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The crystal structures of triphenyl aluminum and lead (II) bromide

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THE CRYSTAL STRUCTURES OF TRIPHENYL ALUMINUM
AND LEAD(II) BROMIDE.**

**Iowa State University of Science and Technology,
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THE CRYSTAL STRUCTURES OF
TRIPHENYL ALUMINUM AND LEAD(II) BROMIDE

by

Hollis Dean McBride

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

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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1966

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PART I. THE STRUCTURE OF TRIPHENYL ALUMINUM

INTRODUCTION

Triphenyl aluminum is known to exist as a dimer; however such a dimer poses an apparent violation of classical bonding theory and thus a knowledge of the structural arrangement of the atoms is necessary in order to hope to understand the chemical bonding involved. The classical bonding theory, first proposed by G. N. Lewis (1), may be briefly expressed by the following principles:

i. The chemical bond is the sharing of an electron pair between two atoms.

ii. Each atom in a compound possesses maximum stability when it achieves a stable rare gas electronic shell.

This simple valence theory in most cases was sufficient to account for the bonding in both ionic compounds, where the inert gas structure is achieved by both anions and cations by a transfer of electrons, and in covalent compounds, where through electron sharing, the shared pairs fill the rare gas shell of both atoms of the bond.

In exception to these rules are the class of compounds, $(AlR_3)_n$ where R is an organic alkyl or aryl substituent. The aluminum and organic substituents can

supply only six electrons for bonding among them. There is, then, no way to form the four bond, eight electron outer shell necessary to achieve the rare gas structure. The case is not solved by forming dimers, for now the eight atom system requires at least seven bonds, though only six electron pairs exist. It is obvious that the classical theory must be extended to understand this type of "electron deficient" compound.

Electron deficient compounds are found, generally, in the combination of a metal--one not sufficiently electropositive to describe the bonding in terms of ions--with non-metallic substances such as hydrides, halides and organic ligands. The discovery of the boron hydrides (2) produced the first example of an electron deficient compound which violated classical theory so severely that the need for a new explanation was obvious. These were, for some time, treated as occurring from properties unique to hydrogen (3, 4), the bonding being explained in terms of a protonated double bond (5). With the discovery of electron deficient organo-metallics, and the need to extend this theory to methylated double bonds, the arrival of the molecular orbital (MO) theory provided an attractive alternate method of explanation.

The molecular orbital treatment provides a complete model for the electron deficient compound where the

classical treatment failed. It provides for a set of orbitals in which the compound has all bonding orbitals filled and where the next possible orbital is a high energy anti-bonding orbital which is empty. Thus, a closed shell structure results and bonds are formed which use all the available orbitals of the metal.

In the case of compounds where electron deficient metals are bridged by non-metallic groups the metal-metal distance would make an important contribution toward substantiating the relative reliability of the protonated double bond or MO theory. The former would be characterized by a strong metal-metal double bond with overlap of the carbon or hydrogen orbitals with the π -bond between the metals. The latter would make the existence of a metal-metal bond merely a question of semantics since one bonding orbital makes use of an orbital from each of two metals as well as the bridging atom. The combination of properties from both the metal-metal and metal-bridge interactions would yield a bonding orbital whose direction is intermediate to that of the extremes, the M-M and M-bridge directions. This type of orbital could be described as a bent orbital since its major axis is not directly between any atom centers. The M-M distance in the latter case therefore could be longer than a M-M single bond distance while the former

theory would predict a shortened M-M distance.

Since atomic distances and spacial arrangements shed much information on what forces constitute bonding, knowledge of the atomic structure of electron deficient compounds should greatly increase understanding of their bonding. Study of the structure of simple organo-aluminum compounds was undertaken because it was felt they would best elucidate the bonding characteristic of the bridging type of electron deficient compounds.

i. Al-C distances are of such distance to minimize stereochemical interference between non-bonding atoms if non-bulky organic substances are used.

ii. The x-ray scattering factors of Al and C are of the same order of magnitude and should provide good resolution of atomic position.

iii. The inclusion of bonds between similar substances of both the classical and electron deficient type allows ready comparison of the bond strengths.

iv. A bridging group such as a phenyl ring can, because of its rigid shape, establish the symmetry of the electron deficient bonding which cannot be established by the atoms participating in the electron deficient bonds themselves.

The structure of the simplest alkyl aluminum,

trimethyl aluminum, has been previously determined in this laboratory by Lewis and Rundle (6). This report will describe the structure of the simplest aryl aluminum, triphenyl aluminum.

Trialkyl aluminum compounds have, in most cases, been found to associate in dimers, trimers, or low order polymers (7). Those compounds which do exist as monomers contain large bulky groups which preclude association because of steric repulsions. Trimethyl aluminum occurs as a dimer (6). Two of the methyls are equidistant between the two aluminums and may be called bridging atoms since they must be equally bonded to each aluminum. The other four methyls are of the classical type; single bonded methyls having bonds to only one aluminum. An accurate structural refinement of trimethyl aluminum shows that the carbon-aluminum skeleton exhibits D_{2h} symmetry (8). Spectroscopic evidence does not substantiate D_{2h} symmetry (9), but this is most likely due to deviation from this symmetry by the hydrogen atoms the positions of which are not easily resolved by x-ray diffraction.

Dimerization would also be predicted in triphenyl aluminum because the energy reduction due to the ensuing electron delocalization would more than compensate for the small steric repulsive effects. Cryoscopic studies

have shown that the degree of association is variable in solution with a temperature dependent molecular association between monomeric and dimeric. Using the ebulliometric method Mole (10) found a two percent solution of triphenyl aluminum to be 80 % associated toward a dimer in benzene and 20 % associated in ether where it is in the form of the dietherate. Perkins and Twentyman (11) found triphenyl aluminum to be dimeric in naphthalene using a Beckman freezing point apparatus. The variable degree of association in solution may be explained from analogy to the work of Muller and Pritchard (12) and Bronstein, et al. (13) who found a rapid exchange in trimethyl aluminum at room temperature, and some exchange at all temperatures above -60° C in several solvents. In a similar manner triphenyl aluminum increases its molecular separation with temperature and ionizing solvent, causing a greater abundance of the monomeric species. Without solvation, neither conditions for mobility nor solvent stabilization of the monomeric species would be present and dimeric triphenyl aluminum would be expected.

The infrared spectrum of triphenyl aluminum resembles mono-substituted benzenes with additional bands; these characteristic intense bands occur at 1185 cm^{-1} and 739 cm^{-1} (14).

Several authors have discussed the theoretical aspects of the bonding in this type of electron deficient compound (5, 15, 16, 17, 18, 19).

Preliminary Results

Triphenyl aluminum may be prepared by reacting aluminum metal and diphenyl mercury in a suitable solvent or as a solid mixture (20). Solvent preparation in xylene produced platelike crystals of triphenyl aluminum, but high reactivity to moisture prevented their transfer without substantial decomposition, thus making them unsuitable for intensity measurements. This transfer was attempted in a specially built dry box, but without success. Small amounts of moisture passing through the rubber gloves was sufficient to partially decompose the crystals before they could be sealed in capillaries. An improvement on the permeability of the gloves used would be necessary before such transfer methods could be used.

Since transfer was unfruitful triphenyl aluminum crystals were prepared directly in the Lindemann glass capillaries. These capillaries are used for collecting x-ray intensity data because of their low absorption of x-rays. Reaction between aluminum turnings and diphenyl mercury as a solid mixture was carried out

in soft glass tubing fused directly to a Lindemann glass capillary. At the reaction temperature of 140°C the volatile mercury and unreacted diphenyl mercury sublime to the cool end of the tubing and may be sealed off. Triphenyl aluminum can then be sublimed at 180°C into the capillary.

Small single crystals of about .1 mm. on an edge were formed in about a week. A liquid decomposition product gradually coated the crystals and prevented growth of any larger crystals¹. Following this procedure a colorless crystal of dimensions .1 x .08 x .07 mm. with well defined faces was obtained and used to acquire single crystal x-ray intensity data.

Weissenberg photographs of zero and first layer diffraction patterns were obtained using Cu radiation to establish the crystal symmetry of triphenyl aluminum. No symmetry other than the center of symmetry required

¹The decomposition product was not identified, although from its solidification temperature it was assumed to be biphenyl. In discussing the problems of decomposition of triphenyl aluminum Mole (10) mentioned that Kenneth Wade found that the decomposition product of triphenyl aluminum is benzene, but it must be assumed that this decomposition was under different conditions, probably from the presence of trace amounts of moisture. In his own literature Wade has only said that benzene is the product of decomposition by HCl addition (21).

by Friedel's law was observed. The crystal symmetry, therefore, is triclinic. Lattice constants, measured from precession photographs using Ni filtered Cu radiation, are

$$\begin{array}{ll} a = 9.392 \pm .013 \text{ \AA} & \alpha = 106.1 \pm .1^\circ \\ b = 10.729 \pm .014 \text{ \AA} & \beta = 110.6 \pm .1^\circ \\ c = 8.280 \pm .015 \text{ \AA} & \gamma = 102.6 \pm .1^\circ \end{array}$$

From the unit cell volume of 711 \AA^3 the calculated density is $0.595(n) \text{ g/cc}$ where n is the number of monomers in the unit cell. By comparison with similar compounds a density somewhat greater than 1.0 would be expected, therefore $d = 1.19 \text{ g/cc}$ and $n = 2$ were assumed.

The distribution of structure factors approximated the expected distribution for a centric crystal (22), and therefore the space group $P\bar{1}$ was assigned. The number and distribution of peaks on the Patterson map also supported this choice.

Solution of the Structure

Establishment of the atomic positions in the unit cell is accomplished by minimization of the difference between the observed and calculated structure factors (F_o and F_c) for the diffracting planes (hkl) of the crystal. The observed structure factors are related to

the intensities of the diffracted x-rays, while the calculated structure factors are, in turn, dependent on the atomic positional and temperature distributional factors. Statistically, these optimum structural parameters are found by minimization of the least square deviations,

$$R_w' = \sum w(hkl) \left(\left| |F_o(hkl)| - |F_c(hkl)| \right| \right)^2,$$

where $w(hkl)$ is a weighting factor dependent upon the probable errors of the observed structure factors. When reporting the reliability of a refinement this is put on an absolute basis, R_w , where

$$R_w^2 = R_w' / \sum w(hkl) |F_o(hkl)|^2,$$

and is called the weighted reliability factor. More commonly used, but with less basis for use, is the unweighted reliability factor, R .

$$R = \sum \left| |F_o(hkl)| - |F_c(hkl)| \right| / \sum |F_o(hkl)|.$$

The calculated structure factors for space group $P\bar{1}$ are given by

$$F_c(hkl) = \sum_n f_n \cos 2\pi (hx + ky + lz),$$

where f_n is the scattering factor of the n^{th} atom including the temperature factor. The observed

structure factors are related to the x-ray intensity obtained from diffraction from crystal planes by

$$F_o(hkl)^2 = sI(hkl)/L(hkl)P(hkl).$$

The scale factor, s , and the Lorenz and polarization factors, LP , scale the observed intensities to an absolute basis, and correct for polarization of the diffracted beam, respectively. Weighting factors are obtained from the probable errors in F_o , $\sigma_f(hkl)$, where

$$w(hkl) = 1/\sigma_f(hkl)^2.$$

The term, σ_f , was evaluated by the finite difference method of Williams (23),

$$\sigma_f = (LP)^{-\frac{1}{2}}(-I^{\frac{1}{2}} + (I + \sigma_i)^{\frac{1}{2}}).$$

This method resolves the problem of treating observations with zero net intensities differently than other measurements as is necessary when using the infinitesimal difference formula,

$$\sigma_f = \sigma_i \times \frac{1}{2}(s/LPI)^{\frac{1}{2}}.$$

The probable error in the intensity, σ_i , is a function of both statistical errors and relative errors in the total intensity measurement, T , background intensity, B , and the white-radiation streaking correction for non-

characteristic wavelength radiation, S. Thus

$$\sigma_i = (T + B + S + K_t T^2 + K_b B^2 + K_s S^2)^{\frac{1}{2}},$$

where K_t , K_b and K_s are the estimates of the error in intensity, background and streaking, respectively, which were estimated as .022, .022 and .25 respectively.

Intensity measurements were obtained on a General Electric XRD-5 x-ray unit equipped with a single crystal orienter and scintillation counter by using the moving crystal, moving counter method and scanning 3.33° in 100 seconds along the diffraction angle, 2θ . Zirconium filtered Mo radiation, a 3° take-off angle, and a 1.2° diffracted beam aperture were used. Observations were made on all diffraction planes for $\sin\theta/\lambda = 0.5$ or less². Those that visually showed no increase in intensity over background were not recorded and not used in the final refinement³. Of 1400 recorded diffraction

²Because of low scattering power of the small, light atom crystal, peak to background ratios were very poor above $\sin\theta/\lambda = .37$. Lack of high angle observations unfortunately greatly reduced resolution of the atomic positions.

³Several methods of treating unobserved reflections, such as Hamilton's method (24), and that of Williams (23) are commonly used. This author does not feel that the use of unobserved reflections in the final refinement leads to a more accurate structure. High probable error in F_o when near background levels, the appreciable chance that the angles establishing the (footnote continued on next page)

angles, 885 reflections were observed above background levels and subsequently used in the refinement. Background intensities were measured for each reflection by offsetting the equatorial angle, ω , 1.5 degrees. Backgrounds were then plotted against 2θ , χ and ϕ , and the resulting graphs used for a corrected background intensity. The net intensity was obtained simply by

$$I = T - B - S.$$

When making a correction for streaking the common procedure is to measure the streaking from a strong reflection versus an offset background. This was done for several strong reflections, and the data from the $3 \cdot 0 \cdot \bar{1}$ reflection was used to make streak corrections. These corrections did not correlate well with actual peak heights measured from the recorder chart. The basis for making the streak correction was then revised, and the amount of streaking was based on the total intensity minus background for the reflections that showed no visible peak on the recorder chart. The new basis lowered the streak measurements by 40 % and improved

(footnote continued from previous page) diffraction planes were incorrectly set, and the lack of a Gaussian distribution due to setting negative intensity measurements to zero mitigate against unobserved improving a refinement.

correlations with chart observations. Streaking was calculated for other reflections by the method of Benson and Fitzwater⁴. No absorption correction was necessary since the light atom absorption is negligible.

A three-dimensional superposition of Patterson function maps was used to find a set of refinable atomic positions. A Patterson function is a representation of all vectors between atomic locations and is given by

$$\begin{aligned}
 P(u,v,w) &= \iiint_0^1 \rho(x,y,z)\rho(x+u,y+v,z+w)dx dy dz \\
 &= \frac{1}{V} \sum_h \sum_k \sum_{l=-\infty}^{\infty} |F(hkl)|^2 \exp 2\pi i(hu+kv+lw).
 \end{aligned}$$

The superposition technique attempts to reduce the Patterson map such that only the vectors from one given atom to the other atoms in the unit cell remain.

The structure factors used in the Patterson function were modified to produce sharper maxima by the method of Jacobson, et al. (25). Oscillations in the Patterson function which would cause false maxima and minima, or "rippling", are reduced to a minimum by combining the normal Patterson function, $P(u,v,w)$, in the proper

⁴Benson, J. and Fitzwater, D.R. Iowa State University, Ames, Iowa. Relation between White Radiation Streaking and \mathcal{Q} . Private Communication. 1963.

portion with the gradient Patterson function,

$$Q(u,v,w) = \iiint_0^1 \nabla \rho(x,y,z) \nabla \rho(x+u,y+v,z+w) dx dy dz.$$

Combining $P(u,v,w)$ and $Q(u,v,w)$ with the normal sharpening function,

$$\exp(-4\pi^2 \sin^2 \theta / \lambda^2) / \hat{f}_0^2,$$

yields the sharpened structure factors,

$$F(hkl)_{\text{sharp}} = (F(hkl) / \hat{f}_0) ((K + \sin^2 \theta / \lambda^2) \exp(-4\pi^2 \sin^2 \theta / \lambda^2))^{\frac{1}{2}}.$$

In this expression \hat{f}_0 is the unitary scattering factor averaged over all the atoms in the unit cell. Jacobson, et al. (25) have found a value of $K = 1/6$ produces optimum resolution.

The Patterson map of triphenyl aluminum showed no single large peak that could be ascribed to an Al-Al vector, but rather many peaks of similar size. Since the C-Al vectors do not pass through the center of symmetry, there are in all cases two equivalent vectors directly superimposed upon each other. The maximum peak height of the C-Al vectors would then be approximately $13 \times 6 \times 2$, very close to the peak height of 13×13 for the Al-Al single vector. A large peak at $x = .76$, $y = .245$, $z = .755$, was superimposed upon the origin and

the resulting minimum function produced many overlapping peaks which failed to describe the molecule. However, the superposition showed peaks at:

	x	y	z
(A)	-.02	.245	.12
(B)	.85	.332	.95
(C)	.76	.245	.755

These had distances (A)-(B) = 2.03 Å, (B)-(C) = 1.44 Å and angle (A)-(B)-(C) = 120°, which are in good agreement with predicted distances of Al-C of 2.00 Å and C-C of 1.40 Å.

A second superposition of (A) on the origin produced only vectors representing the structure. The positions of these vector peaks were centrosymmetric about the midpoint of the vector between the origin and (A) showing a centric Al₂Ph₆ dimer with each aluminum singly bonded to two phenyls and sharing the other two.

Refinement was carried out by least squares methods using the crystallographic least squares program, FITZLSPAR3⁵. Atomic scattering factors used were

⁵Fitzwater, D. R., Benson, J. and Jackobs, J. J. Iowa State University, Ames, Iowa. FITZLSPAR3 Least Squares Package. Private Communication. 1964.

derived by Hansen, et al. (26). An electron density map confirmed the placement of the atoms. The difference between the electron density maps determined from the observed and calculated structure factors was used to find the approximate hydrogen positions. For 12 or 15 hydrogens the density was appreciably greater than background fluctuations on this difference Fourier, but their positions were difficult to resolve accurately because of their low scattering power. Therefore, hydrogens were inserted at theoretically calculated positions⁶, and given a temperature factor, β , of 4.5. They were not refined because of limitations of the parameter handling capacity of the least squares program.

The temperature factor, β , is proportional to the root mean square amplitude of vibration and is a measure of how diffuse the electron density is about the atomic

⁶The calculated hydrogen positions were 1.00 Å from the refined carbon atom centers, directed radially from the center of the phenyl ring. Although the C-H atomic center distance has been found to be 1.09 Å by infrared studies which are based on the motion of the center of mass, the atom placement in x-ray diffraction is based on the apparent center of electron density which is closer to the carbon than the nucleus because of both an increase in electron density in the bond and the large wagging vibrational motion of the hydrogen. It should be noted that calculated positions are in error in cases where there are close atomic approaches because hydrogen bonds are easily distorted to accommodate packing.

center. In calculating the structure factor the scattering factor, f_n , is modified by

$$\exp(-\beta \sin^2 \theta / \lambda^2).$$

The temperature factors for carbon and aluminum were treated anisotropically, in which cases f_n is modified by

$$\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{23}kl - \beta_{31}lh).$$

Initial parameters, derived from the Patterson map for aluminum and carbon positions input in the structure factor calculation with isotropic temperature factors, gave a reliability factor, $R = .204$. Refinement, including insertion of hydrogens in theoretical positions, and anisotropic temperature factors for all carbons and for aluminum lowered R to 0.088. A weighted reliability factor,

$$\Sigma w(|F_o| - |F_c|) / \Sigma w(|F_o|) = 0.067.$$

An evaluation of $R_w' / m - n$, where m is the number of variables and n the number of parameters, gave 0.84, which indicated the weighting scheme was reasonable. The refined atomic positions and temperature factors are given in Table 1. Observed and calculated structure factors are found in Figure 1.

Table 1. Final positional and thermal parameters and their standard errors (in parenthesis) obtained from the least squares refinement of triphenyl aluminum

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al	.4885 (.0004)	.6250 (.0004)	.5568 (.0005)	.0093 (.0006)	.0080 (.0004)	.0130 (.0008)	.0033 (.0004)	.0036 (.0006)	.0037 (.0005)
C _{1a}	.3554 (.0011)	.6876 (.0010)	.3817 (.0014)	.0092 (.0019)	.0081 (.0016)	.0112 (.0028)	.0038 (.0014)	.0026 (.0019)	.0054 (.0017)
C _{2a}	.2552 (.0013)	.6108 (.0011)	.1894 (.0016)	.0130 (.0022)	.0117 (.0018)	.0184 (.0034)	.0050 (.0017)	.0074 (.0023)	.0057 (.0022)
C _{3a}	.1689 (.0013)	.6641 (.0013)	.0700 (.0016)	.0142 (.0023)	.0116 (.0020)	.0174 (.0031)	.0029 (.0018)	.0045 (.0022)	.0071 (.0021)
C _{4a}	.1755 (.0014)	.7979 (.0014)	.1396 (.0020)	.0132 (.0022)	.0151 (.0021)	.0278 (.0040)	.0070 (.0018)	.0084 (.0025)	.0131 (.0025)
C _{5a}	.2714 (.0014)	.8774 (.0011)	.3300 (.0019)	.0166 (.0025)	.0098 (.0018)	.0284 (.0043)	.0051 (.0018)	.0085 (.0028)	.0083 (.0024)
C _{6a}	.3580 (.0011)	.8241 (.0011)	.4486 (.0015)	.0096 (.0020)	.0106 (.0017)	.0198 (.0030)	.0046 (.0015)	.0066 (.0020)	.0085 (.0019)
C _{1b}	.6574 (.0011)	.5681 (.0010)	.4635 (.0014)	.0086 (.0019)	.0092 (.0016)	.0163 (.0028)	.0018 (.0014)	.0057 (.0020)	.0047 (.0017)
C _{2b}	.8186 (.0012)	.6094 (.0010)	.5948 (.0014)	.0095 (.0021)	.0106 (.0016)	.0175 (.0028)	.0038 (.0015)	.0054 (.0021)	.0072 (.0018)
C _{3b}	.9514 (.0012)	.6623 (.0012)	.5622 (.0018)	.0062 (.0021)	.0131 (.0019)	.0242 (.0035)	.0004 (.0015)	.0048 (.0022)	.0021 (.0021)

Table 1 (Continued)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C _{4b}	.9226 (.0015)	.6731 (.0012)	.3938 (.0020)	.0137 (.0027)	.0172 (.0023)	.0298 (.0040)	.0024 (.0019)	.0136 (.0029)	.0093 (.0026)
C _{5b}	.7682 (.0015)	.6376 (.0011)	.2618 (.0017)	.0169 (.0026)	.0120 (.0018)	.0236 (.0034)	.0042 (.0018)	.0139 (.0026)	.0086 (.0020)
C _{6b}	.6385 (.0013)	.5831 (.0010)	.2954 (.0014)	.0143 (.0022)	.0088 (.0016)	.0134 (.0028)	.0032 (.0015)	.0066 (.0021)	.0042 (.0017)
C _{1c}	.5961 (.0012)	.7538 (.0010)	.8185 (.0013)	.0120 (.0021)	.0081 (.0015)	.0134 (.0027)	.0032 (.0015)	.0070 (.0021)	.0034 (.0017)
C _{2c}	.7588 (.0013)	.8416 (.0011)	.9113 (.0015)	.0144 (.0023)	.0083 (.0016)	.0129 (.0030)	.0016 (.0016)	.0070 (.0021)	.0030 (.0019)
C _{3c}	.8275 (.0014)	.9363 (.0012)	.0900 (.0018)	.0198 (.0027)	.0121 (.0019)	.0174 (.0034)	.0023 (.0018)	.0115 (.0026)	-.0002 (.0021)
C _{4c}	.7375 (.0016)	.9536 (.0012)	.1887 (.0015)	.0201 (.0027)	.0127 (.0019)	.0112 (.0029)	.0035 (.0019)	.0043 (.0025)	-.0013 (.0019)
C _{5c}	.5754 (.0016)	.8661 (.0013)	.1015 (.0018)	.0228 (.0032)	.0121 (.0019)	.0219 (.0037)	.0028 (.0021)	.0123 (.0030)	-.0018 (.0022)
C _{6c}	.5088 (.0013)	.7698 (.0012)	.9233 (.0016)	.0112 (.0022)	.0133 (.0019)	.0176 (.0032)	.0024 (.0016)	.0061 (.0023)	-.0007 (.0021)

H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL
1	0	0	40.4	-38.3	5	0	3	5.3	5.7	3	1	-2	43.2	44.1	7	3	-4	17.8	17.6
2	0	0	23.6	-22.8	6	0	3	7.6	-8.7	4	1	-2	29.1	-28.4	0	4	-4	12.5	-13.1
3	0	0	20.6	-20.5	0	1	3	8.8	-7.7	6	1	-2	10.4	-11.5	2	4	-4	11.1	12.3
4	0	0	12.4	13.9	1	1	3	9.7	9.7	0	2	-2	2.9	3.1	0	5	-4	21.5	20.9
4	0	0	13.0	11.3	3	1	3	11.8	11.8	1	2	-2	24.0	-24.2	1	5	-4	23.5	-23.8
6	0	0	15.3	-17.3	4	1	3	14.1	-13.4	2	2	-2	33.3	-32.7	2	5	-4	12.4	12.0
8	0	0	2.5	7.3	0	2	3	21.2	21.0	3	2	-2	7.1	-8.1	5	5	-4	7.3	-8.9
8	0	1	31.2	-29.6	2	2	3	12.3	13.2	4	2	-2	45.5	46.8	6	5	-4	6.2	2.8
1	1	1	3.6	0.7	3	2	3	14.9	-14.9	5	2	-2	10.5	-10.8	0	6	-4	13.4	-13.1
2	1	1	20.2	-20.5	4	2	3	5.6	10.2	6	2	-2	13.3	11.9	1	6	-4	15.6	14.9
3	1	1	8.8	-6.7	0	3	3	10.3	-10.2	8	2	-2	5.9	-1.5	2	6	-4	12.1	-12.0
6	1	1	14.3	-16.7	4	3	3	10.1	-8.7	0	3	-2	33.7	-33.1	5	6	-4	6.5	1.1
7	1	1	13.6	15.1	5	3	3	6.2	5.9	2	3	-2	6.0	6.4	0	7	-4	14.1	14.7
0	2	0	29.1	-28.2	0	4	3	9.0	7.3	3	3	-2	15.3	15.0	2	7	-4	8.2	7.2
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2	1	3	7.4	6.6	3	0	4	7.6	9.8	7	4	-2	6.9	3.8	3	0	-5	9.1	8.3
3	1	3	6.0	-7.1	5	0	4	10.7	-7.1	0	5	-2	9.7	11.1	4	0	-5	6.9	8.1
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2	5	0	12.0	12.1	1	3	4	7.5	-6.5	4	6	-2	14.8	-13.8	2	2	-5	9.2	-9.6
3	5	0	13.7	-11.8	2	3	4	11.2	12.5	5	6	-2	10.0	10.0	5	2	-5	7.0	8.6
4	5	0	8.9	8.9	3	3	4	13.7	-14.1	6	6	-2	11.8	-11.2	7	2	-5	11.9	12.5
1	1	6	6.8	5.4	1	4	4	8.5	1.8	4	7	-2	5.7	2.6	0	3	-5	21.4	21.6
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0	7	0	5.0	-6.7	0	5	4	6.5	-3.0	1	9	-2	14.8	12.3	4	3	-5	13.2	12.0
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0	8	0	5.1	5.8	0	1	5	13.1	-14.3						0	4	-5	6.4	5.1
1	8	0	14.2	-13.9	2	1	5	8.2	-7.4	1	0	-3	19.5	38.8	1	4	-5	12.9	-11.9
2	8	0	7.6	7.5	3	1	5	9.1	8.2	3	0	-3	10.5	-11.2	3	4	-5	18.2	18.0
4	8	0	13.2	12.3	3	1	5	14.8	15.1	4	0	-3	7.1	-7.6	4	4	-5	16.3	-17.6
					2	1	5	7.5	4.3	6	0	-3	13.1	13.4	6	4	-5	10.6	-11.4
					0	5	5	5.8	5.7	9	0	-3	9.3	7.6	0	5	-5	8.0	-8.5
1	0	1	3.3	-1.0						0	1	-3	5.6	7.2	2	5	-5	9.7	-9.3
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6	1	1	7.7	10.0	7	0	-1	17.9	18.2	0	2	-3	10.0	10.8	4	7	-5	8.0	6.1
0	2	1	6.3	-6.3	0	1	-1	24.7	23.5	1	2	-3	13.6	-13.1	5	7	-5	15.3	15.7
1	2	1	7.6	-6.7	1	1	-1	27.0	-26.2	2	2	-3	16.2	-17.1	2	9	-5	5.6	1.0
6	2	1	8.0	-2.8	2	1	-1	74.1	73.9	4	2	-3	26.4	27.3	3	9	-5	5.2	0.4
1	3	1	9.6	8.6	3	1	-1	16.2	-16.6	5	2	-3	19.8	-18.3	0	10	-5		
2	3	1	26.4	-27.1	4	1	-1	18.7	20.4	6	2	-3	24.9	23.7					
3	3	1	9.4	10.2	5	1	-1	11.7	-11.6	0	3	-3	5.8	3.5	0	0	-6	9.9	-12.1
4	3	1	4.9	-4.9	6	1	-1	16.4	16.8	1	3	-3	3.6	-0.5	2	0	-6	16.0	-15.7
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0	4	1	29.2	29.2	1	2	-1	59.2	-57.8	3	3	-3	4.9	-6.4	4	0	-6	11.6	-11.2
1	4	1	10.3	-11.5	2	2	-1	7.4	-8.9	4	3	-3	4.6	2.9	6	0	-6	9.7	-8.7
2	4	1	19.8	20.4	3	2	-1	19.7	19.8	5	3	-3	15.7	-14.1	7	0	-6	11.4	11.8
3	4	1	19.5	-18.3	5	2	-1	5.8	8.1	1	4	-3	6.5	6.5	2	1	-6	10.4	9.3
4	4	1	15.3	15.8	6	2	-1	22.9	-22.0	0	5	-3	9.3	9.0	5	1	-6	17.5	17.1
0	5	1	9.1	-9.5	0	3	-1	64.4	-64.1	1	4	-3	7.3	7.7	0	2	-6	14.8	15.2
2	5	1	23.0	-22.3	1	3	-1	8.7	6.7	4	4	-3	27.8	-28.1	1	2	-6	9.2	-4.2
3	5	1	6.2	5.1	2	3	-1	24.7	-25.6	1	5	-3	16.1	16.5	2	2	-6	7.7	10.1
0	6	1	5.0	-5.0	3	3	-1	14.4	13.5	3	5	-3	7.0	9.2	4	2	-6	17.9	9.4
2	6	1	11.3	-12.0	4	3	-1	6.4	-7.4	4	5	-3	21.1	-21.6	5	2	-6	17.5	-17.5
1	7	1	12.1	-10.6	5	3	-1	8.9	-8.7	0	6	-3	23.9	23.9	6	3	-6	10.2	-10.4
2	7	1	11.6	9.7	6	3	-1	14.2	13.5	0	6	-3	12.9	-12.7	1	3	-6	15.8	15.6
1	8	1	10.3	-7.7	7	3	-1	8.4	7.2	1	6	-3	10.7	9.9	2	3	-6	11.8	-10.6
					0	4	-1	18.7	19.5	2	6	-3	8.9	-9.3	3	3	-6	12.2	12.1
1	0	2	5.9	-7.8	1	4	-1	31.8	-31.1	3	6	-3	9.7	8.9	4	3	-6	22.6	-22.0
2	0	2	19.7	19.0	2	4	-1	18.6	19.0	4	6	-3	9.2	-7.5	1	4	-6	7.0	-7.5
3	0	2	11.6	-13.3	3	4	-1	13.0	12.3	5	6	-3	7.2	6.2	2	4	-6	4.1	4.7
4	0	2	8.5	7.2	4	4	-1	2.7	2.2	6	6	-3	8.9	-11.2	3	4	-6	8.4	-7.3
5	0	2	12.6	-11.6	6	4	-1	14.2	13.0	0	7	-3	6.1	5.2	0	5	-6	7.3	7.3
6	0	2	16.2	17.1	0	5	-1	3.8	-2.8	1	7	-3	5.9	-2.5	4	5	-6	7.7	-7.2
0	1	2	10.6	-9.1	1	5	-1	12.2	12.8	2	7	-3	6.1	6.4	0				

The Structure

Triphenyl aluminum crystallizes as a dimer with two of the phenyl groups bonded equally to both aluminums in the dimer forming a bridge between the monomer units as shown in Figure 3. The dimer skeleton, Figure 2, has bridging carbons forming an acute angle

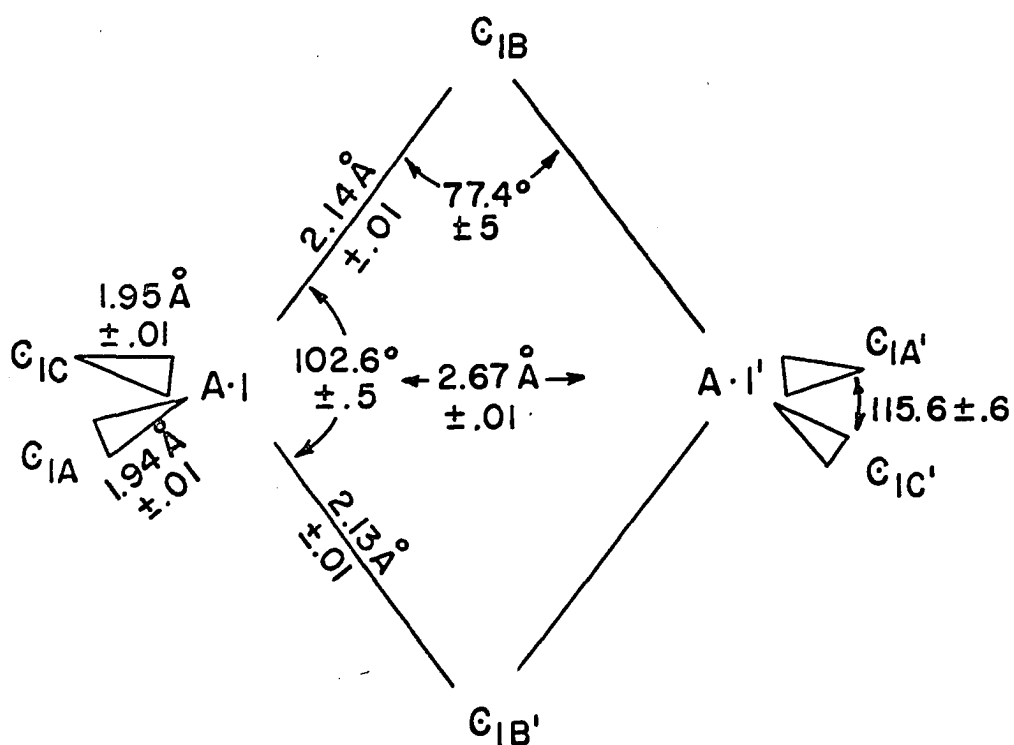


Figure 2. The atomic skeleton arrangement about the aluminum atoms in triphenyl aluminum

between metals similar to those found in trimethyl aluminum (6), and in polymeric dimethyl beryllium (27) and dimethyl magnesium (28). A complete listing of

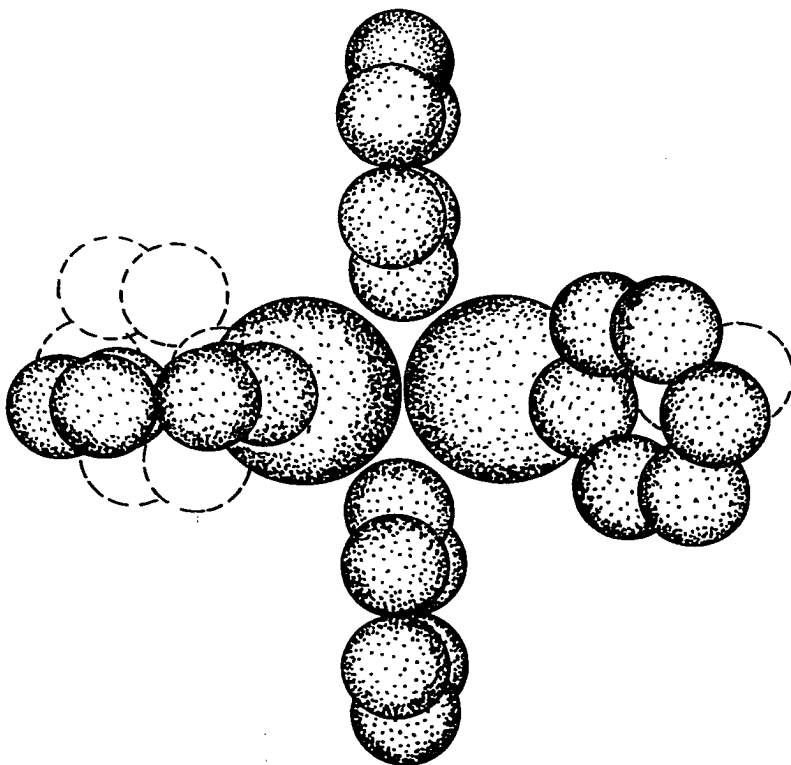


Figure 3. The triphenyl aluminum dimer

angles and bond distances in the bridged skeleton are found in Table 2, and are compared to the similar measurements for trimethyl aluminum. The carbon-carbon distances in the phenyl groups are found in Table 3. These were calculated using a modified ORFFE function and error computer program (29). The packing of dimers in the unit cell is shown in Figure 4. A description of the important structural features follows.

The two aluminum to carbon distances in the bridge average 2.135 \AA , and the aluminum-carbon non-bridging distances average 1.945 \AA . These are considerably shorter than the aluminum to alkyl-carbon bridge distance of 2.15 \AA in trimethyl aluminum (8) and the alkyl single bond distances of 1.98 \AA in trimethyl aluminum, 2.00 \AA in $\text{KF} \cdot 2\text{Al}(\text{C}_2\text{H}_5)_3$ (30), and 2.02 \AA in $\text{LiAl}(\text{C}_2\text{H}_5)_4$ (31). The $\text{Al}(\text{C}_2\text{H}_5)_4^-$ ionic character in the last case would create a slightly longer distance than that corresponding to a normal single bond.

The bond angles about the aluminum are such that the angle between the non-bridging carbons, $\text{C}_{1a}-\text{Al}-\text{C}_{1c}$, is 115.5° , greater than a tetrahedral angle, while the angle between the bridging carbons, $\text{C}_{1b}-\text{Al}-\text{C}_{1b}'$, is 102.6° , less than the tetrahedral angle. See Figure 4 for the method of labeling atoms. The angle between bridging carbons, as will be clarified later, should

Table 2. Interatomic distances and angles of the central bridging skeleton of triphenyl aluminum^a

Atoms	Triphenyl aluminum	Trimethyl Aluminum
	Distances (Å)	
Al-C _{1a} (terminal)	1.94 ± .01	1.98 ± .01
Al-C _{1c} (terminal)	1.95 .01	1.98 .01
Al-C _{1b} (bridging)	2.13 .01	2.15 .01
Al-C _{1b'} (bridging)	2.14 .01	2.15 .01
Al-Al	2.67 .01	2.604 .005
	Angles (°)	
Al-C _{1b} -Al'	77.4 ± .5	74.6 ± .3
C _{1a} -Al-C _{1c}	115.5 .6	122.8 .5
	Angles between normals (°)	
C _{1b} -Al-C _{1b'} and		
C _{1a} -Al-C _{1c}	91.4 .6	90.0 .5
Al-C _{1b} -Al and		
Phenyl ring "b"	84.7 .8	

^aThe interatomic distances and angles are compared with similar measurements in the aliphatic carbon bridge of trimethyl aluminum (8).

Table 3. Interatomic distances and angles within the phenyl rings, including standard errors

Atom	Distance	Error	Atom	Angle	Error
C _{1a} -C _{2a}	1.41	± .02 Å	C _{1a} -C _{2a} -C _{3a}	123.8	± 1.2°
C _{2a} -C _{3a}	1.38	.02	C _{2a} -C _{3a} -C _{4a}	119.4	1.2
C _{3a} -C _{4a}	1.37	.02	C _{3a} -C _{4a} -C _{5a}	120.3	1.2
C _{4a} -C _{5a}	1.39	.02	C _{4a} -C _{5a} -C _{6a}	119.3	1.2
C _{5a} -C _{6a}	1.37	.02	C _{5a} -C _{6a} -C _{1a}	121.3	1.2
C _{6a} -C _{1a}	1.41	.02	C _{6a} -C _{1a} -C _{2a}	114.9	1.1
C _{1b} -C _{2b}	1.40	.02	C _{1b} -C _{2b} -C _{3b}	123.0	1.1
C _{2b} -C _{3b}	1.40	.02	C _{2b} -C _{3b} -C _{4b}	118.8	1.1
C _{3b} -C _{4b}	1.37	.02	C _{3b} -C _{4b} -C _{5b}	120.9	1.2
C _{4b} -C _{5b}	1.36	.02	C _{4b} -C _{5b} -C _{6b}	119.3	1.2
C _{5b} -C _{6b}	1.39	.02	C _{5b} -C _{6b} -C _{1b}	123.2	1.0
C _{6b} -C _{1b}	1.40	.02	C _{6b} -C _{1b} -C _{2b}	114.7	1.1
C _{1c} -C _{2c}	1.40	.02	C _{1c} -C _{2c} -C _{3c}	123.0	1.2
C _{2c} -C _{3c}	1.36	.02	C _{2c} -C _{3c} -C _{4c}	119.5	1.1
C _{3c} -C _{4c}	1.38	.02	C _{3c} -C _{4c} -C _{5c}	120.2	1.1
C _{4c} -C _{5c}	1.39	.02	C _{4c} -C _{5c} -C _{6c}	119.6	1.1
C _{5c} -C _{6c}	1.36	.02	C _{5c} -C _{6c} -C _{1c}	122.8	1.2
C _{6c} -C _{1c}	1.39	.02	C _{6c} -C _{1c} -C _{6c}	115.0	1.1

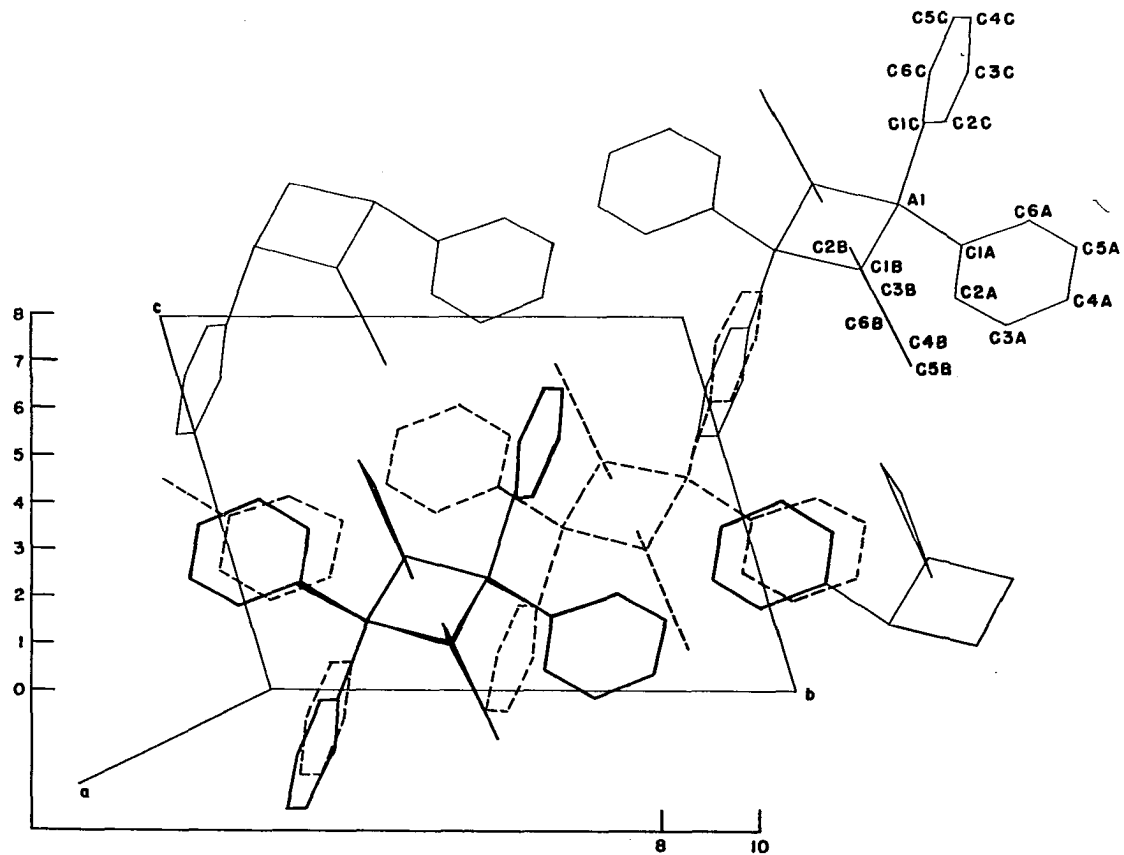


Figure 4. Molecular packing in triphenyl aluminum;
 projection on the yz plane

not be confused with the orbital direction of the bridged bond. The acute Al-C_b-Al' bridging angle of 77.4° is somewhat larger than the 74.6° found in the alkyl aluminum. The larger angle allows a longer Al-Al distance, 2.67 Å, than the 2.604 Å found in trimethyl aluminum.

The bridging phenyl rings lie very nearly perpendicular to the plane formed by the aluminums and two C_{1b} carbons; the angle between ring and plane normals being 84.7°. The C₁ carbon on each of the phenyls is drawn toward the dimer center, thus distorting the otherwise equiangular (120°) phenyl ring. The C₂-C₁-C₆ angle in each phenyl ring is ~ 115°, which is 5° more acute than found for other phenyl angles. In conjunction with this, the C₁-C₂ and C₁-C₆ distances are increased to 1.40 Å as compared to a 1.38 Å average for all phenyl distances in the molecule.

A set of orthogonal coordinates for the molecule, using the transformation matrix,

$$\begin{pmatrix} -.22826 & .93917 & .25667 \\ .92505 & .29142 & -.24363 \\ .30361 & -.18182 & .93529 \end{pmatrix},$$

which places the Al-Al vector along the x axis and the C_{1b}-C_{1b'} vector along the y axis, is included as Table 4 in order to show, numerically, the extent of deviation from the highly symmetrical, D_{2h} symmetry, model.

Table 4. Orthogonalized coordinates for the triphenyl aluminum dimer^a

Atom	x ^b	y	z	Atom	x	y	z
Al	1.33	0.00	0.00	C1a	2.33	0.05	-1.65
C1b	0.01	1.66	0.04	C2a	1.81	0.01	-2.95
C2b	-0.11	2.39	1.22	C3a	2.58	0.12	-4.09
C3b	-0.15	3.79	1.25	C4a	3.94	0.22	-3.98
C4b	-0.07	4.48	0.08	C5a	4.50	0.24	-2.71
C5b	0.08	3.82	-1.10	C6a	3.74	0.15	-1.58
C6b	0.09	2.44	-1.22	C1c	2.40	-0.11	1.63
				C2c	2.70	0.98	2.45
				C3c	3.51	0.89	3.52
				C4c	4.13	-0.30	3.85
				C5c	3.84	-1.41	3.07
				C6c	3.00	-1.31	2.00

^aThe origin is the center of symmetry of the dimer. The x axis lies along the Al-Al vector; the y axis approximately along the C_{1b}-C_{1b'} vector.

^bAll distances are in Angstroms.

Intermolecular distances between dimers correspond to normal van der Waals interaction distances of 2.40 Å for H-H contacts and 2.95 Å for H-C contacts, or longer in most cases. Calculated hydrogen positions show several shorter intramolecular distances; these are H_{2a}-H_{2b'}, 2.15 Å; H_{2a}-H_{6b}, 2.37 Å; H_{2c}-C_{2b}, 2.65 Å;

$H_{6c}-C_{6b}$, 2.93 Å. The deviation from a theoretical model which exhibits D_{2h} symmetry is in such a direction as to shorten the H-H distances and lengthen the H-C distances above. Since the calculated positions for the hydrogen atoms did not take into account these non-bonded interactions, strain relief could result, changing these positions, and making the actual intramolecular distances longer.

Bonding Properties

Triphenyl aluminum is an electron deficient compound. Electron deficiency occurs when an atom with more low energy orbitals than valence electrons, typically a metal, combines with atoms containing no unused electron pairs (16) giving rise to an apparent excess of atomic orbitals over electrons available to fill them. Bonds are formed to create the maximum possible delocalization of electrons such that all the available orbitals of the metallic atom are used (32).

The Al-C bonds in triphenyl aluminum are of two types, a "classical" bond with a full two electron complement between two atom centers, and a non-classical bond between the bridging carbon and aluminum atoms. This latter bond contributes about half as much electron density between each carbon and aluminum as does a

classical bond, as is seen by the increase in bond length of 0.19 Å for the Al-C_b bond distance as compared with the classical Al-C_a bond distance.

An empirical equation derived by Pauling (33) for partial bonds predicts a 0.21 Å extension for a bond order of 1/2. If two orbitals were available to provide for resonance shortening, the distance corresponding to a bond number of 1/2 would be expected to be 0.18 Å longer than a single bond.

This approximation of single and half bonds is more closely followed by the similar bridging skeleton in trimethyl aluminum, Me₃Al, where there is little contribution from the electrons in the three C-H bonds. In Me₃Al the difference between the two bond types is 0.17 Å. This difference follows more closely the predicted distances if there were two orbitals participating, and indeed, Gillespie (15) has calculated that the promotion energy necessary to utilize high energy 3d orbitals is reasonable. His calculations show that a five orbital carbon atom could be obtained, and that the resulting sp³d hybrid orbitals would have an angle of 70° between them. Prior infrared and structural studies show normal hydrogen-carbon interactions (5). The alternative of placing the electron, one each in the two bonding sp³d orbitals would produce a paramagnetic compound, which

has not been observed.

In triphenyl aluminum the bond order of both the two-centered and bridged bonds would be expected to be greater than the corresponding bonds in Me_3Al . The easily delocalized π -system of the phenyls would contribute some electron density to the Al-C bonds. That this occurs may be observed in the shorter Al-C distances in triphenyl aluminum than in trimethyl aluminum, 1.945 vs. 1.98 Å for the two-centered bond and 2.135 vs 2.15 Å for the bridged bond. The greater shortening in the first case is most likely due to a more favorable bond direction for π -overlap.

The electron donating effect of the π -electrons of the phenyl groups can be noted by the longer $\text{C}_1\text{-C}_2$ and $\text{C}_1\text{-C}_6$ distances (1.40 Å average) than other C-C distances in the rings (1.38 Å average). From the short C-C distances it appears that the contribution of electron density from other than the $\text{C}_1\text{-C}_2$ and $\text{C}_1\text{-C}_6$ bonds is small.

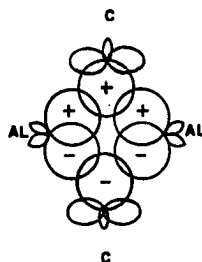
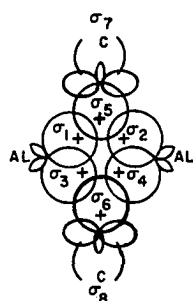
Two major approaches have been postulated to explain the formation of an electron deficient bridged structure. The first, which may be called a "methylated double bond" consists of a direct Al-Al double bond with the free phenyl orbitals overlapping the π orbital of the double bond. The long Al-Al distance, 2.67 Å, versus

the sum of the single bond covalent radii of Al of 2.54 Å, makes use of this concept alone unprofitable. The second approach, by making use of the molecular orbital concept, incorporates both the methylated double bond and a bond directed between the aluminum atoms and the bridging carbon. These bonding orbitals would, then, be formed by the combination of two aluminum and one carbon atomic orbitals forming a bonding, three-center, molecular orbital.

Using the known spacial arrangement of the atoms, the molecular orbitals could be made up by expressing these orbitals in terms of linear combinations of the atomic orbitals, with appropriate coefficients to minimize the energy. From the position of the non-bridging phenyl groups in particular, it would be expected that a choice of coefficients such that hybrids between sp^2 and sp^3 on the aluminum would be most appropriate. Using the sp^2 hybrid, the equivalent of the methylated double bond could be explained in terms of the aluminums each contributing an sp^2 and a p orbital which interact with the two carbon sp^2 orbitals. Two bonding orbitals would be formed, one having the predominate character of a direct Al-Al overlap and the other predominately carbon sp^2 and aluminum p overlap. The two remaining sp^2 orbitals on the aluminum are used for bonding to the non-bridging

phenyls. In the case of sp^3 hybrid orbitals, two of the tetrahedral sp^3 hybrid orbitals would be utilized to bond with non-bridging carbons. For the latter orbitals, symmetry (assuming it is D_{2h}) would allow for the combination of atomic orbitals illustrated in Figure 5. The aluminum sp^3 and carbon sp^2 orbitals form two bonding MO's, a_{1g} and b_{2u} , which are filled by the four available electrons. The bond shortening from the case of an aliphatic bridging carbon occurs because the phenyl p orbitals also form bonding orbitals, b_{1g} and b_{3u} , with the aluminum sp^3 orbitals, delocalizing the phenyl π -electron system, and increasing the electron density in the Al-C bond. If the phenyl group were rotated 90° around the C_1-C_4 axis no π -overlap would occur, and no bond shortening over the alkyl case would be expected.

Care must be taken when speaking of the bridging angle of a three-centered bond. Measurements by x-ray determine the center of electron density of the atom. Only in the case of a two-centered bond would this atom position have to fall along the bonding orbital. The major axis of the three-centered bonding orbital in triphenyl aluminum would have a less acute angle than the Al- C_{1b} -Al angle that was measured, as demonstrated in Figure 6.

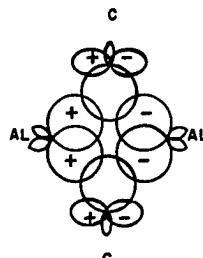
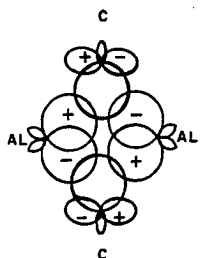


$$\phi_1 = \frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) \quad \phi_2 = \frac{1}{\sqrt{2}}(\sigma_5 + \sigma_6)$$

$$\chi_{\sigma_{1g}}^b = N(\phi_1 + \lambda \phi_2) \quad \chi_{\sigma_{1g}}^a = N(\phi_1 - \lambda \phi_2)$$

$$\phi_5 = \frac{1}{2}(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4) \quad \phi_6 = \frac{1}{\sqrt{2}}(\sigma_5 - \sigma_6)$$

$$\chi_{b_{2u}}^b = N(\phi_5 + \lambda \phi_6) \quad \chi_{b_{2u}}^a = N(\phi_5 - \lambda \phi_6)$$



$$\phi_3 = \frac{1}{2}(\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4) \quad \phi_4 = \frac{1}{\sqrt{2}}(\sigma_7 - \sigma_8)$$

$$\chi_{b_{1g}}^b = N(\phi_3 + \lambda \phi_4) \quad \chi_{b_{1g}}^a = N(\phi_3 - \lambda \phi_4)$$

$$\phi_7 = \frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4) \quad \phi_8 = \frac{1}{\sqrt{2}}(\sigma_7 + \sigma_8)$$

$$\chi_{b_{3u}}^b = N(\phi_7 + \lambda \phi_8) \quad \chi_{b_{3u}}^a = N(\phi_7 - \lambda \phi_8)$$

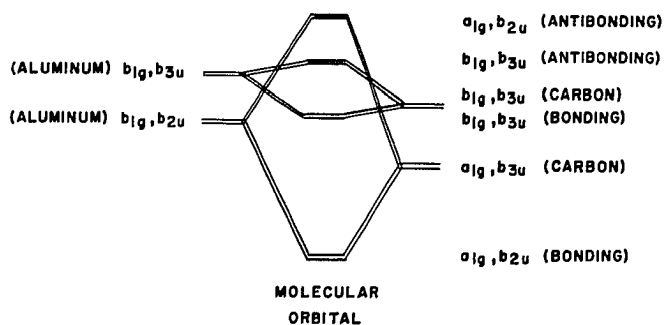
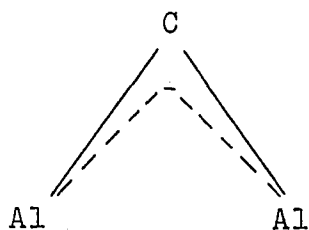


Figure 5. The molecular orbitals contributing to the three-centered bonds in triphenyl aluminum



————— Indicates the direction between atom centers
 ----- Indicates the direction of the bonding orbital

Figure 6. The direction of the three-center orbital

Proper linear combination of the orbitals due to the two extreme aluminum hybrids, sp^3 and sp^2 , approximates the obtained structure. Deviations from the MO predicted symmetry, such as the 5° tilt of the phenyl ring from D_{2h} symmetry, can be explained as an attempt to relieve the strain of the non-bonding H-C interactions. The C_{2v} symmetry about each aluminum, which MO calculations predict, also is violated. The C_{1a} -Al- C_{1c} plane normal is at an angle of 91.6° to the C_{1b} -Al- C_{1b}' plane normal. Any combination of aluminum sp^3 and sp^2 bonding characteristics would leave these plane normals perpendicular. The lack of orthogonality, again, indicated that repulsions between non-bonded phenyls necessitate that deviations from calculated optimum bond angles occur. As the size of the organic portion of the molecule increases steric effects would be expected to play a more major role in determining the exact configuration.

CONCLUSIONS

Structural studies of the group III A organo-metallics have done much to illuminate conditions necessary for maximum stabilization of electron deficient compounds.

In the III A periodic row only aluminum has the optimum bonding radius to combine with organo-substituents to delocalize electrons through dimerization. The short boron-carbon bonding distance would cause high energy H-H interactions between monomers precluding dimerization of organo-borons. All known triorgano-borons are monomeric (34). Organo-gallium and indium dimers are precluded by the M-C_b bonds which would, if the dimer contained the acute angles necessary for forming carbon bridges, cause M-M interactions less than the single bond distances of the metal. Trimethyl gallium is monomeric, yet more stable than Me₃Al (35). Triphenyl gallium is monomeric, also (20). Trimethyl indium forms a tetramer, but is bonded through direct metal-metal bonds rather than carbon bridges (36).

All known hydrocarbon organo-aluminums tend toward dimerization unless precluded by steric interference of bulky groups as in the case of tri-isopropyl aluminum (5) and tri-isobutyl aluminum (37). Some organo-aluminums,

such as $\text{Me}_2\text{AlPMe}_2$ and Me_2AlOMe (38) are trimers, while others, such as Me_2AlF (39) and Me_2AlH (40) are polymers. In Me_2AlH the short Al-H distance would exclude the possibility of dimerization because of the short Al-Al distance created; therefore, the polymer is to be expected. The bonding in organo-aluminum halides is less clear cut. In general, dimers with halogen bridges are predicted. Brockway (41) found Me_2AlCl to be a dimer with chlorine bridges by electron diffraction. Amma's (40) uncompleted x-ray refinement of MeAlCl_2 does not find the expected Cl bridges.

Little is known about compounds which might be expected to be monomeric for electronic reasons. Attempts to prepare $(\text{CF}_3\text{CH}_2\text{CH}_2)_3\text{Al}$ by several methods have ended in failure⁷. Known aluminum aryls with electron withdrawing substituents have not been characterized as to association.

From structural studies the following conclusions may be drawn:

- i. To produce maximum stability in electron deficient compounds association will occur by formation of a multi-centered bond using all of the available

⁷Mellon, E. University of Florida, Gainesville, Florida. Private Communication. 1966.

orbitals to provide maximum delocalization of electrons.

ii. Although maximum overlap occurs in a model with high symmetry, disruption of this symmetry does not preclude association.

iii. This association can be prevented by steric factors.

iv. A bond with greater electron density can be produced by using bridging groups which can donate electrons.

v. The extent of disruption of association by lowering electron density in a bridged bond by use of electron withdrawing groups is unknown.

PART II. THE STRUCTURE OF LEAD(II) BROMIDE

INTRODUCTION

In the previous section on triphenyl aluminum a well defined example of an electron deficient compound was discussed. That the object of this study, lead(II) bromide, could also be another example of an electron deficient compound is not so obvious.

The bonding in lead bromide may be due to only ionic interactions based on a spherical Pb^{++} ion with a $6s^2$ core, or may be due to partial covalent bonding (18) in which case if we assume two electrons remain paired, in the $6s$ core, there remains three valence orbitals (the $6p$ orbitals) though only two valence electrons--the conditions which give rise to possible electron deficiency.

The crystal structure of lead bromide was first investigated by Nieuwenkamp and Bijvoet (42). The structure was found to be isomorphous with lead chloride (43). Both structures were assigned to the centric space group, $Pnma$. Halide atoms with two different environments are found. One is part of a continuous chain of leads and halide and has two short Pb-Br bonds while the other contains only one short Pb-Br bond. Each lead, therefore, has three-fold primary coordination resulting from short bonds to two chain halides and one non-chain halide. This three-fold primary coordination

would be expected if the bonds had partial covalent character.

Assuming this covalent character a halide and two leads in the chain might be expected to use but one bonding orbital and form a bridged bond similar to that discussed earlier in triphenyl aluminum, or more exactly, that of the halide bridge in compounds of the type $(\text{Me}_2\text{AlCl})_2$ (41). However it must also be noted that the halide has unshared electron pairs which could participate in a second bond particularly if these bonds have significant ionic character, and the three-centered bond does not of necessity exist.

A halide with only one covalent bond would be expected to contribute more electron density to a lead-halide bond than one bridging two lead atoms and, therefore, be shorter in length. Yet neither of the previous structural refinements of these halides confirmed the prediction. Nieuwenkamp and Bijvoet found both types of bonds in PbBr_2 to be 3.0 \AA . Braekken found the single bond to be longer, 2.86 \AA , than the chain bond, 2.81 \AA , in the lead chloride.

In studies on lead chloride, done concurrently with this refinement of lead bromide, Sahl and Zemann (44) and Sass, Brachett, and Brachett (45) found the lead-chloride chain bond to be longer than the non-chain bond.

The measurements of Sahl and Zemann indicated distances of 2.90 and 2.86 Å respectively, while those of Sass, et al. found bond distances of $2.91 \pm .02$ and $2.80 \pm .02$ Å. Tin(II) chloride has also been found to have three short bonds and a Sn-Cl chain isomorphous to PbBr_2 (46, 47). The non-chain bond was again the shortest.

Because of the somewhat conflicting evidence, particularly in the case of PbBr_2 , we decided to reinvestigate this salt to obtain more accurate bond distances.

Preliminary Results

The previously reported diffraction pattern from lead bromide was confirmed to have orthorhombic $2/m \ 2/m \ 2/m$ symmetry with extinction conditions $hk0$, $h = 2n$ and $Ok\ell$, $k + \ell = 2n$. Further, the alternate layers in k were systematically similar in intensity, a result which indicated all atoms lie on or near a mirror in y . Lattice constants were measured, using a back reflection Weissenberg camera and Cu radiation, to be

$$\begin{aligned} a &= 8.06 \pm 0.01 \text{ \AA} \\ b &= 4.732 \pm 0.006 \text{ \AA} \\ c &= 9.55 \pm 0.01 \text{ \AA} \end{aligned}$$

These compare favorably with improved lattice constants obtained by Calingaert (48) from x-ray powder studies.

These were

$$\begin{aligned} a &= 8.0461 \text{ \AA} \\ b &= 4.7249 \text{ \AA} \\ c &= 9.5255 \text{ \AA}. \end{aligned}$$

From the measured density of 6.66 g/cc (49), the number of molecules to the unit cell is calculated to be four, giving a calculated density of 6.64 g/cc.

All earlier work on the lead dihalides have assigned their atomic arrangements to the centric space group, Pnma. This requires all atoms to be in four-fold special positions, and the aforementioned similarity of alternate layers in b requires that the type of special position be the mirror plane at $y = 1/4$. The four-fold set of special positions at $y = 1/4$ in Pnma is equivalent to the four-fold general set of positions of the acentric space group Pn2₁a (IUC nomenclature Pna2₁) for $y = 1/4$. Table 5 shows the equivalent positions possible in Pnma and Pn2₁a. An acentric structure closely approximating a centric structure would give a pattern of diffraction similar to the centric structure. Extensive data are necessary to determine whether the actual structure is centric, or only approximates a centric molecule.

Table 5. Possible equivalent positions in lead bromide

Space group	Pnma	Pn2 ₁ a
Number of positions	4	4
Point symmetry	m	1
Equivalent positions	x 1/4 z 1/2-x 3/4 1/2+z \bar{x} 3/4 \bar{z} 1/2+x 1/4 1/2-z	x y z 1/2-x 1/2+y 1/2+z \bar{x} 1/2+y \bar{z} 1/2+x y 1/2-z

Plate-like crystals of lead bromide were grown by sublimation. Crystals were also grown from water; the diffraction pattern showing them to be identical to the sublimed PbBr_2 , but their needle shape made them less suitable for diffraction studies. Before accumulating x-ray intensity data a crystal was cut into a rectangular prism .06 x .06 x .02 mm. on an edge to reduce the effect of absorption. For lead bromide, which has as absorption coefficient, μ , equal to 661 cm.^{-1} the optimum crystal diameter, based on a cylindrical crystal, is $1.5/\mu \text{ cm.}$, or .02 mm. (50):

Solution of the Structure

Intensity data were accumulated on an General Electric XRD-5 x-ray unit equipped with a single crystal

orienter and using Zr filtered Mo radiation. A moving crystal, moving counter technique with a 200 second and 3.33° scan along 2θ was used to measure individual intensities. Intensity measurements were collected for 736 Bragg reflections; all reflections up to $\sin\theta/\lambda = .85$ or $k = 4$, whichever was least. The angle settings for the reflections were calculated using SCO-5 computer program⁸. Individual background radiation corrections for each reflection were made by offsetting ω by 1.5 degrees and rescanning the reflection. The intensity measurements were corrected for absorption using a modified polyhedral absorption correction program written by Busing (51). A summation, using an 8 x 8 x 8 point weighted grid to represent the crystal volume, evaluated the transmission factor,

$$A(\phi, \chi, 2\theta) = 1/V \iiint \exp(-\mu(R_i + R_d)) dx dy dz.$$

R and R_d are the distances travelled by the incident and diffracted beam within the crystal. The detector response time was measured to be 4 microseconds and used to correct for lost counts of the scintillation counter.

⁸Williams, D. E. Ames Laboratory, Atomic Energy Commission, Ames, Iowa. SCO-5 Angle Calculation Program. Private Communication. 1961.

It was found that using 80 % of the maximum count rate, I_{\max} , and a time, t , equal to the duration $I = 1/2 I_{\max}$, a Gaussian type rate curve could be closely approximated for the response time correction. Corrections for non-characteristic radiation streaking, for Lorentz and polarization errors and calculations of standard deviations in the measured structure factors used in weighting the reliability of the structure factor were made using a procedure similar to that described in the preceding section on triphenyl aluminum. Modifications were necessary to account for the absorption by the crystal in the calculation of I and σ_i .

$$I = (T - B - S) / A.$$

$$\sigma_i = (T + B + S + K_t T^2 + K_b B^2 + K_s S^2 + K_a (I/A)^2)^{\frac{1}{2}}.$$

The infinitesimal difference method was used to compute σ_f .

$$\sigma_f = \sigma_i \times \frac{1}{2} (s/LPI)^{\frac{1}{2}}.$$

The transmission factor, A , ranged from a minimum of .02 to a maximum of .36. This high and variable absorption caused the measurement of the crystal dimensions to be the largest source of error in the measured data. Correspondingly, in calculating standard deviations, the

percent error in the absorption correction was estimated as 12 %. The corresponding errors in the reflection intensity and background intensity were estimated as 4 %, and the streak error at 6 %. Hamilton's method (24) was used to treat unobserved reflections. The statistical treatment assumed a centric structure. The minimum intensity necessary to be called observed was taken as $2\sigma_i$.

Preliminary methods normally used to determine whether a crystal structure is centric or acentric fail unless the choice is between a markedly acentric or centric structure. Statistical methods using the distribution of structure factors predict a centric structure when the atomic arrangement has many atoms near or in special positions (22). A Patterson function map showed maxima at $y = 1/2$ and $y = 0$ only, which is consistent with both a centric structure with all atoms at $y = 1/4$ and $y = 3/4$ or an acentric structure with all atoms near $y = 1/4$ and $y = 3/4$.

A preliminary least squares refinement, assuming a centric structure, and including anisotropic temperature factors, was carried out using ORFLS least squares program (52), and produced a structure with $R = .115$ and $R_w = .077$. The factor $(R_w / (m - n))^{1/2}$ was 0.67 indicating errors were estimated higher than actually existed.

In order to be able to correct for the high anomalous dispersion occurring in lead bromide for Mo radiation, FITZLSPAR3 least squares refinement program was used for the final refinement. The atomic scattering factor may be written

$$f_n = (f_0 + \Delta f' + i \Delta f'') \exp(-\beta_{11} h^2 - \beta_{22} k^2 - \beta_{33} l^2 - \beta_{12} hk - \beta_{23} kl - \beta_{31} lh)$$

where $\Delta f'$ and $\Delta f''$ are the real and imaginary corrections to f_0 for the anomalous phase shift. The values for f_0 were taken from Hartree - Fock - Slater wave function calculations of Hansen, et al. (26).

The values of f' and f'' for $\sin\theta/\lambda = 0$ are due to Dauben and Templeton (53) and the corrections for other values of $\sin\theta/\lambda$ are calculated from Berghuis, et al. (54). The imaginary dispersion corrections, $\Delta f''$, was handled by incorporation in the least squares refinement using the method of Ibers and Hamilton (55). The extent of phase shift by anomalous dispersion may be seen from the magnitude of the non-zero values of BCAL in Figure 7, the observed and calculated structure factors corresponding to the centric model. BCAL is the imaginary part of F_c ,

$$F_c = ACAL + i BCAL.$$

In order to make as few assumptions as possible independent centric and acentric least squares refinements were carried out. The calculated structure factor for mirror symmetry in space group Pnma is

$$F_c = 4 \cos 2\pi\left(hx - \frac{h+k+l}{4}\right) \cos 2\pi\left(lz + \frac{h+l}{4}\right).$$

For space group Pn2₁a the structure factor is

$$F_c = 4 \cos 2\pi\left(hx - \frac{h+k+l}{4}\right) \cos 2\pi\left(ky + \frac{k}{4}\right) \cos 2\pi\left(lz + \frac{h+l}{4}\right) \\ + 4i \cos 2\pi\left(hx - \frac{h+k+l}{4}\right) \sin 2\pi\left(ky + \frac{k}{4}\right) \cos 2\pi\left(lz + \frac{h+l}{4}\right).$$

At $y = 1/4$ the two equations are identical.

The refinement utilized 690 structure factors; the remainder were not used because of irregularities in their background intensities. A weighted reliability factor, R_w of .0769 was obtained in the centric refinement, while a reliability factor of .0760 was obtained in the acentric refinement. The values of R were .1023 and .1015, respectively.

The significance of the decrease in R_w from .0769 to .0760 by refining the structure acentrically rather than centrically can statistically be evaluated by means of Hamilton's significance test (56). There is an increase of eight variables in the acentric refinement. For a reliability factor ratio, $R_c/R_{ac} = 1.012$, and 690 pieces

of data the significance test establishes that the structure falls between the 5 and 10 % confidence levels of being acentric. This statistical method, therefore, concludes that the probability is greater than 90 % that the structure has no center of symmetry.

The reliability of the conclusion the structure is acentric is dependent upon the applicability of this statistical method. The method requires errors in data to be random. But the standard deviation of the y parameters (including temperature factors in the y direction) are a factor of 10 greater than in the x and z parameters, primarily caused by the short y axis and the small amount of high angle data in that direction. Since the variables which are different for acentric and centric refinements are all parameters in the y direction, and the reliability of y parameters is less than the reliability of all parameters, the reliability factor is, then, too low when considering only shifts in the y direction. Therefore, it is proper to conclude that the probability that the structure is acentric is less than 90 %, and that the question of which representation is better, the acentric or centric, still contains doubt.

It should be noted that this does little to change the discussion of bonding which follows. The primary change that occurs when going from centric to acentric is

to split the degenerate bond pairs between atoms on the two different layers at $y = 1/4$ and $y = 3/4$. Since in the overall bonding picture interest is centered in the average bond length for a given type of bond, the centric structure will be used predominately in the discussion.

Atomic parameters for both acentric and centric structural refinements are given in Table 6. Bond

Table 6. Atomic parameters with standard errors (in parenthesis) for the centric and acentric refinements of lead(II) bromide

	Pb		BrII		BrI	
	Acentric	Centric	Acentric	Centric	Acentric	Centric
x	.23482 (.00013)	.23478 (.00013)	.35715 (.00027)	.35720 (.00026)	.02022 (.00030)	.01989 (.00028)
y	.25000	.25000	-.25680 (.00308)	-.25000	.23425 (.00267)	.25000
z	.41135 (.00013)	.41133 (.00013)	.57739 (.00026)	.57740 (.00026)	.66323 (.00031)	.66304 (.00030)
β_{11}	.00979 (.00016)	.01023 (.00016)	.00761 (.00028)	.00756 (.00029)	.00791 (.00030)	.00744 (.00030)
β_{22}	.02958 (.00072)	.02955 (.00068)	.01860 (.00136)	.01869 (.00128)	.02267 (.00184)	.02344 (.00137)
β_{33}	.00587 (.00010)	.00597 (.00011)	.00407 (.00021)	.00406 (.00022)	.00477 (.00023)	.00490 (.00023)
β_{12}	.00184 (.00106)		.00228 (.00213)		-.00503 (.00161)	
β_{13}	-.00122 (.00011)	-.00124 (.00012)	.00019 (.00021)	.00007 (.00022)	.00104 (.00023)	.00113 (.00023)
β_{23}	.00171 (.00093)		-.00188 (.00232)		-.00182 (.00157)	

angles and distances, calculated using ORFFE function and error program (29) are given in Tables 7 and 8, respectively. The symmetry and interatomic distances for the centric lead bromide structure are shown in Figure 8.

Table 7. Angles about lead with corresponding standard errors for the acentric and centric refinements of lead(II) bromide

A - Pb - B		S_A^a	T_A^b	S_B	T_B	Acentric		Centric	
						Angle	Err.	Angle	Err.
Br _I	Br _{II}	1	0	1	0	75.3	± .3 ^o	76.4	± .1 ^o
Br _I	Br _{II}	1	0	1	2	77.4	.3		
Br _{II}	Br _{II}	1	0	1	2	103.4	.2	103.4	.2
Br _I	Br _I	1	0	4	3	79.7	.2	78.8	.1
		1	0	4	4	78.0	.2		
Br _I	Br _{II}	4	1	1	0	74.3	.3	75.4	.1
		4	0	1	2	76.6	.3		
Br _{II}	Br _{II}	2	0	1	0	125.0	.5	125.9	.1
		2	0	1	2	126.8	.5		
Br _{II}	Br _{II}	2	0	4	0	68.8	.3	68.9	.1
		2	0	4	4	68.9	.3		
Br _I	Br _I	4	3	4	4	94.8	.2	94.9	.2
Br _I	Br _{II}	1	0	2	0	131.2	.1	131.1	.1
Br _I	Br _{II}	1	0	4	0	123.8	.1	123.9	.1

^aIn generating atoms A and B the symmetry transformation, $S = 1, 2, 3, 4$ represents x, y, z ; $1/2 - x, 1/2 + y, z - 1/2$; $1/2 + x, 1/2 - y, 3/2 - z$; $1 - x, 1/2 + y, 1 - z$, respectively.

^bIn generating atoms A and B the unit cell translation, $T = 0, 1, 2, 3, 4$ represents $0, 0, 0$; $0, -1, 0$; $0, 1, 0$; $-1, 0, 0$; $-1, -1, 0$, respectively.

Table 8. Interatomic distances with corresponding standard errors for the acentric and centric refinements of lead(II) bromide

Atoms	S ^a	T ^b	Acentric		Centric	
			Dist.	Error	Dist.	Error
Pb-Br _I	1	0	2.964	± .005	2.965	± .005
Pb-Br _{II}	1	0	3.040	.015	3.015	.004
Pb-Br _{II}	1	1	2.989	.015		
Pb-Br _{II}	2	0	3.276	.006	3.274	.005
Pb-Br _{II}	4	0	3.291	.005	3.291	.005
Pb-Br _I	4	3	3.160	.013	3.211	.005
Pb-Br _I	4	4	3.269	.013		
Pb-Br _I	2	0	3.843	.011	3.891	.005
Pb-Br _I	2	1	3.939	.011		
Br _{II} -Br _I	1	0	3.667	.017	3.696	.005
Br _{II} -Br _I	1	1	3.721	.017		
Br _{II} -Br _{II}	4	0	3.618	.006	3.619	.006
Br _{II} -Br _{II}	4	1	3.618	.006		
Br _{II} -Br _I	3	0	3.722	.017	3.669	.007
Br _{II} -Br _I	3	1	3.616	.017		
Br _{II} -Br _I	4	4	3.813	.006	3.808	.005
Br _I -Br _I	4	0	3.928	.007	3.924	.007
Br _I -Br _I	4	1	3.928	.007		
Br _{II} -Br _I	2	1	4.083	.006		

^aIn generating the second atom listed S = 1,2,3,4 represents the symmetry transformations, x,y,z; 1/2 - x, 1/2 + y, z - 1/2; 1/2 + x, 1/2 - y, 3/2 - z; 1 - x, 1/2 + y, 1 - z, respectively. The first atom is at x,y,z.

^bIn generating the second atom listed T = 0,1,2,3,4 represents the unit cell translations, 0,0,0; 0,-1,0; 0,1,0; -1,0,0; -1,-1,0, respectively.

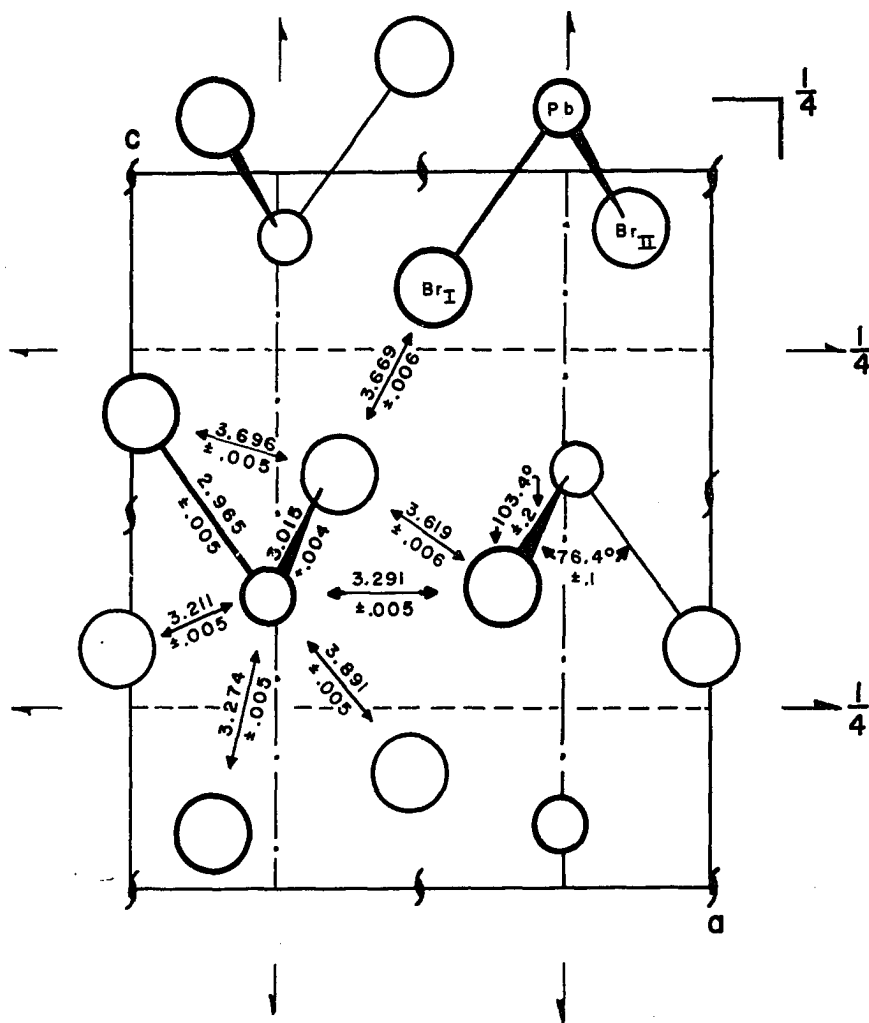


Figure 8. Molecular packing and symmetry elements for lead(II) bromide in centric space group Pnma (Darker atoms are at $1/4$ in y , lighter atoms at $3/4$ in y .)

Structural Properties

The lead atoms have three-fold primary coordination, shown in Figure 9, at around 3.0 \AA and four more short bonds from 3.16 to 3.30 \AA . Two more bromines lie at approximately 3.89 \AA . The bonds to the three primary bromines are shorter than the sum of the ionic radii of 3.17 \AA and must have some covalent character. The four secondary bonds are predominantly ionic in character. The bromines at 3.89 \AA are $.7 \text{ \AA}$ longer than the energetically minimum ionic separation and have little bonding character. The coordination around the lead might be described as a trigonal prism of bromine atoms with the other three bromines directed outward at the half-heights of the prism faces.

The three-fold primary coordination about the lead includes a single Br_I bond at a distance of 2.967 \AA , and an infinite chain of $\text{Br}_{II}-\text{Pb}-\text{Br}_{II}-\text{Pb}$ parallel to the b axis with the average Br-Pb distance of 3.015 \AA . The continuous chain $\text{Br}_{II}-\text{Pb}-\text{Br}_{II}-\text{Pb}$ angle is 103.4° while the two $\text{Br}_I-\text{Pb}-\text{Br}_{II}$ angles average 76.4° .

Divalent lead contains two electrons outside the 5d shell which do not participate in bonding, and two valence electrons for bonding. If the two non-valence electrons remain paired in the $6s^2$ orbital, the three

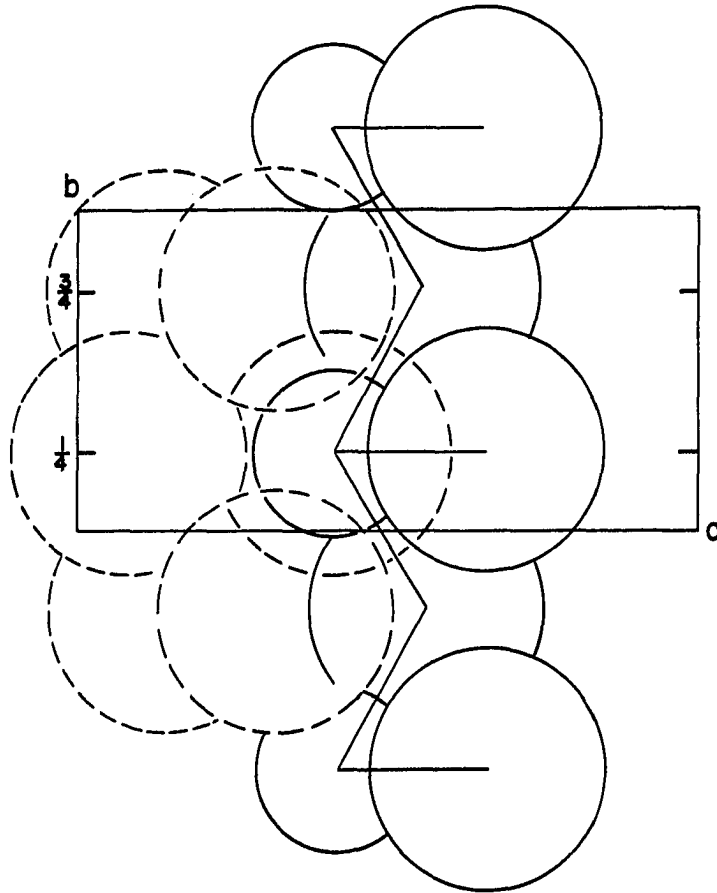


Figure 9. Coordination about lead in lead(II) bromide (The smaller atoms are lead, larger, bromine. Solid atoms represent covalent bonding; broken atoms represent ionic bonding.)

6p orbitals would be available for covalent bonding. The two 76.4° and one 103.4° angles, which average 85.4° , would be better represented by bonds formed from p orbitals than from any s character which would tend to change bond angles from the 90° of a p orbital toward the 109° typical for an sp^3 orbital.

Two possibilities arise when considering the orbitals used by Br_{II} in bridging to two lead atoms. The bonding may be of the three-centered type using one bromine orbital, or Br may supply both electrons to a second bonding orbital, forming two two-centered bonds.

The appropriateness of either possible model to the experimentally determined lead bromide structure can best be evaluated by determining the expected configuration for maximum overlap due to the covalent bonding, and then evaluating what changes might be expected from ionic interactions.

Both bromine and lead would be expected to use primarily p orbital bonding in a two bonded model giving rise to the configuration of Figure 10. All angles

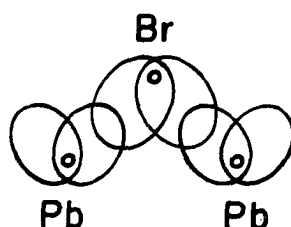


Figure 10. A model representing 2-centered bonding

would be 90° . The Pb-Br_I and Pb-Br_{II} bonds would have the same bond character except that the Br_{II} would need to withdraw more electron density from the Pb-Br_{II} bond than Pb-Br_I since it has fewer unshared electrons, and thereby the Pb-Br_{II} bond would be slightly longer. No Pb-Pb bonding is occurring and this distance should be long. And finally, if each bridging bromine (Br_{II}) uses two electron pairs in bonding, a formal negative charge would be placed on the electropositive lead, hence it would be reasonable to assume more ionic character would exist in all bonds to create a condition with a more equitable distribution of charge. From electronegativity differences a Pb-Br bond would be predicted to have 22 % ionic character (57). The two bonded model would be expected to have greater ionic character than that.

On the other hand, a three-centered bond would contain only about half the electron density per unit area of the two-centered bond and ionic character would not necessarily be increased. As shown in Figure 11, two

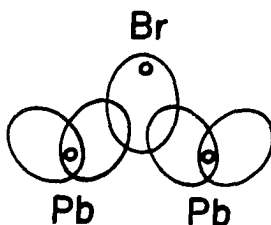


Figure 11. A model representing 3-centered bonding

lead orbitals would overlap one Br_{II} orbital to form the three-centered bond. To obtain maximum overlap the Pb-Pb distance would be as short as possible, consistent with only partial Pb-Pb covalent bonding. The more diffuse Pb- Br_{II} bonds should be considerably longer than Pb- Br_{I} bonds.

The actual structure does not conform to any of the expectations of the three-centered model. The 4.73 Å Pb-Pb distance and 103.4° Pb- Br_{II} -Pb angle would produce poor overlap of the orbitals involved. Assuming a linear relation between bond extension and ionic character, and using the sum of the covalent and ionic radii of 2.86 and 3.17 Å respectively, a single bond of 2.96 Å would have 58 % ionic character, far greater than expected for a three-centered bond. The difference between the 2.965 Å Pb Br_{I} bond and 3.015 Å Pb Br_{II} bond is only .05 Å. Even assuming only 42 % covalent character, a bond of order 1/2 would be .09 Å longer than a bond of order one. By any of several other arguments it would be predicted that a three-centered bond would have greater than 42 % covalent character and that the difference between the two types of bonds would be even greater.

On the other hand the data shows reasonable agreement with the two bond model. The long Pb-Pb

distance, high ionic character in the short bonds, and small difference in length between Pb-Br_{II} and Pb-Br_{I} are consistent with the model. The acute 76.4° $\text{Br}_{\text{I}}-\text{Pb}-\text{Br}_{\text{II}}$ bond and short $\text{Br}_{\text{I}}-\text{Br}_{\text{II}}$ distance of 3.70 \AA would not be predicted from the model. The Br-Br repulsions should leave Br_{I} in the plane at $y = 1/4$, but repulsions should make the $\text{Br}_{\text{I}}-\text{Pb}-\text{Br}_{\text{II}}$ angle obtuse.

That this does not occur must be the result of the longer ionic interactions about each lead. That steric factors are very pronounced is easily seen from the number of short Br-Br non-bonded distances ranging down to 3.62 \AA . This is in contrast to a Br-Br van der Waal distance which has an energy minimum at 3.90 \AA . The data best show this tight packing by the restricted motion of the bromine atoms. This may be seen in the fact that the temperature factor of the lead, although a much heavier atom with more inertia, shows it to have greater motion than the bromine.

Also affected by these short Br-Br distances are the Pb-Br ionic interactions. In the compromise to reach an energy minimum the average Pb-Br ionic distances are $.1 \text{ \AA}$ longer than the normal ionic radius of 3.17 \AA . It is also probable that the covalent distances have also been elongated by these non-bonded interactions and the calculated value of 58 % ionic properties should

be considered a maximum. The main point here is that the ionic interactions could greatly distort the bonding and since these short ionic bonds are all on the "back" side of the molecule, the force to make the $\text{Br}_I\text{-Pb-Br}_{II}$ angle acute appears to be appreciable.

Although a comparison was made between the lead bromide bridging structure and the aluminum halide bridging compounds, an attempt to equate the bonding in the two compounds should not be made. Known halogen-aluminum bridging compounds have non-bridging distances close to the covalent single bond distance, and a bond extension of about $.1 \text{ \AA}$ for the bridge (41, 58). Only the Al-Br-Al angle of close to 90° shows favoritism toward a two-bonded bromine. The bonding may thus be quite different from the PbBr_2 case.

This refinement has shown that, in lead bromide, a mixture of covalent and ionic interactions occur, that the covalent bonding utilizes all remaining available orbitals to complete the sixth shell inert gas structure of lead, and that a bromine which is covalently bonded to two leads will have a somewhat longer interatomic bonding distance than a bromine bonded to only one lead. The results also support a model in which the chain bromine atoms use two bonding orbitals to form two covalent bonds to the adjacent lead atoms.

RESEARCH PROPOSALS

1. Study of organo-aluminum compounds have shown much about how steric effects influence dimerization, but little about the electron density necessary to make the electron poor, bridged bond stable. It appears very likely that the donation of the electron rich phenyl group has a major effect in stabilizing the dimer since it is sterically more cramped than non-branched aliphatic dimers. Use of electron withdrawing and donating phenyl substituents and measurement of their relative association (by cryoscopic methods) could give indication of the stability of the bridged bond. Several substituted phenyl aluminum compounds have been prepared (59), but characterized only by melting point. Electron withdrawing groups would not only lower the stability of the bridged bond, but also the stability of the aluminum phenyl single bond. It would be interesting to find which bond is most affected by the decrease in electron density; i.e., whether a monomeric organo-aluminum can be found because of electronic rather than steric reasons.
2. The structure of diphenyl zinc, as an example of

a covalent electron deficient (near) transition metal compound, would provide an interesting study. Its four valence orbitals could be filled by bridged bonding similar to diphenyl magnesium, or, as might be more expected, Zn-Zn bonding could occur.

3. A LCAO-MO treatment of triphenyl aluminum could be used to study the relative sp^2 - sp^3 orbital participation, and thereby the strength and direction of the three-centered bond. Lipscomb and coworkers (60) have developed methods for SCF calculations by building on models of this type with simpler structures.
4. It would be interesting to calculate the energy minimum from non-bonded carbon and hydrogen potential functions in triphenyl aluminum and compare these with the actual and molecular orbital models.

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APPENDIX

The crystal structure of π -cyclopentadienyl- π -cycloheptatrienyl vanadium (CCV) was first studied by Gordon Engebretson in this laboratory. The quality of the data however was very poor and only partial refinement could be carried out, only enough to establish the general orientation of the vanadium to the carbon rings. The partial refinement was reported in a note (61).

The problem of refinement was turned over to this author and, after accumulation of new data, the refinement was completed. The result of that refinement is reported here.

Background

$C_5H_5VC_7H_7$ was prepared by King and Stone (62). The compound is paramagnetic with one unpaired electron, which substantiates the stoichiometry as $C_5H_5VC_7H_7$ rather than $C_5H_5VC_7H_8$; the latter necessarily having two unpaired electrons. They proposed that the structure contained a vanadium "sandwiched" between a five and seven member ring, forming a π -bonded complex. No structural substantiation of π -cycloheptatrienyl metal complexes had been reported prior to Engebretson's study, and reservations as to their existence had been raised (63).

As a π -complex the structure of CCV would be closely analogous to ferrocene (64, 65, 66). Ionically it may be written $C_5H_5^-V^0C_7H_7^+$, each ring containing a six π -electron system which contributes a major share to the bonding. In the more rigorous molecular orbital description, by analogy to the description of Moffitt (67) for the iron-carbon bonding of ferrocene, the vanadium-carbon bonding is the result of the overlap of a combination of d_{xz} and d_{yz} orbitals with the π orbitals of the rings. Two orbitals, symmetrical around the z axis, are formed by the combination, which bond with the π system of all carbons of each ring. Approximately one electron pair bond is formed, and the symmetry allows free rotation of the rings. This theoretical molecular orbital description would require the rings to be approximately planer and perpendicular to an axis (z) through the vanadium.

Ferrocene (65), and several similar π -complexes, have been found to be disordered in the crystalline state. This is not surprising considering the possibility of free rotation described above which would mean only non-bonded interactions would provide forces which would act to localize the positions of the ring atoms. This also helps to explain failure of several earlier structural studies which were based on an ordered structure, including

the previous x-ray studies of CCV, to refine.

Structural Solution

A single crystal was chosen from a sample of CCV supplied by F. G. A. Stone, and mounted for intensity studies. Crystal symmetry was confirmed to be orthorhombic, Pnma, and the lattice constants were measured using a back reflection Weissenberg camera to be

$$\begin{aligned} a &= 11.052 \pm .014 \text{ \AA} \\ b &= 10.825 \pm .016 \text{ \AA} \\ c &= 7.934 \pm .007 \text{ \AA} \end{aligned}$$

Data were taken on a General Electric XRD-5, single crystal orienter using Mo radiation. A moving crystal, 100 second scan along 2θ was used to record the intensity diffracted from each reflection. Of 1450 reflections observed, 680 were not appreciably above the background and not used in the refinement. The threshold for calling a reflection observed was set at a low $1.5 F_{\min}$, rather than the more normal $3 F_{\min}$. Reflections were in general weak, and many fell in this range.

Background intensities of scattered radiation were taken for each reflection. This was found to be high for all crystals tested, and created an unfavorable peak to background ratio causing higher than normal uncertainty

in the data. The extremely high background gave indication the crystal packing might not be ordered.

The data were corrected for non-characteristic radiation streaking by using as a standard the intensity of several unobserved reflections having high streaking relative to normal background intensity, and the relationships of streaking to diffraction angle derived by Fitzwater and Benson⁹. Corrections for absorption were not deemed necessary. Since the crystal symmetry falls in the same orthorhombic space group as PbBr_2 the relationships used for calculating structure factors for PbBr_2 could be also used to calculate the structure factors for CCV.

A Patterson function map was calculated and clearly showed the vanadium position, but had too many maxima to define only a single ordered set of carbon rings. An ordered set of atomic positions was refined using as the initial values the final positions of Engebretson, and a reliability factor of 14.6 % was obtained.

An electron density map showed that the data could best be fit by placing some of the electron density in

⁹Fitzwater, D. R. and Benson, J. Iowa State University, Ames, Iowa. Relation between White Radiation Streaking and 2θ . Private Communication. 1963.

the positions obtained by rotating the C_7H_7 ring 25.7° and the C_5H_5 ring 36° . This rotation retains an atom on the mirror plane, a necessary condition for a static model in the space group Pnma.

Two sets of positions are then possible for each carbon atom to be refined, and the positions which contain the minority of electron density are hereafter called the disordered positions. Since the sum of the ordered and disordered positions for each atom must have an intensity scattering power equal to one carbon atom fractional atoms were put at possible positions. These were then varied by alternately using electron density calculations and least squares minimizations until the electron density difference map showed no weighting in favor of the ordered or disordered set of positions and the least squares deviation was a minimum. For the final refinement

$$\Sigma w(|F_o| - |F_c|) / \Sigma w|F_o| = 0.074.$$

Unfortunately the extent of disorder was not well established by this study. This is partly due to the experimental difficulties of a disordered structure; high background from a more diffuse thermal distribution and added parameters to refine. A major source of error which prevented accurate refinement was a mistake in the

computer program which calculated the structure factors. The calculations for the inclusion of the temperature parameters for two of the 8 equivalent positions was in error and not found until after the completion of the refinement. Although the error would not shift atom positions greatly, it is not easily estimated. From the standard errors in the C_5H_5 ring disorder, where we are already working with a small fraction of the electron density of a carbon atom, it appears that the effect on the system was appreciable. In the following discussion conclusions should be metered by these limitations.

Discussion

The basic structure consisting of vanadium atoms sandwiched between two parallel rings is substantiated by this study and shown in Figure 12, which also shows the packing of the molecule. It is also found that the exact orientation of the aromatic rings cannot be localized. Refined atomic coordinates and structure factors are given in Table 9 and Figure 13, respectively.

In the space group $Pnma$, if the static positions are considered, two $C_7H_7-C_5H_5$ relative ring orientations may occur as shown in Figure 14. One atom of each ring must be on the mirror plane, and may be either cis to

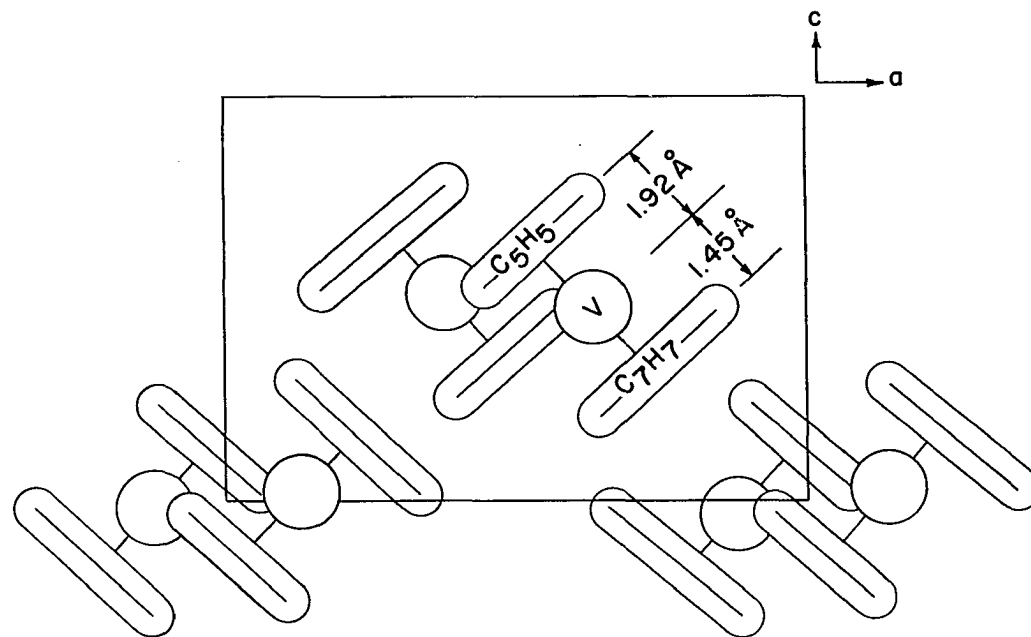


Figure 12. Relative orientation of π -cyclopentadienyl- π -cycloheptatrienyl vanadium molecules in the unit cell

Table 9. Final positional and thermal parameters and their standard errors (in parenthesis) obtained from least squares refinement of π -cyclopentadienyl- π -cycloheptatrienyl vanadium

Atom	x	y	z	β
CH1	.3427 (.0042)	.2500	.0220 (.0056)	3.154 (0.749)
CH2	.3038 (.0029)	.3681 (.0033)	.0783 (.0039)	3.520 (0.684)
CH3	.2145 (.0029)	.3993 (.0029)	.1996 (.0041)	3.267 (0.605)
CH4	.1405 (.0036)	.3154 (.0029)	.3024 (.0034)	2.908 (0.470)
CP1	.1030 (.0038)	.2500	-.2427 (.0057)	3.776 (0.721)
CP2	.0506 (.0022)	.3570 (.0025)	-.1707 (.0032)	3.579 (0.513)
CP3	-.0412 (.0021)	.3169 (.0021)	-.0510 (.0036)	3.460 (0.413)
CH1D	.1423 (.0122)	.2500	.3054 (.0109)	3.925 (1.888)
CH2D	.1737 (.0055)	.3666 (.0061)	.2475 (.0078)	3.298 (1.224)
CH3D	.2628 (.0070)	.3952 (.0063)	.1236 (.0089)	3.861 (1.371)
CH4D	.3328 (.0052)	.3153 (.0052)	.0312 (.0082)	3.045 (0.999)
CP1D	-.0577 (.0173)	.2500	-.0326 (.0287)	4.055 (3.762)
CP2D	.0113 (.0102)	.3468 (.0101)	-.1133 (.0137)	2.035 (1.868)
CP3D	.0904 (.0104)	.3102 (.0104)	-.2249 (.0141)	2.083 (1.869)

Table 9 (continued)

Atom	x	y	z	β_{11}	
V	.1445 (.0004)	.2500	.0361 (.0006)	.0048 (.0001)	
	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
	.0068 (.0001)	.0092 (.0001)	-.0001 (.0001)	-.0006 (.0001)	-.0001 (.0001)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	
H = 0																								
0	0	40.9	39.6	11	8	11.8	10.1	2	2	-32.6	-17.1	6	6	14.8	-12.8	6	1	8.0	2.8	10	10	17.1	17.1	
0	0	53.4	52.0	11	9	15.9	-15.2	4	4	24.1	-25.7	2	2	17.1	-17.1	6	2	11.0	10.4	10	10	29.8	29.8	
0	0	16.0	16.3	11	10	12.1	-13.3	3	3	13.3	-12.0	1	1	20.2	-20.3	6	3	11.0	10.3	10	10	20.2	20.2	
0	0	10.7	10.7	11	11	12.4	-13.6	5	5	9.2	-7.3	1	1	19.2	-18.2	6	4	12.3	12.3	10	10	19.2	19.2	
0	0	176.1	-179.3	11	12	13.9	-14.1	4	4	26.0	-23.2	1	1	62.9	-64.5	6	5	11.1	11.1	10	10	62.9	62.9	
0	0	8.4	12.8	10	10	12.2	-12.5	5	5	12.6	13.1	1	1	31.2	-33.2	6	6	9.6	9.6	10	10	31.2	31.2	
0	0	29.9	39.9	10	11	11.1	11.8	5	5	19.9	14.5	1	1	11.6	-14.9	6	7	23.7	-26.9	10	10	11.6	11.6	
0	0	21.6	-22.2	10	12	11.1	11.8	4	4	21.6	20.6	1	1	7.8	-10.0	6	8	11.1	11.3	10	10	7.8	7.8	
0	0	11.3	16.7	10	13	11.3	11.8	3	3	14.5	16.5	1	1	15.0	15.0	6	9	11.1	11.3	10	10	15.0	15.0	
0	0	11.3	16.7	10	14	11.3	11.8	2	2	14.5	16.5	1	1	30.9	31.7	6	10	11.1	11.3	10	10	30.9	31.7	
0	0	11.3	16.7	10	15	11.3	11.8	1	1	14.5	16.5	1	1	10.7	10.7	6	11	11.1	11.3	10	10	10.7	10.7	
0	0	11.3	16.7	10	16	11.3	11.8	1	1	14.5	16.5	1	1	23.6	22.5	6	12	11.1	11.3	10	10	23.6	22.5	
0	0	11.3	16.7	10	17	11.3	11.8	1	1	14.5	16.5	1	1	16.2	13.4	6	13	11.1	11.3	10	10	16.2	13.4	
0	0	11.3	16.7	10	18	11.3	11.8	1	1	14.5	16.5	1	1	8.0	8.0	6	14	11.1	11.3	10	10	8.0	8.0	
0	0	11.3	16.7	10	19	11.3	11.8	1	1	14.5	16.5	1	1	16.2	13.4	6	15	11.1	11.3	10	10	16.2	13.4	
0	0	11.3	16.7	10	20	11.3	11.8	1	1	14.5	16.5	1	1	39.2	39.2	6	16	11.1	11.3	10	10	39.2	39.2	
0	0	11.3	16.7	10	21	11.3	11.8	1	1	14.5	16.5	1	1	42.2	42.2	6	17	11.1	11.3	10	10	42.2	42.2	
0	0	11.3	16.7	10	22	11.3	11.8	1	1	14.5	16.5	1	1	15.3	15.6	6	18	11.1	11.3	10	10	15.3	15.6	
0	0	11.3	16.7	10	23	11.3	11.8	1	1	14.5	16.5	1	1	16.6	16.6	6	19	11.1	11.3	10	10	16.6	16.6	
0	0	11.3	16.7	10	24	11.3	11.8	1	1	14.5	16.5	1	1	11.7	11.7	6	20	11.1	11.3	10	10	11.7	11.7	
0	0	11.3	16.7	10	25	11.3	11.8	1	1	14.5	16.5	1	1	24.7	24.7	6	21	11.1	11.3	10	10	24.7	24.7	
0	0	11.3	16.7	10	26	11.3	11.8	1	1	14.5	16.5	1	1	23.0	22.5	6	22	11.1	11.3	10	10	23.0	22.5	
0	0	11.3	16.7	10	27	11.3	11.8	1	1	14.5	16.5	1	1	22.0	22.0	6	23	11.1	11.3	10	10	22.0	22.0	
0	0	11.3	16.7	10	28	11.3	11.8	1	1	14.5	16.5	1	1	17.7	16.4	6	24	11.1	11.3	10	10	17.7	16.4	
0	0	11.3	16.7	10	29	11.3	11.8	1	1	14.5	16.5	1	1	14.4	14.4	6	25	11.1	11.3	10	10	14.4	14.4	
0	0	11.3	16.7	10	30	11.3	11.8	1	1	14.5	16.5	1	1	8.4	8.4	6	26	11.1	11.3	10	10	8.4	8.4	
0	0	11.3	16.7	10	31	11.3	11.8	1	1	14.5	16.5	1	1	14.0	14.0	6	27	11.1	11.3	10	10	14.0	14.0	
0	0	11.3	16.7	10	32	11.3	11.8	1	1	14.5	16.5	1	1	14.6	14.6	6	28	11.1	11.3	10	10	14.6	14.6	
0	0	11.3	16.7	10	33	11.3	11.8	1	1	14.5	16.5	1	1	19.0	19.0	6	29	11.1	11.3	10	10	19.0	19.0	
0	0	11.3	16.7	10	34	11.3	11.8	1	1	14.5	16.5	1	1	16.7	16.7	6	30	11.1	11.3	10	10	16.7	16.7	
0	0	11.3	16.7	10	35	11.3	11.8	1	1	14.5	16.5	1	1	15.6	15.6	6	31	11.1	11.3	10	10	15.6	15.6	
0	0	11.3	16.7	10	36	11.3	11.8	1	1	14.5	16.5	1	1	8.1	8.1	6	32	11.1	11.3	10	10	8.1	8.1	
0	0	11.3	16.7	10	37	11.3	11.8	1	1	14.5	16.5	1	1	15.1	15.1	6	33	11.1	11.3	10	10	15.1	15.1	
0	0	11.3	16.7	10	38	11.3	11.8	1	1	14.5	16.5	1	1	8.1	8.1	6	34	11.1	11.3	10	10	8.1	8.1	
0	0	11.3	16.7	10	39	11.3	11.8	1	1	14.5	16.5	1	1	16.1	16.1	6	35	11.1	11.3	10	10	16.1	16.1	
0	0	11.3	16.7	10	40	11.3	11.8	1	1	14.5	16.5	1	1	17.4	17.4	6	36	11.1	11.3	10	10	17.4	17.4	
0	0	11.3	16.7	10	41	11.3	11.8	1	1	14.5	16.5	1	1	10.8	10.8	6	37	11.1	11.3	10	10	10.8	10.8	
0	0	11.3	16.7	10	42	11.3	11.8	1	1	14.5	16.5	1	1	19.7	19.7	6	38	11.1	11.3	10	10	19.7	19.7	
0	0	11.3	16.7	10	43	11.3	11.8	1	1	14.5	16.5	1	1	21.4	21.4	6	39	11.1	11.3	10	10	21.4	21.4	
0	0	11.3	16.7	10	44	11.3	11.8	1	1	14.5	16.5	1	1	20.7	20.7	6	40	11.1	11.3	10	10	20.7	20.7	
0	0	11.3	16.7	10	45	11.3	11.8	1	1	14.5	16.5	1	1	21.3	21.3	6	41	11.1	11.3	10	10	21.3	21.3	
0	0	11.3	16.7	10	46	11.3	11.8	1	1	14.5	16.5	1	1	14.0	14.0	6	42	11.1	11.3	10	10	14.0	14.0	
0	0	11.3	16.7	10	47	11.3	11.8	1	1	14.5	16.5	1	1	8.5	8.5	6	43	11.1	11.3	10	10	8.5	8.5	
0	0	11.3	16.7	10	48	11.3	11.8	1	1	14.5	16.5	1	1	14.9	14.9	6	44	11.1	11.3	10	10	14.9	14.9	
0	0	11.3	16.7	10	49	11.3	11.8	1	1	14.5	16.5	1	1	54.9	54.9	6	45	11.1	11.3	10	10	54.9	54.9	
0	0	11.3	16.7	10	50	11.3	11.8	1	1	14.5	16.5	1	1	24.3	24.3	6	46	11.1	11.3	10	10	24.3	24.3	
0	0	11.3	16.7	10	51	11.3	11.8	1	1	14.5	16.5	1	1	39.1	39.1	6	47	11.1	11.3	10	10	39.1	39.1	
0	0	11.3	16.7	10	52	11.3	11.8	1	1	14.5	16.5	1	1	20.2	20.2	6	48	11.1	11.3	10	10	20.2	20.2	
0	0	11.3	16.7	10	53	11.3	11.8	1	1	14.5	16.5	1	1	28.1	28.1	6	49	11.1	11.3	10	10	28.1	28.1	
0	0	11.3	16.7	10	54	11.3	11.8	1	1	14.5	16.5	1	1	16.1	16.1	6	50	11.1	11.3	10	10	16.1	16.1	
0	0	11.3	16.7	10	55	11.3	11.8	1	1	14.5	16.5	1	1	17.0	17.0	6	51	11.1	11.3	10	10	17.0	17.0	
0	0	11.3	16.7	10	56	11.3	11.8	1	1	14.5	16.5	1	1	13.1	13.1	6	52	11.1	11.3	10	10	13.1	13.1	
0	0	11.3	16.7	10	57	11.3	11.8	1	1	14.5	16.5	1	1	33.9	33.9	6	53	11.1	11.3	10	10	33.9	33.9	
0	0	11.3	16.7	10	58	11.3	11.8	1	1	14.5	16.5	1	1	14.9	14.9	6	54	11.1	11.3	10	10	14.9	14.9	
0	0	11.3	16.7	10	59	11.3	11.8	1	1	14.5	16.5	1	1	8.4	8.4	6	55	11.1	11.3	10	10	8.4	8.4	
0	0	11.3	16.7	10	60	11.3	11.8	1	1	14.5	16.5	1	1	10.2	10.2	6	56	11.1	11.3	10	10	10.2	10.2	
0	0	11.3	16.7	10	61	11.3	11.8	1	1	14.5	16.5	1	1	15.6	15.6	6	57	11.1	11.3	10	10	15.6	15.6	
0	0	11.3	16.7	10	62	11.3	11.8	1	1	14.5	16.5	1	1	50.2	50.2	6	58	11.1	11.3	10	10	50.2	50.2	
0	0	11.3	16.7	10	63	11.3	11.8	1	1	14.5	16.5	1	1	19.9	19.9	6	59	11.1	11.3	10	10	19.9	19.9	
0	0	11.3	16.7	10	64	11.3	11.8	1	1	14.5	16.5	1	1	11.1	11.1	6	60	11.1	11.3	10	10	11.1	11.1	
0	0	11.3	16.7	10	65	11.3	11.8	1	1	14.5	16.5	1	1	13.6	13.6	6	61	11.1	11.3	10	10	13.6	13.6	
0	0	11.3	16.7	10	66	11.3	11.8	1	1	14.5	16.5	1	1	20.0	20.0	6	62	11.1	11.3	10	10	20.0	20.0	
0	0	11.3	16.7	10	67	11.3	11.8	1	1	14.5	16.5	1	1	18										

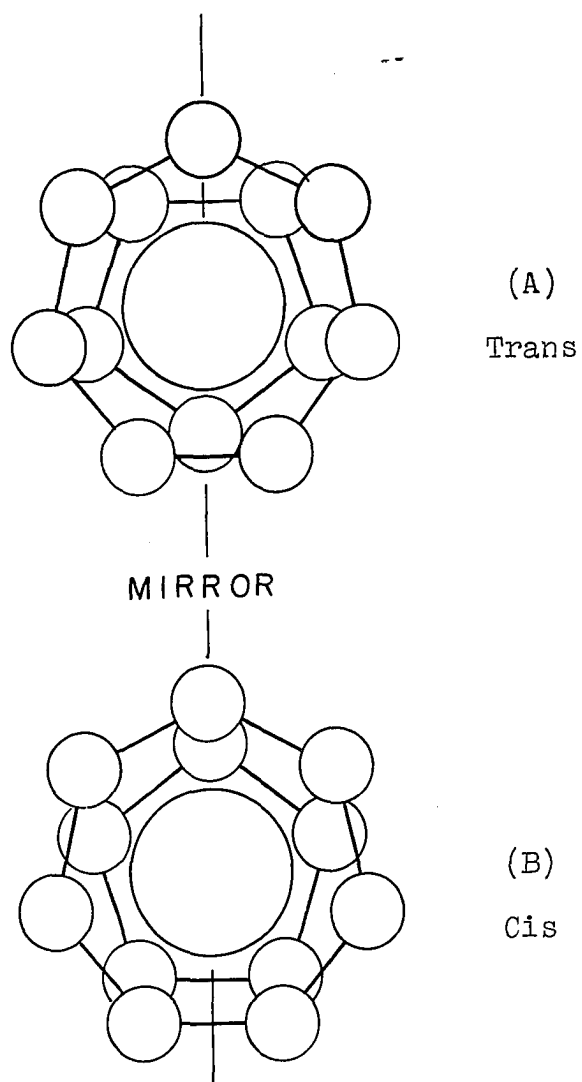


Figure 14. Possible relative orientations of aromatic rings in π -cyclopentadienyl- π -cycloheptatrienyl vanadium

the atom of the other ring (B) or trans (A). When considering packing in the crystal lattice there are two possible positions for each ring, therefore, four relative orientations are possible, two cis and two trans. The refinement shows that all four positions are occupied by carbons.

The refinement found minimum standard deviation occurring when the C_7H_7 was distributed 67 % to 33 % between its two possible positions, one differing from the other by a rotation of 25.7° . The C_5H_5 had a minimum at 84 % and 16 % in its positions which differ by a rotation of 36° . The major positions for each ring find the atoms on the mirror plane cis to one another.

The reliability of the 2/1 ratio between C_7H_7 positions is good; the standard deviation averages $.010 \text{ \AA}$ for the major position and $.015 \text{ \AA}$ for the minor and the electron density map is consistent. However, the reliability of the 5/1 ratio between C_5H_5 is not good. The standard deviation of the minor position is $.04 \text{ \AA}$ compared to $.008 \text{ \AA}$ for the major, and the individual atom densities show marked variation in the electron density map.

In a study of a similar compound, $C_7H_7CrC_5H_5$,

Russell and Rundle¹⁰ found a similar disorder of 2/1 in the C_7H_7 ring, but no disorder in the C_5H_5 ring. Ferrocene also has a 2/1 disorder (65).

The above analysis assumes a static model with oscillations occurring about a fixed position. A better way to view the model might be to consider a dynamic aromatic ring where atoms spend equal time in positions related by the mirror, thereby relieving the possible misconception that one atom must lie on the mirror plane. The higher probability of the rings being oriented in a cis configuration is primarily due to the fact that this cis configuration has only one short C_7H_7 - C_5H_5 non-bonded interaction, while in the trans orientation there are two short C_7H_7 - C_5H_5 distances. (See Figure 14.) Rotation would be expected to occur, the freedom of which is dependent on the non-bonded interactions.

All V-C distances are of the same order, 2.18 to 2.27 Å. Distances of 1.45 and 1.92 Å were calculated for the perpendicular distance to the V- C_7H_7 plane and the V- C_5H_5 plane respectively. The non-bonded contact distances between C_5H_5 and C_7H_7 carbons are of the order of van der Waals minimum non-bonded contacts, of 3.42 to

¹⁰Russell, D. R. The University, Leichester, England, and Rundle, R. E. Ames Laboratory, Atomic Energy Commission, Ames, Iowa. Private Communication. 1963.

to 3.76 Å and heavily influence the V-C distance. Therefore dicyclopentatrienyl sandwich compounds should not be stable since C-C contacts would be prohibitively short.