular to the axis of rotation on the Weissenberg camera and Weissenberg data were obtained using a short oscillation range about the c-axis. Mo Kα radiation was used in this work which obtained data to $\ell = 8$, with (0·0·10) barely perceptible. The exposure times for all work was about thirty hours. This last operation, however, required seventy hours. Timed exposures were used in all work with molybdenum radiation.

## Unit cell and space group

The lattice symmetries of the ($hk0$), ($hk1$), ($0k\ell$) and ($h0\ell$) levels were all $C_{2\ell}$. Precession pictures taken at small $\bar{\mu}$ angles with no screen by precessing about the b-axis all showed $C_{2\ell}$ symmetry. The same was true when the a-axis was precessed about. This evidence indicates that beryllium chloride belongs in the orthorhombic crystal class. Reflections ($hk\ell$) are present only when $h + k + \ell = 2n$; ($h0\ell$), only with $h=2n, \ell=2n$; ($0k\ell$), only with $k=2n, \ell=2n$.

The space group is, therefore, either $D_{2h}^{26}$ - I bam or $C_{2v}^{21}$ - I ba (30).

The lattice constants were all measured on precession photographs, $a_o = 9.86$, $b_o = 5.36$, $c_o = 5.26$Å. The handbook specific gravity of beryllium chloride is 1.899 25°/4, which is in good agreement with the density 1.91 gms./cm$^3$, determined by use of the above lattice constants, and assuming four $BeCl_2$ molecules per body-centered unit cell.

Determination of atomic positions

All reflection intensities were determined by visual estimation. These were suitably corrected for the Lorentz-polarization factor (31, 32) and converted to structure factors. It is to be noted that the X-ray data were not the best, the "spots" being badly elongated.

In either space group the chlorine atom positions are $\pm$ (xy0, $x\bar{y}$ 1/2) + 000, 1/2 1/2 1/2 and the beryllium positions are (00z), 00 1/2 + z) + 000, 1/2 1/2 1/2, where z = 1/4 if the space group is I bam. This is, then, a three parameter problem. The two chlorine parameters could have been easily fixed by trial and error, but the Patterson technique was employed. A two-dimensional projection was made onto the (001) plane (Figure 8), and suitable chlorine parameters were found. The function used was

$$P_{xy} = \sum_{0}^{\infty}\sum_{0}^{\infty} F^2_{hk0} \cos 2\pi hx \cos 2\pi ky.$$

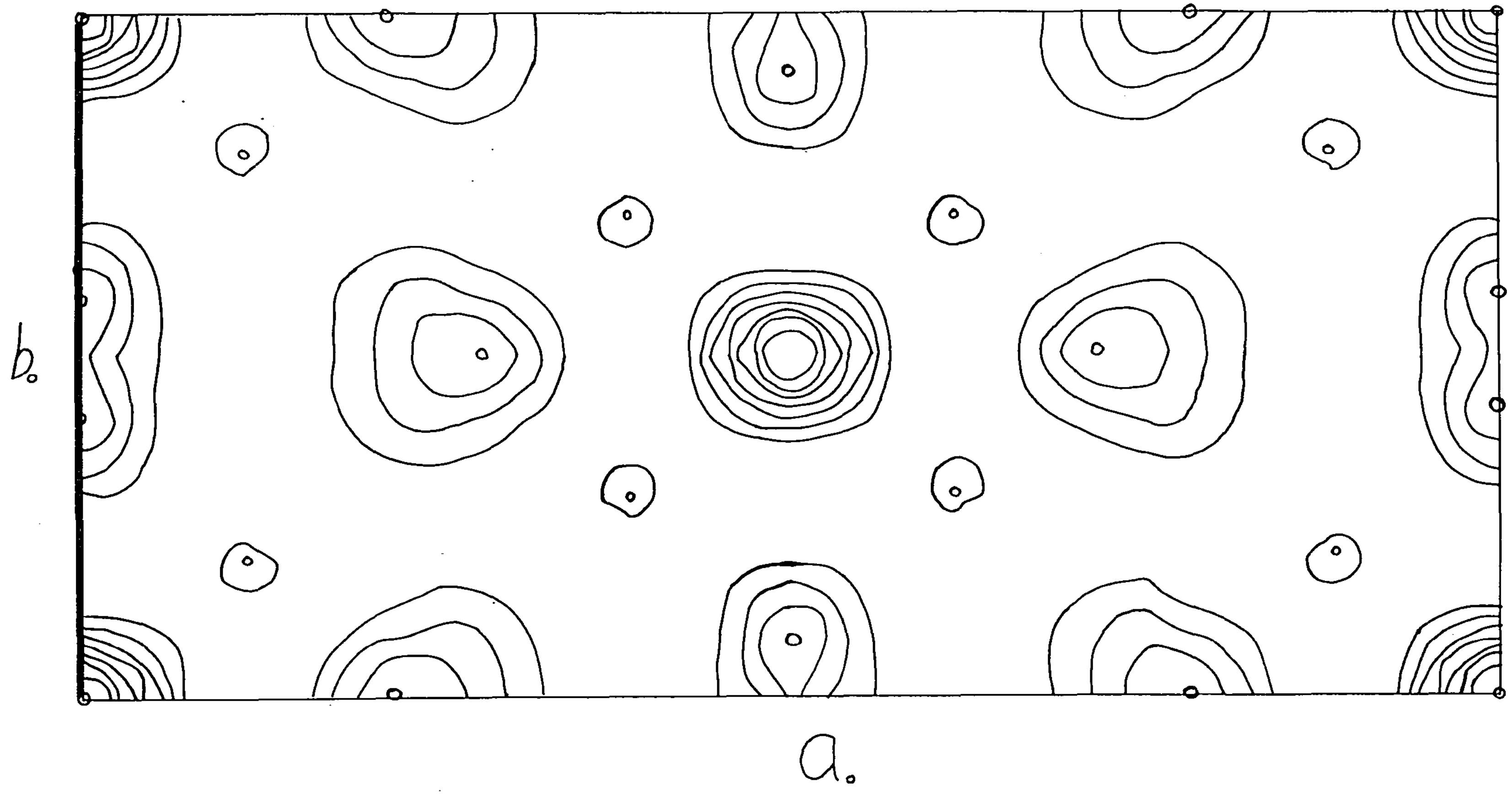


Fig. 8. The Patterson projection onto the ab plane, beryllium chloride.

These rough parameters were refined by a two dimensional Fourier (Figure 9),

$$\rho_{xy} = \sum_{0}^{\infty} \sum_{0}^{\infty} \pm F_{hk0} \cos 2\pi hx \cos 2\pi ky.$$

Successive Fouriers using observed structure factors and calculated phases were run until all structure factor signs became static. The structure factor signs used were obtained from the calculated values,

$$F_{hk0} = 4 f_{Be} + 8 f_{Cl} \cos 2\pi hx_{Cl} \cos 2\pi ky_{Cl}.$$

To complete the refinement, the back shift technique (47) was utilized. The peak positions were determined in the manner described in that paper. The results of this analysis are:

$$x_{Cl} = 0.109 \pm 0.001$$
$$y_{Cl} = 0.203 \pm 0.002,$$

the errors being estimated by Cruickshank's method (50). For the orthorhombic system the standard deviation, $\sigma$, of any parameter, $x_i$, is given by

$$\sigma(x_i) = \frac{\sigma(A_{hi})}{\partial^2\rho/\partial r^2} = \frac{\left\{\sum (4\pi^2/a_i^2V)^2_{hk\ell}\, h_i^2(\Delta F)^2\right\}^{1/2}}{2pN(p/\pi)^{3/2}}.$$

Here $\Delta F$ represents the difference between observed and calculated structure factors, p is a constant set equal in this case to 4.69, and N is the atomic number of the atom whose position's accuracy is being checked. The series termination error (57) was less than 0.001 parameter units in

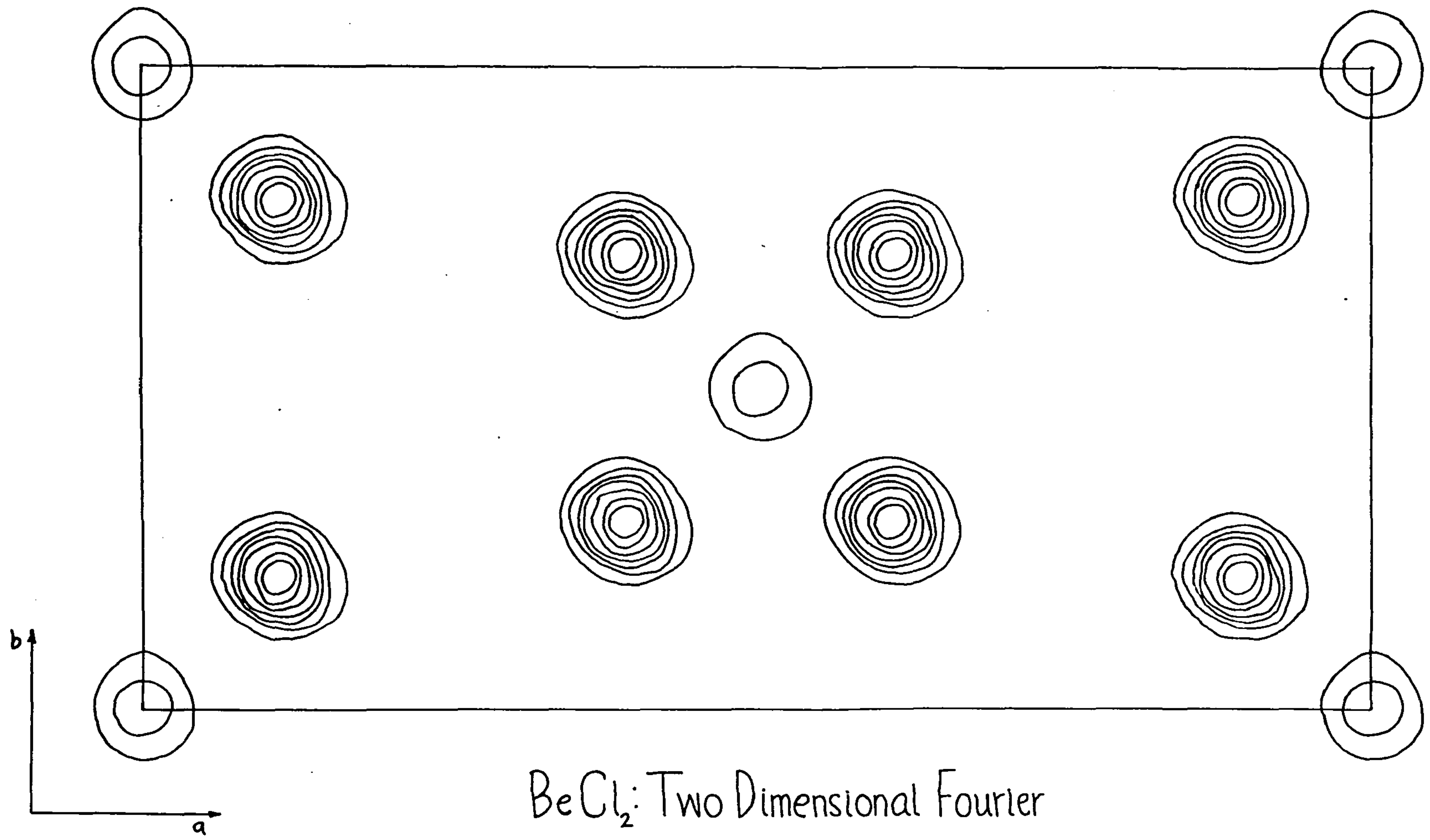


Fig. 9. The Fourier projection onto the ab plane, beryllium chloride.

both x and y.

The z parameter of the beryllium was handled purely by trial and error methods using the ($00\ell$) data. Since reflections ($00\ell$) with $\ell$ greater than eight could not be obtained, the z parameter was found to be less accurately determined. The result was $z_{Be} = 0.25 \pm 0.02$ parameter units. Although the error is fairly high here, it can be said that $z_{Be}$ really is 1/4, and that the space group of beryllium chloride is I bam.

General ($hk\ell$) data were calculated by the use of:

$$F_{hk\ell} = 4\, f_{Be}(-1)^{\ell/2} + 8 \cos^2 2\pi \frac{h+k+\ell}{4} \cos 2\pi \left(hx + \frac{\ell}{4}\right)$$

$$\times \cos 2\pi(ky - \ell/4) \cos 2\pi \ell z$$

when $\ell$ is even. When $\ell$ is odd, the beryllium contribution is zero. To compare the observed data with the calculated, the observed data were corrected for the temperature and absorption effects. The temperature factor by which the observed structure factors were multiplied was

$\exp(+B \sin^2 \theta/\lambda^2)$. B was found to be equal to $3.9 \mathring{A}^2$. This value was determined by applying the method of least squares to the data. The observed data also contain an absorption correction which was determined by the method of Bradley (58) assuming a circular cross section. A mass absorption coefficient, $\mu$, was calculated to be 175 $cm^{-1}$. The diameter of the needle used in obtaining X-ray data was

0.36mm, so $\mu r$ equals 3.2. An absorption curve was plotted on this basis, using Bradley's data. The absorption corrections were picked off at appropriate $\sin^2 \theta/\lambda^2$ values for each reflection.

The temperature factor is probably asymmetric since $(00\ell)$ data can be obtained at somewhat higher $\sin \theta/\lambda$ values than (hk0) data. This is, however, a minor defect and was disregarded. The usual evaluation of the reliability of the structure was made; R equals 0.19 for all data

$$(R \equiv \sum \left||F_{obsd}| - |F_{calcd}|\right| / \sum |F_{obsd}| ).$$

A listing of the observed and calculated structure factors may be seen in Table 7.

Table 7. Comparison of observed and calculated structure Factors for beryllium chloride.

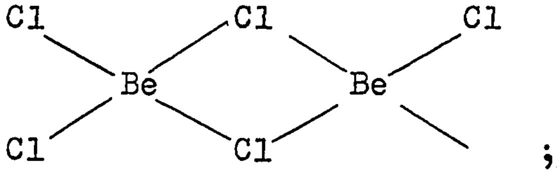
| Indices | $F_{obsd}$/ | $F_{calcd}$ | Indices | $F_{obsd}$ | $F_{calcd}$ |
|---|---|---|---|---|---|
| 200 | 60 | +42 | 350 | 16 | -21 |
| 400 | 74 | -72 | 550 | 46 | -51 |
| 600 | 31 | -31 | 211 | 110 | -92 |
| 800 | 51 | +52 | 411 | 25 | -31 |
| 10•0•0 | 46 | +56 | 611 | 50 | +55 |
| 12•0•0 | 25 | -13 | 811 | 46 | +43 |
| 020 | 86 | -67 | 10•1•1 | 47 | -29 |
| 040 | 29 | +33 | 121 | 32 | -31 |
| 110 | 58 | +45 | 321 | 37 | -40 |
| 310 | 7 | - 1 | 521 | 14 | +11 |
| 510 | 9 | -12 | 721 | 33 | +36 |
| 710 | 12 | +10 | 921 | 0 | + 4 |
| 910 | 22 | +24 | 11•2•1 | 55 | +29 |
| 220 | 8 | - 3 | 231 | 45 | +46 |
| 420 | 65 | +69 | 431 | 24 | +17 |
| 620 | 36 | +40 | 631 | 35 | -33 |
| 820 | 19 | -27 | 831 | 30 | -26 |
| 10•2•0 | 41 | -33 | 141 | 35 | +39 |
| 12•2•0 | 26 | +22 | 341 | 43 | +53 |
| 130 | 37 | -35 | 541 | 23 | -16 |
| 330 | 35 | +34 | 741 | 68 | -53 |
| 530 | 50 | +57 | 251 | 0 | - 1 |
| 730 | 0 | - 3 | 451 | 0 | - 2 |
| 930 | 51 | -37 | 161 | 33 | -33 |
| 11•3•0 | 14 | - 8 | 361 | 46 | -56 |
| 240 | 13 | +13 | 561 | 21 | +14 |
| 440 | 14 | -14 | 202 | 24 | +11 |
| 640 | 16 | - 6 | 402 | 76 | -78 |
| 10•4•0 | 18 | +23 | 602 | 31 | -46 |
| 150 | 46 | +54 | 802 | 35 | +37 |

Table 7 (Continued).

| Indices | $F_{obsd}$ | $F_{calcd}$ | Indices | $F_{obsd}$ | $F_{calcd}$ |
|---|---|---|---|---|---|
| 10·0·2 | 35 | +40 | 10·2·2 | 44 | -48 |
| 12·0·2 | 35 | -23 | 132 | 44 | -48 |
| 112 | 13 | + 3 | 332 | 18 | +17 |
| 312 | 21 | -13 | 532 | 29 | +40 |
| 512 | 22 | -27 | 732 | 0 | - 3 |
| 022 | 69 | -73 | 932 | 47 | -46 |
| 222 | 21 | -20 | 042 | 30 | +18 |
| 422 | 44 | +46 | 242 | 17 | - 2 |
| 622 | 18 | +25 | 442 | 17 | -27 |
| 822 | 39 | -40 | 152 | 37 | +38 |
| | | | 352 | 20 | -34 |
| | | | 552 | 44 | -58 |

## Discussion of the Structure

The structure of beryllium chloride is isomorphous with dimethylberyllium and silicon disulfide (3, 24). The salient feature of all three compounds is the polymeric chains



the repeat unit will be a four membered ring with the two nonmetal atoms occupying opposite corners. In beryllium chloride these chains run parallel with the c-axis and pack rather like circular cylinders. The chlorine-chlorine distance between chains is 3.85Å, which is somewhat larger, but near previously observed van der Waals distances which range from 3.6 to 3.8Å.

It is to be noted that bonding in the molecule takes place in such a manner that all the orbitals of the beryllium are utilized. The bond distances give some clue as to the bonding. The beryllium-chlorine distance is 2.02Å versus 2.05Å given by the sum of the covalent radii of Pauling (8). This would indicate a bond order of one. If Pauling's metallic radius (12) is adapted, the sum is 1.883Å. This value makes the bond order uncertain.

Investigation of the bond angles gives more exact information about the nature of the bonding. The compound is similar to dimethylberyllium, but shows interesting differences. In dimethylberyllium the ∠ C-Be-C is 114°, greater than tetrahedral, whereas the corresponding ∠ Cl-Be-Cl is only 98.2°, very much less than tetrahedral. The resulting angles ∠ Be-C-Be and ∠ Be-Cl-Be are 66° and 81.8° respectively. Dimethylberyllium was described earlier in this thesis as an 'electron-deficient' compound in which the two beryllium atoms move close together toward the direction of greatest charge density of the single carbon bridge tetrahedral orbital. In beryllium chloride the bridge angle is not as acute as that in dimethylberyllium and the explanation for that compound cannot hold for beryllium chloride, so beryllium chloride is not 'electron-deficient'. The bond angles found in the chloride are, however, quite similar to those found in silicon disulfide. Silicon disulfide is undoubtedly a coordinate-covalent compound, and by inference so is beryllium chloride. The bond angles are entirely reasonable for this. The orbital configuration about the beryllium should be tetrahedral, the bond angle 109°; the chlorine should use two p-orbitals at 90°. Obviously, to form a ring both must undergo strain, and some compromise must occur. The result is entirely reasonable, the Cl-Be-Cl is ten degrees less than that angle usually found between p-orbitals. One feels then that the angles found in beryllium chloride characterize coordinate-covalent bond- in bridge compounds containing tetrahedral metal atoms.

Since beryllium chloride is a strained molecule, the question arises as to whether or not the bond orbitals and directions are coincident. The molecule may adjust to the strain either by changing its orbital angle or by allowing the orbitals to overlap so that their directions are askew. This latter case would mean that maximum overlap would not be attained. Of the two possibilities, the latter seems the more reasonable if the qualitative results of the cyclopropane calculation (60) are applied here. It was found in that case that the energy required to distort the orbital angle of carbon was far greater than that lost by not attaining maximum overlap.

All the above is based on the assumption that beryllium chloride is covalent-coordinate in character. It is natural to wonder whether or not the compound might be ionic. The physical properties of the compound are covalent, the compound is readily soluble in ether and benzene. The crystal structure study itself shows that the main structural data detail is the polymeric chain which is analogous to that found in silicon disulfide which is to be classified as coordinate-covalent. Ionic character of the beryllium-chlorine bond may be calculated using Pauling's scale of electronegativities (8), the result indicates 44 per cent ionic character. This should be compared with 39 per cent for the hydrogen-oxygen bond in water. This evidence coupled with the low conductivity of fused beryllium chloride is sufficient to confirm beryllium chloride as covalent.

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