Crystal structure of some ring systems containing group III and group V elements

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PREFACE

This thesis describes research in Chemical Crystallography carried out during three years spent in the Chemistry Department in Durham University.

I am indebted to my supervisor, Dr. H.M.M. Shearer for continual guidance and encouragement and for suggesting the problems. I would like to thank Prof. G.E. Coates and Dr. K. Wade and their research students for providing the compounds.

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SUMMARY

The work in the first part of this thesis describes the crystal structure analysis of the trans-ethylideneaminodimethylborane dimer $(MeHCNBMe_2)_2$. The structure was solved from the three dimensional Patterson function with the aid of superposition methods, and the atomic parameters refined by F_o syntheses and least-squares calculations to a residual of 0·121 for the 645 observed reflections. The molecule was found to contain a planar four-membered boron-nitrogen ring system with a double bond attached directly to nitrogen and to be the trans isomer.

Part II describes the crystal structure analysis of the 2,2'-dimethylbutylidene-3-aminodimethylaluminium dimer, $(Bu^tMeCNAlMe_2)_2$. Evaluation of the three dimensional Patterson function gave the solution to the structure. Refinement of the atomic parameters showed the space group to be the centrosymmetric Cmca rather than Aba2. The final value for the residual was 0·114 for the 524 reflections observed. This structure was shown to be similar to $(MeHCNBMe_2)_2$ as it contains an aluminium-nitrogen four membered ring system with a double bond attached to nitrogen and to be the trans isomer.

The crystal structure analysis of dimethylphosphinatodimethylgallium, $(Me_2GaO_2PMe_2)_2$, is described in part III. Over the 726 reflections observed, the final value of R was 0·086. The dimer contains an eight membered ring system in which the gallium atoms are bridged by

two phosphinate groups. The ring conformation is such that contacts across the ring and methyl contacts round the ring are comparable with the closest intermolecular contacts.

CONTENTS

TABLES

STRUCTURE REFINEMENT

X-rays are scattered by the electrons in atoms. The atoms possess finite volume and phase differences arise between rays scattered from different parts of the atom. The differences increase with increasing scattering angle and the atomic scattering factor, f_o, falls off with sin θ. The atoms in a crystal lattice have finite amplitudes of oscillation. The frequency of these vibrations is less than the frequency of the X-rays so that, as the thermal motions of corresponding atoms are not in phase, the scattering is further reduced with increasing Bragg angle. The vibrations can be described as an ellipsoid of vibration. This can be represented as a tensor, $\underset{\sim}{U}$, with six independent components. The amplitude U, for a reflection with Miller indices hkl, is given by,

$$U = U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*$$

and the expression for the atomic scattering, f, by

$$f = f_o \exp \quad - 8\pi^2U(\sin\theta/\lambda)^2$$

For an isotropic vibration this is expressed as $f = f_o \exp \quad - B(\sin\theta/\lambda)^2$ where B, the Debye factor, is $8\pi^2U$.

The resultant of waves scattered by the whole contents of the unit cell in a particular direction is the structure factor, F_{hkl}

$$F_{hkl} = \sum_{0}^{n} f_j e^{2\pi i(hx_j/a + hy_j/b + lz_j/c)}$$

where the summation is over all the n atoms in the unit cell, atom j having coordinates x_j, y_j, z_j.

This complex quantity can be expressed as an amplitude, $F_{hkl} = \sqrt{A^2 + B^2}$ together with a phase angle, α, where $\alpha_{hkl} = \tan^{-1}(B/A)$.

$$A = \sum_{0}^{n} f_j \cos 2\pi\,(hx_j/a + ky_j/b + lz_j/c)$$

$$B = \sum_{0}^{n} f_j \sin 2\pi\,(hx_j/a + ky_j/b + lz_j/c)$$

The structure factor can also be represented by the expression

$$F_{hkl} = \frac{V}{abc}\int_0^a\int_0^b\int_0^c \rho(xyz)\,e^{2\pi i\,(hx/a + ky/b + lz/c)}.dx.dy.dz.$$

Where $\rho(xyz)$ is the electron density at the point xyz in the unit cell, the number of electrons in the volume dx.dy.dz. being $\rho(xyz)$ dx.dy.dz.

As $\rho(xyz)$ is a periodic function it can be represented as a Fourier series.

$$\rho(xyz) = \sum_{-\infty}^{\infty}\sum\sum A_{pqr}\,{}^{2\pi i\,(px/a + qy/b + rz/c)}$$

Substituting this in the expression for F_{hkl} and integrating, all terms are zero except those where p = -h, q = -k and r = -l.

Thus $F_{hkl}/V = A\,(\bar{h}\ \bar{k}\ \bar{l})$

and $\rho(xyz) = \frac{1}{V}\sum_{-\infty}^{\infty}\sum\sum F_{hkl}\,e^{-2\pi i\,(hx/a + ky/b + lz/c)}$

Fourier Methods.

F_o synthesis.

Evaluation of the expression for the electron density using the observed values for the structure factors, F_o, combined with the phases of structure factors based on the postulated atomic parameters, F_c, gives a high concentration of electron density in the region of atomic sites. Re-estimates of the atomic coordinates from these peaks give a set of F_c in better agreement with the F_o's hence leading to further refinement.

Not all the reflections can be observed experimentally and only a finite number of terms are available to include in the summation. This gives rise to termination of series effects where the peaks are surrounded by diffraction ripples which can cause the observed peaks to be displaced from their true positions.

If the structure is being solved by heavy atom methods, peaks due to the atoms not included in the calculation of structure factors appear in the F_o synthesis and hence their coordinates can be found.

Refinement by this method ends when the signs of the F_c for a centro-symmetric space group are no longer changing.

$F_o - F_c$ synthesis.

If, instead of F_o, the difference between the magnitude of the observed and calculated structure factors, $(|F_o| - |F_c|)$, are used as coefficients in the Fourier series, the systemmatic errors due to the termination of series are eliminated. The resultant synthesis gives the difference between the observed electron density and that for the postulated model and indicates corrections to the positional and thermal parameters for each atom.

The coordinate corrections can be estimated from the first derivatives of $\rho_o - \rho_c$. The value of the electron density at a distance r from the centre of an atom can be approximated by the expression

$\rho_o(r) = \rho_o(o) \exp(-pr^2)$.

Expanding this and ignoring all terms past the second gives

$$\rho_o(r) = \rho_o(o) \quad (1 - pr^2).$$

If the error in r is δr then

$$\rho_o(r) - \rho_c(r) = \rho_o(o)(1 - p(r-\delta r)^2) - \rho_c(o)(1 - pr^2).$$

Assuming that the shapes of ρ_o and ρ_c are identical but are displaced then, if $D_r = \rho_o(r) - \rho_c(r)$, $\left(\frac{\delta D_r}{\delta r}\right)_{r = o} = -\rho_o(o)2p\delta r$.

$$\text{Hence} \quad \delta r = \left(\frac{\delta D}{\delta r}\right)_{r = o} \Big/ 2p\rho_o(o)$$

Values of p and $\rho_o(o)$ can be found from the shape of the peak for each atom from an F_o synthesis.

Anisotropic corrections to the thermal parameters can be found from the curvatures of $(\rho_o - \rho_c)$ and the correction to an isotropic temperature factor can be determined from the value of D at an atomic site. If isotropic temperature parameters have been used to calculate the set of F_c then the principle axes of the ellipsoid of vibration are in the directions of principal curvature of D at the atomic site.

Schomaker (1957) derives the following equations giving the corrections to scaling and thermal parameters.

If h_1, h_2 and h_3 are the components of 2 sin θ/λ along the principal axes of the ellipsoid of vibration and T is the assumed isotropic temperature factor, then

$$\rho_o(r) = (1 + \Delta K) \int_o^{h_o} f_o \, T \exp ((\Delta B_1 h_1^2 + \Delta B_2 h_2^2 + \Delta B_3 h_3^2)/4) \exp(-2\pi i h r) . V . dh.$$

where h_o is the limit of the observed reflections and the ΔB's are the changes in the temperature parameter and ΔK the error in the scale factor.

He derives the following four equations:

$$D(o) + \rho_o(o) - \rho_c(o) = 4\pi \, I_2 \Delta K - \frac{\pi}{3} \, I_4 \, (\Delta B_1 + \Delta B_2 + \Delta B_3)$$

$$D_1''(o) = - \frac{16}{3} \pi^3 I_4 \Delta K + \frac{4}{15} \pi^3 I_6 \, (3\Delta B_1 + \Delta B_2 + \Delta B_3)$$

$$D_2''(o) = - \frac{16}{3} \pi^3 I_4 \Delta K + \frac{4}{15} \pi^3 I_6 \, (\Delta B_1 + 3\Delta B_2 + \Delta B_3)$$

$$D_3''(o) = - \frac{16}{3} \pi^3 I_4 \Delta K + \frac{4}{15} \pi^3 I_6 \, (\Delta B_1 + \Delta B_2 + 3\Delta B_3)$$

The $D''(o)$ are the curvatures of $\rho_o - \rho_c$ and I_2, I_4 and I_6 are integrals of the form $I_n = \int_o^{h_o} h^n \, f_o \, T . \, dh.$

These are analagous to the equations derived by Cruikshank (1956), which give the corrections to the thermal parameters referred to the reciprocal axes.

If the scaling is assumed correct and the first equation ignored, Schomakers equations simplify to those produced by Cochran (1951).

Method of Least-Squares

This method adjusts the scale and atomic parameters so that the sum of the weighted squares of the differences in magnitudes of the observed and calculated structure factors, R, is minimised.

$$R = \sum_{hkl} W(|F_o| - |F_c|)^2 = \sum_{hkl} W\Delta^2$$

where

$$\Delta = |F_o| - |F_c|$$

For R to be a minimum $\delta R/\delta p_j = 0$ where p are the parameters of F_c and j is one of the n atoms.

Cochran, 1948, has shown that the methods for determining corrections to the atomic parameters by least-squares refinement and the difference synthesis are formally equivalent and identical if the least squares weights, w, are equal to $1/f_{hkl}$.

The structure factors least-squares parameter corrections are computed by solving a set of normal equations derived as follows:

for R to be a minimum $\frac{\delta R}{\delta p_j} = o = \sum \frac{W\Delta\delta|F_c|}{\delta p_j}$ .... (1)

Expanding Δ as a function of its parameters using the first two terms only of the Taylor Series, where p represents a set of parameters and the set of errors in these, gives

$$\Delta(p + \epsilon) = \Delta(p) - \sum_{i=1}^{n} \epsilon_i \cdot \frac{\delta F_c}{\delta p_i}$$

This approximation is valid only for small parameter changes as F_c is not a linear function of these. As F_c is a linear function of the scale factor, the normal equations are valid for large scale changes if the changes in the other parameters are small.

As

$$\Delta(p + \epsilon) = o, \qquad \Delta(p) = \sum_{n=1}^{n} \epsilon_i \frac{\delta F_c}{\delta p_i}$$

Substituting this in equation (1) gives a set of n equations, the normal equations.

$$\sum_{i=1}^{n}\left\{ \sum_{hkl} W\left(\frac{\delta|F_c|}{\delta p_j} \cdot \frac{\delta|F_c|}{\delta p_i}\right)\right\} \epsilon_i = \sum_{hkl} W\Delta \frac{\delta|F_c|}{\delta p_j}$$

The partial derivatives of F_c with respect to the coordinates are evaluated as follows: $|F_c| = A\cos\alpha + B\sin\alpha$

$$\frac{\delta|F_c|}{\delta p_j} = \left(\frac{\delta A}{\delta p_j}\right)\cos\alpha + \left(\frac{\delta B}{\delta p_j}\right)\sin\alpha + (-A\sin\alpha + B\cos\alpha)\left(\frac{\delta\alpha}{\delta p_j}\right)$$

where

$$-A\sin\alpha + B\cos\alpha = o$$

$$A_j = f_j \cos 2\pi(hx/a + ky/b + lz/c)$$

and

$$B_j = f_j \sin 2\pi(hx/a + ky/b + lz/c)$$

then

$$\frac{\delta A}{\delta x_j} = \frac{-2\pi h f_j}{a}\sin 2\pi(hx/a + ky/b + lz/c)$$

$$= \frac{-2\pi h B_j}{a}$$

and $$\frac{\delta B_j}{\delta x_j} = \frac{2\pi h \cos 2\pi}{a}(hx/a + ky/b + lz/c) = \frac{2\pi h}{a} A_j$$

Hence

$$\frac{\delta |F_c|}{\delta p_j} = \frac{2\pi h}{a}(A_j\cos\alpha - B_j\sin\alpha)$$

The partial derivatives with respect to the thermal parameters can be found similarly. They are of the form.

$$\frac{\delta |F_c|}{\delta U_{11,j}} = -2\pi^2 h^2 a*^2 \, |F_c|$$

as $\frac{\delta A}{\delta U_{11,j}} = -2\pi^2 h^2 a*^2 A_j$ and $\frac{\delta B}{\delta U_{11,j}} = -2\pi^2 h^2 a*^2 B_j$

The overall scale factor for the F_o is determined as the inverse scale factor for the F_c and $\frac{\delta |F_c|}{\delta G} = \frac{|F_c|}{G}$ where the F_c include this scale factor.

With the availability of larger, faster computers, it is possible to use the full matrix treatment to solve the normal equations directly in some cases. Usually some approximation is made. Use of the diagonal terms only of the matrix leads to very slow refinement as this neglects any interaction between parameters.

In the block diagonal approximation suggested by Cruikshank et.al., 1961, corrections to the coordinates and temperature parameters are found by calculating a series of 3 x 3, 6 x 6 and 1 x 1 matrices together with their right hand sides. The 3 x 3 matrix allows for the interactions between the coordinates of an atom due to the axes not being orthogonal and the 6 x 6 matrix allows for the interactions between the anisotropic thermal parameters of an atom.

The effect of a change of overall scale factor on the temperature parameter corrections is found from a 2 x 2 matrix.

These were the approximations made in the least-squares computer program used for the work described in this thesis. Other programs use a series of 9 x 9 or 4 x 4 matrices to allow for the interactions between all the parameters of an atom.

When using approximations of this kind it is found that fewer cycles of refinement are needed if the shifts obtained from the least squares equations are multiplied by a partial shift or "fudge" factor. In the block diagonal approximation used a partial shift factor of 0.8 was applied to all the shifts.

For the parameters to have minimum e.s.d.'s each of the structure factors should be weighted so that $w = k/\sigma^2_{F_{hkl}}$. The e.s.d. in the parameter p_j is given by

$$\sigma^2(p_j) = (a^{-1})_{p_{jj}} w\Delta^2/(m-n)$$

where $(a^{-1})_{jj}$ is an element of the matrix inverse to the full matrix, a_{ij}, of the normal equations, m is the number of experimental observations and n the number of parameters. Rather than giving each reflection a weight of K/Δ^2, a weighting function with only a few parameters is used and these are adjusted to give average values of $w\Delta^2$ that are constant for reflections within ranges of value F_o and/or $\sin\theta/\lambda$.

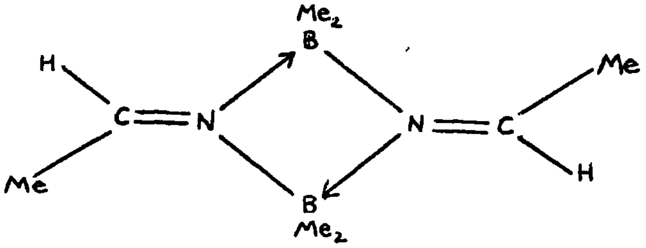
For the work in this thesis F_o syntheses were used to complete the structure determination by locating atoms whose coordinates could not be found by Patterson methods. Refinement of atomic parameters was carried out by structure factors least squares calculations. Difference syntheses were computed to check the least-squares results for unforseen errors e.g. disordering and in an attempt to locate hydrogen atoms.

The Crystal Structure of trans-ethylideneaminodimethylborane dimer

$(Me_2BNCHMe)_2$

Introduction

Hydroboration of methyl cyanide using dimethyl borohydride gives two products with the same chemical analysis and very similar infra-red spectra, one a liquid and the other a solid. Vapour density determinations and cryoscopic measurements in benzene indicate that the molecule contains two $Me_2BNCHMe$ units, and the i.r. spectra shows bands that could correspond to a carbon-nitrogen double bond stretching frequency. The similarity of these two compounds suggest that they are cis and trans isomers with the following structure for the trans compound. (Lloyd and Wade, 1964).



As yet no complete structure analysis has been carried out for a compound containing a boron-nitrogen four membered ring with a double bond attached directly to it. The crystal structure analysis confirms that, in the crystalline state, this compound has the structure suggested and is the trans isomer.

Experimental

Crystals.

Crystals elongated in the direction of the 'c' axis were found to form on the sides of a flask containing $(Me_2BNCHMe)_2$ crystals left standing at the pressure of their own vapour. The crystals were air sensitive but could be cut and mounted on glass fibres in air and were found to be satisfactorily protected by a coating of shellac.

Crystal data.

The unit cell dimensions were obtained from photographs of the hko and hol nets taken with Cu Kα radiation and of the okl and hol nets using Mo Kα radiation and the precession method. The greatest error in these is probably that in centering the crystal and is thought to be of the order of 0·3%. The dimensions given are the mean values obtained using the different radiations, the greatest difference in the corresponding values being 0·3%.

Monoclinic. $a = 6{\cdot}55\text{Å}$, $b = 11{\cdot}92\text{Å}$, $c = 7{\cdot}89\text{Å}$, $\beta = 105^\circ 23'$

$\lambda(\text{Mo K}\alpha) = 0{\cdot}7107\text{Å}$, $\lambda(\text{Cu K}\alpha) = 1{\cdot}5418\text{Å}$

$V = 592{\cdot}73\text{Å}^3$, $Z = 4$ $Me_2BNCHMe$ units, $F(000) = 184$ electrons

$D_m = 0{\cdot}93$ gm cm^{-3}, $D_x = 0{\cdot}929$ gm cm^{-3}

Absorption $\mu(\text{Cu K}\alpha) = 2{\cdot}2$ cm^{-1}, $\mu(\text{Mo K}\alpha) = 0{\cdot}65$ cm^{-1}

Observed reflections:

hol when h = 2n

oko when k = 2n

hkl no conditions.

This uniquely determines the space group as $P2_1/a$, (C_{2h}^5).

The density for four $Me_2BNCHMe$ units per unit cell of 0·929 gm cm^{-3} calculated using the above cell dimensions is the same as the value of 0·93 gm cm^{-3} obtained by differential flotation of the crystals in a methyl cyanide water mixture. Each of the four asymmetric units of the space group is occupied by one $Me_2BNCHMe$ unit. If the compound is dimeric in the crystalline state, then each dimer must possess a centre of symmetry and the methyl carbons on the carbons attached to nitrogen must be trans.

Collection of Intensities.

Partial three dimensional data was recorded photographically using Zr-filtered Mo radiation and the precession method for the okl-2kl nets and Ni-filtered Cu radiation and the equi-inclination Weissenberg method for the hko-hk5 nets.

The intensities were estimated visually by comparison with a graduated scale, the elongated reflections only on the Weissenberg nets being used.

Length corrections (Phillips, 1956) were applied to these reflection on the nets hkl-hk3 at the same time as the usual Lorentz and polarisation corrections. For the nets hk4 and hk5 the length of spots with the same sin θ values were found to vary across the film so estimates of the lengths were obtained by direct measurements.

No correction for absorption was made.

The structure factors were correlated using factors calculated from the common reflections by a modified Rollett least-squares method. They numbered 475 of which 174 appeared on more than one net.

Structure Determination

The structure was solved by calculation of the three-dimensional Patterson function. The atomic parameters were refined by F_o and $F_o - F_c$ syntheses and finally by least squares calculations.

The three dimensional Patterson function was calculated, the expression

$$P(uvw) = \frac{4}{V} \sum_{0}^{h} \sum_{0}^{k} \sum_{0}^{l} [W_{hkl} |F_{hkl}|^2 \cos 2\pi(hu + lw) + W_{\bar{h}kl} |F_{\bar{h}kl}|^2 \cos 2\pi(-hu + lw)] \cos 2\pi kv$$

being evaluated at intervals in u of 0·262Å, in v of 0·263Å and in w of 0·298Å.

The expression used for w_{hkl} was $1/\{f \exp(-2{\cdot}5\sin^2\theta/\lambda^2)^2\}$ where f is the theoretical value for the scattering for the sin θ value for each F_{hkl}.

A statistical analysis of the intensities of the hko reflections (Wilson, 1942) gave an apparently low estimate of the overall temperature factor of 2·8Å^2 for the atoms in the molecule. The expression used for w_{hkl} gives a set of coefficients intermediate to those from point atoms at rest and point atoms.

The Patterson function was solved by choosing a sharply defined peak 4.8Å from the origin as arising from the single weight vector due to C3' - C3 and superimposing this on the origin. (see fig. I). This three-dimensional superposition gave regions of positive overlap in positions consistent with all six atoms in the asymmetric unit, but for C4 there was a choice of two peaks, one of which was eliminated by further superpositions. The appearance of this spurious peak was probably due to the boron-nitrogen vector orientated similarly to the C3 - C4 vector.

The coordinates obtained from the superposition were as follows and gave interatomic distances and angles consistent with the proposed dimeric structure.

Atom	x	y	z	Å
N	0.92	0.60	0.79	
C1	-0.92	1.79	-1.58	
C2	0.92	0.60	-2.10	
C3	1.44	1.79	1.18	
C4	2.10	1.79	2.63	
B	0.13	0.60	-0.92	

A set of structure factors was calculated using these coordinates. The value of the residual, R, was 0.59 where

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

Structure Refinement

Refinement was carried out at first from a three dimensional F_o synthesis computed at the same intervals as the Patterson function using the signs of the calculated structure factors with their observed magnitudes.

The expression used was

$$p(xyz) = \frac{4}{V} \sum_{o}^{h} \sum_{o}^{k} \sum_{o}^{l} \left[F_{hkl}^{h+k\,=\,2n} \cos 2\pi(hx + lz) + F_{hk\bar{l}} \cos 2\pi(hx - lz) \right] \cos 2\pi ky \; +$$

$$\sum_{o}^{h} \sum_{o}^{k} \sum_{o}^{l} \left[F_{hkl}^{h+k\,=\,2n+1} \sin 2\pi\,(hx + lz) + F_{hk\bar{l}} \sin 2\pi(hx - lz) \right] \sin 2\pi ky$$

This gave well defined peaks in positions corresponding to five of the atomic sites, and with heights consistent with their atomic number. The carbon peak heights were between 4 and 5 e Å^{-3}. The sixth peak, corresponding to C2, was much more smeared out along b. The y-coordinate of C2 was adjusted until calculated structure factors gave a residual of 0·47. Two further cycles of refinement caused the residual to fall to 0·39 and then to 0·31. At this stage the coordinate shifts were of the order of 0·1Å.

Refinement was continued by calculating an $F_o - F_c$ synthesis.

The shifts in the coordinates were derived by means of the expression (see Introduction).

$$\delta r = \frac{\dfrac{d(\rho_o - \rho_c)}{dr}}{2\rho_o(o)p}$$

with the atomic positions being moved in the direction of maximum gradient. Values of $\rho_o(o)$ and p were obtained by plotting $\log \rho_r$ against r^2 for C2 and N.

Temperature factor corrections for the atoms were calculated, assuming (wrongly) the scaling to be correct, from the values of the electron density at the atomic sites. The simplified expression $\rho_o - \rho_c = -\pi I_4 \Delta B$ and the suggested value for I_4 (Schomaker, 1957) were used. Where $\rho_o - \rho_c$ is negative at the atomic sites the temperature factors are too low.

Structure factors calculated using these corrections to the coordinates and temperature factors gave a residual of 0·29. As $\Sigma|F|_o$ and $\Sigma|F_c|$ for these structure factors were still very different the scale and temperature factors were corrected as follows.

Structure factors for the hko and okl nets were used to plot values of $\ln(\Sigma|F|_o / \Sigma|F|_c)$ against $\sin^2\theta$ for ranges of $\sin\theta$. From the intercept and slope of this line, K, the scale factor, and the change in B can be measured.

$$KF_o = F_c \exp(-\Delta B \sin^2\theta/\lambda^2)$$

$$\ln(\Sigma|F_o|/\Sigma|F_c|) = \ln(1/K) - \Delta B\sin^2\theta/\lambda^2$$

The values of B used were found to be too high and K too low. Altering the scale and temperature factors in this way improved the residual from 0·29 to 0·265.

A second difference map was computed which resulted in a residual of 0·215. At this stage the coordinate shifts were of the order of 0·02Å.

As a least-squares computer program was now available, refinement was continued isotropically for all six atoms to a residual of 0·177, the average shift after five cycles being 0·002Å. All six atoms were then refined anisotropically to a residual of 0·139.

Hydrogen atoms.

At this stage in the refinement a difference map was computed which showed peaks of height about 0·25 e.A^{-3} that could all be explained as being due to the hydrogen atoms and all the hydrogen atoms could be accounted for in this way. The mean C-H distance for the methyl hydrogens ranged from 0·83 to 1·1Å with a mean value of 1·03Å. The C-C-H angles ranged from 102° to 131° with a mean value of 112°. The single hydrogen, H7, was 1·21Å from C4.

Structure factors calculated including all ten hydrogen atoms in these positions gave, after one further cycle of refinement of the atoms other than hydrogen a residual of 0·1204, the final value.

The final cycle of refinement.

No. of planes = 646, $\sum|F_o| = 3681{\cdot}45$, $\sum|F_c| = 3639{\cdot}38$, $R = 0{\cdot}1207$, $R' = 0{\cdot}0313$.

In the final cycles refinement the weighting scheme used was $w = 1/(a + |F_o| + c(F_o)^2)$.

w appears in the quantity R', which is that minimised in the least-squares calculations.

$$R' = \sum w \frac{(|F_o| - |F_c|)^2}{\sum w |F_o|^2}$$

In the last cycle of refinement values of a of 3·2 and c of 0·3 were used. The final shifts in the coordinates ranged from 0·03 to 0·15 of the corresponding e.s.d., the average value being 0·004Å. The average shift in temperature factors, for this cycle was 0·0002Å^2. These shifts varied from 0 to 0·12 of the corresponding e.s.d.

The final values of the atomic coordinates are shown in table I and the thermal parameters in table II. The unobserved planes were not included in the refinement, but none of these were found to be significantly greater than their minimum observable value. The final values of the structure factors are listed in table V.

The scattering curves quoted in International Tables for X-ray Crystallography Volume III, page 202, were used.

Table I. $(Me_2BNCHMe_2)_2$

Atomic Coordinates and their e.s.d.'s

Atom	x	y	z	σ(x)	σ(y)	σ(z)	Å
N	0·7066	0·7515	0·5872	0·0036	0·0036	0·0041	
C1	-0·7789	1·5803	-1·8933	0·0074	0·0058	0·0071	
C2	1·4288	-0·1259	-1·6144	0·0063	0·0070	0·0075	
C3	1·5535	1·6238	1·2468	0·0052	0·0052	0·0060	
C4	1·9978	1·7607	2·7625	0·0065	0·0065	0·0072	
B	0·1745	0·4231	-1·0208	0·0056	0·0053	0·0064	
H1	2·1000	2·0000	0·4000				
H2	-0·5400	2·4000	-2·3000				
H3	-1·4500	1·8000	-1·3000				
H4	-1·3500	1·3000	-2·8500				
H5	1·3000	1·5000	3·4000				
H6	3·0000	1·5000	3·2000				
H7	1·9100	2·5300	3·0240				
H8	1·9100	0·5960	-1·5780				
H9	1·0920	-0·5960	-2·3670				
H10	1·9100	-0·8940	-0·9200				

Table II. $(Me_2BNCHMe_2)_2$

Thermal parameters in Å^2 and their e.s.d.'s in 10^3 Å^2 in brackets.

Atom	U_{11}	U_{22}	U_{23}	U_{12}	U_{23}	U_{13}
N1	0·0358(2)	0·0455(2)	0·0313(3)	-0·0025(1)	-0·0039(3)	0·0074(2)
C1	0·0895(5)	0·0609(3)	0·0672(5)	0·0035(3)	0·0213(3)	-0·0081(4)
C2	0·0678(4)	0·1002(5)	0·0748(5)	-0·0115(4)	-0·0189(4)	0·0399(4)
C3	0·0505(3)	0·0605(3)	0·0517(4)	-0·0038(2)	-0·0128(3)	0·0060(3)
C4	0·0615(3)	0·0857(4)	0·0683(5)	-0·0099(3)	-0·0252(3)	-0·0001(3)
B	0·0446(3)	0·0472(3)	0·0422(4)	-0·0040(2)	0·0064(2)	0·0103(3)

The isotropic temperature factor used for all the hydrogen atoms had the value 0·1106.

Table III. $(Me_2BNCHMe)_2$

Bond distances and angles.

B-C1	1·602Å	0·008Å
B-C2	1·620	0·008
B-N	1·588	0·006
B-N'	1·596	0·006
N-C3	1·272	0·006
C3-C4	1·468	0·007
B-N mean	1·592	0·004
B-C mean	1·611	0·006
B-N-B'	93·6°	0·3°
N-B-N'	86·4	
C1-B-C2	116·9	0·4
N-C3-C4	125·2	0·5
B-N-C3	131·4	0·4
B'-N-C3	134·7	0·4°

Description of the Structure

As expected from the chemical evidence, the molecule is dimeric and contains a four-membered boron-nitrogen ring with a double bond attached to nitrogen. It is the trans isomer. The interatomic distances and angles together with their estimated standard deviations are shown in Table III and also in Fig. I. The lengths of the chemically equivalent bonds B-N and B-N' and also B-C1 and B-C2 do not differ significantly from one another and their mean values are illustrated in the figure and are included in the table.

The ring bonds are formally single and the average B-N distance of 1·592 ± 0·004Å is the same as that of 1·591 ± 0·006Å in $(BCl_2NMe_2)_2$ (Hess, 1963) which also contains a four-membered boron-nitrogen ring. This close agreement arises in spite of the nitrogen atoms being formally sp^2 hybridised in the present work and sp^3 hybridised in the other case. In both instances the bond angles in the rings are nearly 90° and the atomic orbitals involved in the ring formation must depart considerably from their formal hybrid states. Similar lengths are found in other compounds. The B-N distance in $(CH_3)_2NBF_3$ (Geller and Hoard, 1951) is 1·58Å and in the $[BH_2(NH_3)_2]^+$ ion (Nordman, 1959) it is 1·58 ± 0·02Å.

The carbon-nitrogen double bond, $N{=}C_3$, has a length of 1·272Å, the same as in $(Bu^tMeCNAlMe_2)_2$. This value is also found for dimethylglyoxime (Merritt and Lanterman, 1952). The mean B-C distance of

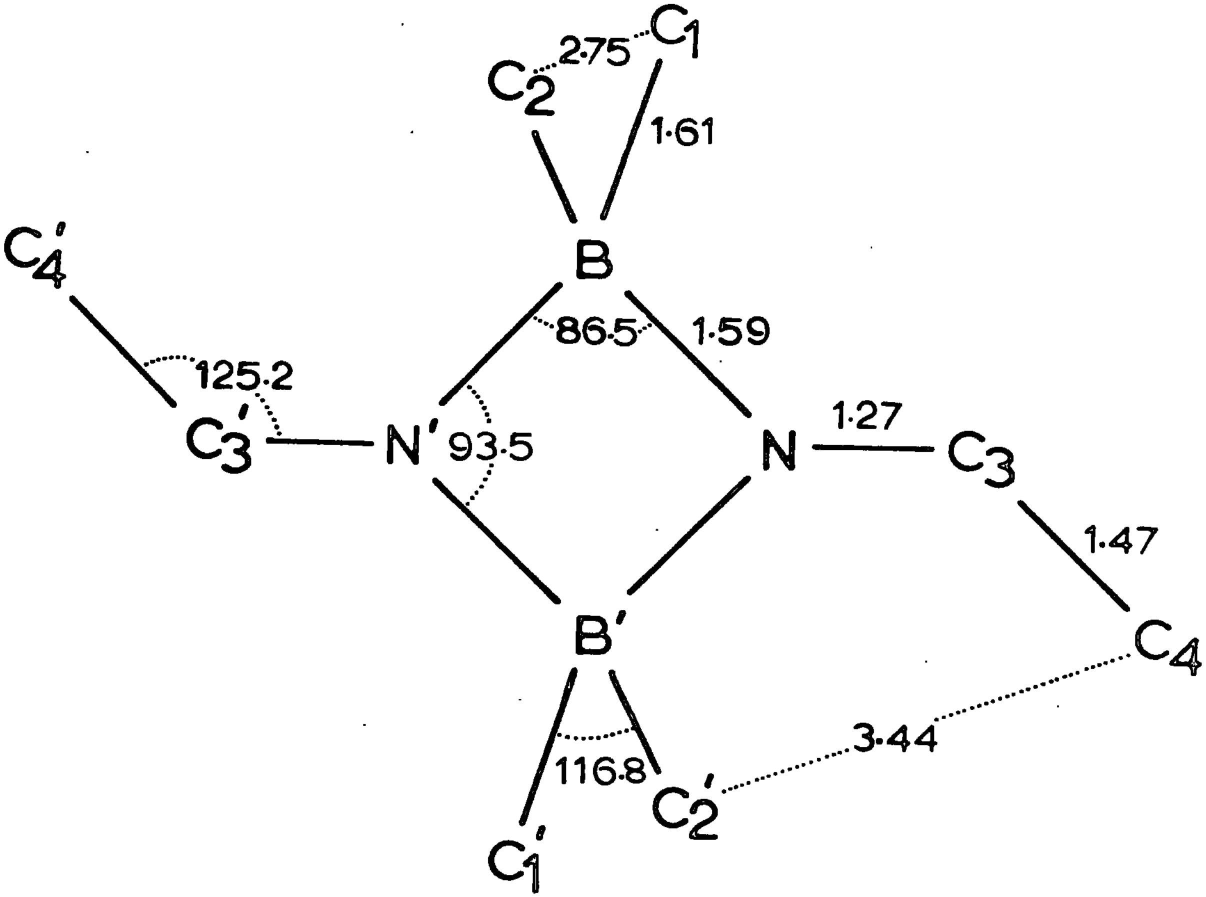


FIG. I. $(Me_2BNCHMe)_2$

1·611 ± 0·006Å is the same as that in tetramethyl diborane (Hedberg and Schomaker, 1951).

However the C3-C4 distance of 1·468 ± 0·007Å is much shorter than that expected for a bond involving atoms in sp^2 and sp^3 hybrid states. Pauling (1960) estimates the shortening for a C-C single bond adjacent to a C=C double bond as of the order of 0·02Å. No comparable shortening is found in $(Bu^tMeCNAlMe_2)_2$ and in dimethylglyoxime the corresponding distance is 1·53Å. On the basis of the significance tests proposed by Cruickshank (1953), the difference between the above value and that of 1·53 ± 0·01Å is highly significant. The molecular librations will lead to an apparent shortening in the bond lengths and the effect would be expected to be greatest for this terminal bond. However only a part of the shortening can be explained in this way.

The ring angle at nitrogen is greater than 90°. This might be expected from its formal sp^2 hybrid nature and its greater electronegativity than boron. However in $(BCl_2NMe_2)_2$ where all the ring atoms are formally sp^3 hybridised, the angle at boron is 93·1° compared with 86·4° in the present work. With the reduction in the ring angle at boron from the tetrahedral value, the angle C1-B-C2 is increased to 116·8° and leads to a C1-C2 distance of 2·75A.

The B'-N-C3 angle of 134·7° is greater than B-N-C3 which is 131·7°. This distortion increases the distances between C4 and the methyl carbons on B' to 3·44 and 3·45Å. Similarly the increase in the angle N-C3-C4 to 125·2°, greater than the trigonal value, increases the non-bonding contacts involving C4.

The equation of the mean plane through B, N, C3 and the atoms related by the centre of symmetry is

$$0{\cdot}769x' - 0{\cdot}633y + 0{\cdot}076z' = 0$$

where the atoms are referred to orthogonal axes parallel to a, b and c*.

The distances of the atoms from this plane are as follows:

N	0·009Å
C1	-1·353
C2	1·391
C3	0·004
C4	0·061
B	0·000

C4 is therefore at a distance of 0·06Å from the mean plane.

The equation of the mean plane through B, C1, C2 and the atoms related by the centre of symmetry is

$$0{\cdot}489x' + 0{\cdot}695y + 0{\cdot}527z' = 0$$

where the atoms are referred to axes as above. The distances of the atoms from this plane are:

B	-0·006Å
C1	0·002
C2	0·002

and the atoms are co-planar. The angle between the two mean planes is 89°.

The temperature parameters are generally greater for atoms furthest from the molecular centre and are smallest for the boron and nitrogen atoms. In addition the values appear smaller for nitrogen than for boron which is consistent with some increased concentration of electrons at nitrogen.

The intermolecular contacts of less than 4·4Å are listed in Table IV where the second atom is situated at the position indicated in the Table. The two contacts of less than 4Å are from C2 to C3 and C4 of the next molecule along a. Figs. II and III show the molecular packing.

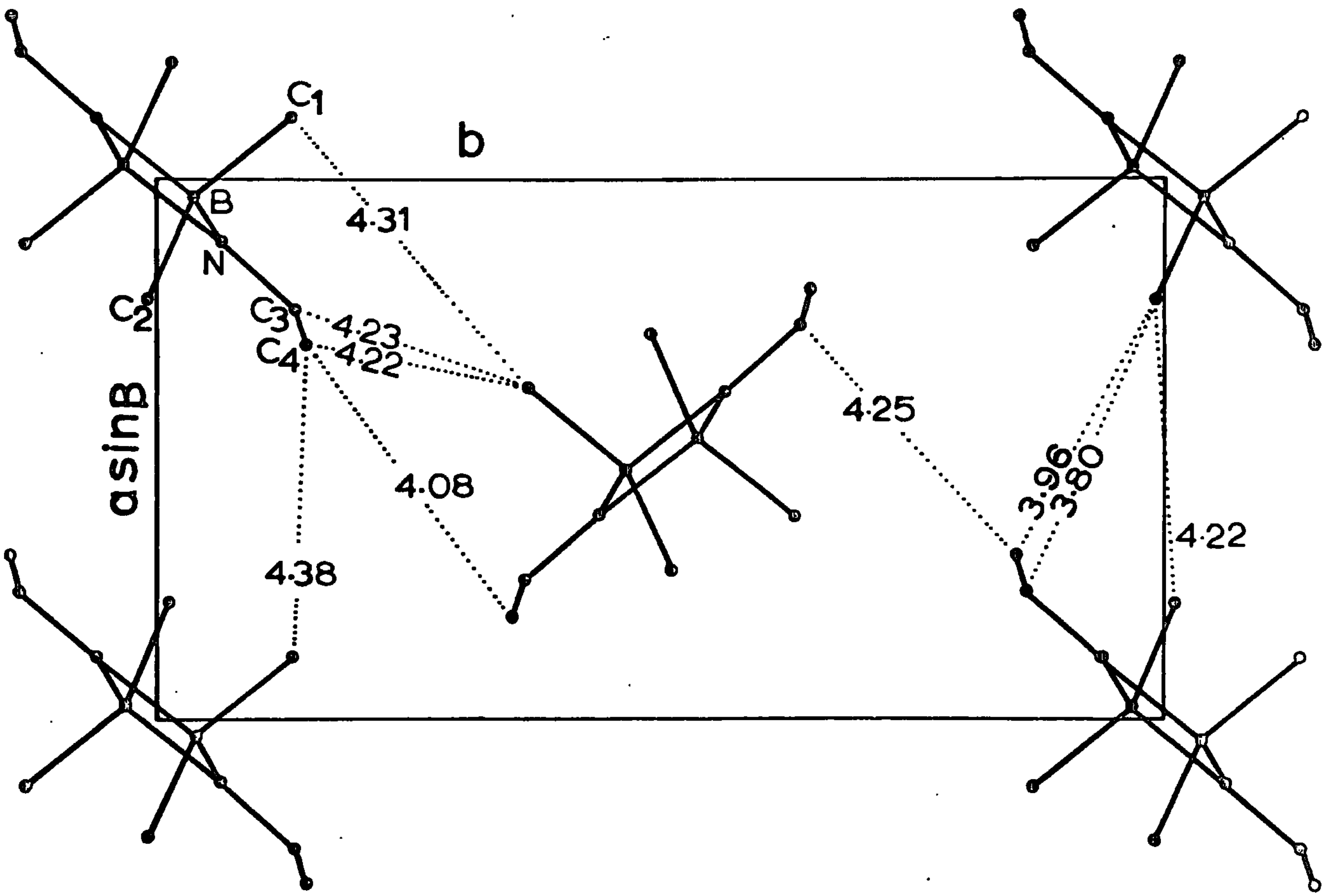


FIG. II. $(Me_2BNCHMe)_2$ 001 projection

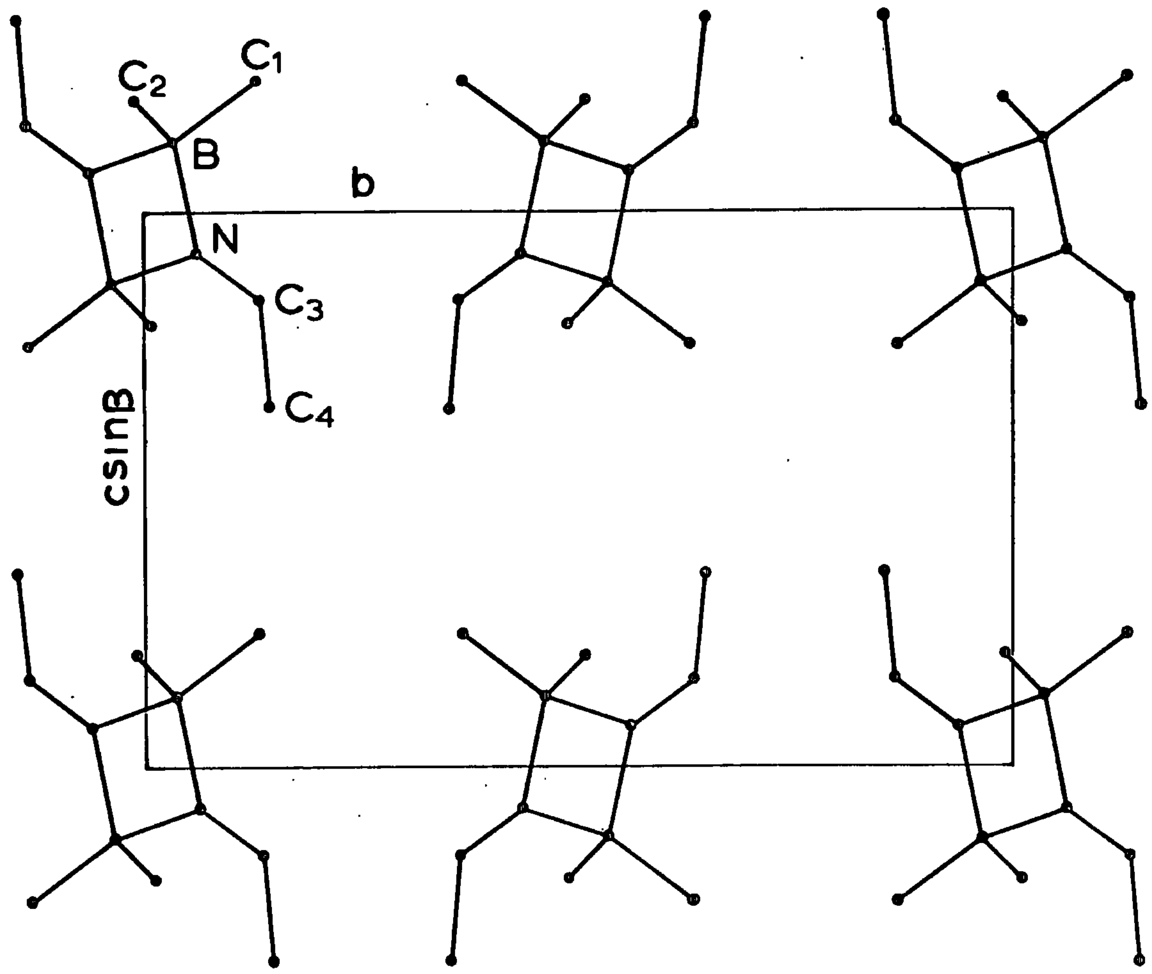


FIG. III. $(Me_2BNCHMe)_2$ 100 projection

Table IV. $(Me_2BNCHMe)_2$

Non bonding contacts.

Intramolecular contacts.

C1	C2	2·745
C2'	C4	3·454
C1'	C4	3·442

Intermolecular contacts.

C2	C3	$1-x,\bar{y},\bar{z}$	3·80A°
C2	C4	$1-x,\bar{y},\bar{z}$	3·961
C4	C4	$x-\frac{1}{2},\frac{1}{2}-y,z$	4·08
C4	C2	$x,y,1+z$	4·16
C2	C2	$1-x,\bar{y},\bar{z}$	4·221
C2	C4	$x-\frac{1}{2},y-\frac{1}{2},\bar{z}$	4·22
C2	C3	$x-\frac{1}{2},y-\frac{1}{2},\bar{z}$	4·23
C3	C3	$x-\frac{1}{2},\frac{1}{2}-y,z$	4·25
C4	C1	$1+x,y,1+z$	4·27
C1	C1	$\frac{1}{2}+x,\frac{1}{2}-y,z$	4·32
C3	C4	$x-\frac{1}{2},1-y,z$	4·38

TABLE V. $(Me_2BNCHMe_2)_2$.

Observed and calculated structure factors.

h	k	l	10Fo	10Fc
0	0	1	246	383
0	0	2	281	-336
0	0	3	144	-151
0	0	4	128	-140
0	0	5	22	-10
0	0	6	<48	-15
0	0	7	50	-53
0	1	1	126	-139
0	1	2	19	7
0	1	3	205	-220
0	1	4	57	-47
0	1	5	82	83
0	1	6	<48	-14
0	1	7	36	-38
0	2	0	338	417
0	2	1	261	316
0	2	2	25	-27
0	2	3	121	-143
0	2	4	41	-35
0	2	5	23	-26
0	2	6	34	-45
0	3	1	72	-89
0	3	2	96	-101
0	3	3	168	-176
0	3	4	62	-68
0	3	5	<12	3
0	3	6	39	-47
0	3	7	36	-33
0	3	8	<51	9
0	3	9	36	32
0	4	0	227	-251
0	4	1	81	73
0	4	2	72	65
0	4	3	58	-51
0	4	4	33	20
0	4	5	25	-14
0	5	1	23	27
0	5	2	55	-66
0	5	3	45	45
0	5	4	61	-56
0	5	5	159	-158
0	5	6	56	-58
0	5	7	<51	14
0	5	8	43	31
0	5	9	43	40
0	6	0	115	114
0	6	1	51	-45
0	6	2	135	-139
0	6	3	58	-51
0	6	4	<15	-10
0	6	5	60	53
0	6	6	56	59
0	7	1	21	-17
0	7	2	40	39
0	7	3	36	49
0	7	4	47	-43
0	7	5	60	-50
0	8	0	56	55
0	8	1	62	-62
0	8	2	117	-102
0	8	3	54	-48
0	8	4	34	32
0	8	5	79	73
0	9	1	<15	9
0	9	2	48	43
0	9	3	<15	9
0	9	4	35	27
0	9	5	60	50
0	10	0	101	-101
0	10	1	44	-47
0	10	2	<14	-4
0	10	3	<17	8
0	10	4	43	47
0	10	5	21	25
0	11	1	41	39
0	11	2	28	27
0	11	3	39	39
0	11	4	49	46
0	12	0	49	-43
0	12	1	19	-17
0	12	2	18	16
0	12	3	27	26
0	12	4	13	15
0	13	1	<11	10
0	13	2	23	25
0	13	3	36	41
0	13	4	11	12
1	1	-6	63	-55
1	1	-5	60	-72
1	1	-4	67	79
1	1	-3	81	79
1	1	-2	73	-65
1	1	-1	379	426
1	1	0	319	438
1	1	1	136	137
1	1	2	13	-11
1	1	3	205	-212
1	1	4	83	-114
1	1	5	60	-15
1	1	6	44	-59

h	k	l	10Fo	10Fc
1	2	-6	42	-38
1	2	-5	52	54
1	2	-4	212	221
1	2	-3	91	95
1	2	-2	17	-10
1	2	-1	247	-239
1	2	0	257	-299
1	2	1	102	101
1	2	2	151	-172
1	2	3	101	-112
1	2	4	94	99
1	2	5	<13	1
1	2	6	45	-57
1	3	-6	37	-24
1	3	-5	35	33
1	3	-4	<11	1
1	3	-3	81	78
1	3	-2	39	33
1	3	-1	385	-415
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1	3	1	480	525
1	3	2	108	110
1	3	3	61	-68
1	3	4	174	-175
1	3	5	83	-96
1	3	6	50	33
1	4	-6	106	116
1	4	-5	89	60
1	4	-4	49	56
1	4	-3	62	59
1	4	-2	64	-62
1	4	-1	38	-45
1	4	0	15	21
1	4	1	159	-160
1	4	2	82	-80
1	4	3	23	-22
1	4	4	84	-87
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1	5	1	137	137
1	5	2	52	63
1	5	3	55	-50
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1	5	5	17	22
1	5	6	51	52
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1	6	-3	60	-56
1	6	-2	67	-57
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1	8	2	36	33
1	8	3	<17	-2
1	8	4	47	40
1	9	-3	18	-17
1	9	-2	62	-64
1	9	-1	62	-67
1	9	0	42	-32
1	9	1	27	-22
1	9	2	21	-15
1	9	3	31	35
1	9	4	60	57
1	9	5	29	26
1	10	-5	23	-22
1	10	-4	16	11
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1	10	-2	45	-44
1	10	-1	42	-36
1	10	0	26	20
1	10	1	58	63
1	10	2	36	36
1	10	3	44	40

h	k	l	10Fo	10Fc
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1	11	-3	29	24
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1	11	0	48	-44
1	11	1	31	25
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1	12	-3	23	-30
1	12	-2	23	-23
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1	12	0	51	42
1	12	1	27	25
1	12	2	39	33
1	12	3	30	30
1	13	-4	19	22
1	13	-3	23	24
1	13	-2	11	12
1	13	-1	<13	3
1	13	0	11	-12
1	14	-3	21	-23
1	14	-2	<9	-2
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1	14	0	9	9
1	14	2	15	15
1	15	-1	16	21
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2	0	-2	403	411
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2	0	5	169	-177
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2	1	-4	54	62
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2	4	-3	61	62
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2	4	-1	99	-85
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2	4	1	150	131
2	4	2	77	84
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3	3	5	38	28
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3	4	-4	23	17
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3	8	-3	<17	-8
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3	9	-3	42	-35
3	9	-2	<14	1
3	9	-1	22	15
3	9	0	18	-16
3	9	1	<16	7
3	9	2	53	54
3	9	3	41	35
3	10	-5	17	21
3	10	-4	21	20
3	10	-3	<17	-4
3	10	-2	17	-14
3	10	-1	23	20
3	10	0	37	37
3	10	1	26	21
3	10	2	13	15
3	11	-5	22	-24
3	11	-4	<15	2
3	11	-3	<16	10
3	11	-2	13	13
3	11	-1	<15	13
3	11	0	<43	-8
3	11	1	<15	-7
3	11	2	18	-15
3	11	3	<13	-12
3	11	4	23	31
3	12	-2	33	35
3	12	-1	<13	-1
3	12	0	11	-9
3	12	1	22	18
3	12	2	13	15
3	13	-3	19	24
3	13	-2	12	13
3	13	-1	<11	-10
3	13	0	13	-13
3	13	1	<10	-22
3	13	2	16	-18
4	0	-5	93	88
4	0	-4	47	-57
4	0	-3	153	-139
4	0	-2	122	-127
4	0	-1	75	58
4	0	0	<37	21
4	0	1	87	-67
4	0	2	<13	2
4	0	3	78	-73
4	0	4	99	-97

h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc
4	1	-5	19	-17	4	6	-5	21	-19
4	1	-4	33	-14	4	6	-4	37	-40
4	1	-3	111	-97	4	6	-3	49	-52
4	1	-2	11	-5	4	6	-2	28	-30
4	1	-1	86	73	4	6	-1	70	70
4	1	0	44	-51	4	6	0	64	73
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4	1	2	<13	-10	4	6	2	44	45
4	1	3	<12	6	4	6	3	<17	17
4	1	4	60	61	4	6	4	15	-18
4	1	5	25	22	4	7	-5	19	15
4	2	-5	82	83	4	7	-4	<17	7
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4	2	-2	51	-43	4	7	-1	57	-57
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4	2	1	29	15	4	7	2	48	46
4	2	2	67	-54	4	7	3	31	26
4	2	3	36	-31	4	7	4	14	18
4	3	-4	70	-38	4	8	-4	49	-42
4	3	-3	120	-106	4	8	-3	44	-39
4	3	-2	63	-56	4	8	-2	<14	1
4	3	-1	25	-24	4	8	-1	57	54
4	3	0	54	-60	4	8	0	42	47
4	3	1	42	-32	4	8	1	34	36
4	3	2	29	22	4	8	2	39	41
4	3	3	68	66	4	8	3	<16	-1
4	3	4	77	78	4	8	4	13	-13
4	3	5	32	26	4	9	-2	27	25
4	4	-5	29	32	4	9	-1	45	40
4	4	-4	<16	-5	4	9	0	15	-15
4	4	-3	30	-40	4	9	1	32	-24
4	4	-2	<12	1	4	9	2	13	-10
4	4	0	22	29	4	9	3	<14	5
4	4	1	<15	11	4	9	4	22	24
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4	4	3	20	29	4	10	-4	<15	4
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4	5	0	39	-29	4	10	4	31	29
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4	5	4	15	16	4	12	-4	17	17

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4	12	-2	<10	6
4	12	-1	<11	-2
4	12	0	<32	-9
4	12	1	18	-23
4	13	-3	19	25
4	13	-2	<7	9
4	13	-1	<8	-8
4	13	0	6	0
5	1	-5	37	39
5	1	-4	<16	-5
5	1	-3	90	-85
5	1	-2	81	-74
5	1	-1	47	-36
5	1	0	26	-26
5	1	1	<16	24
5	1	2	18	-11
5	1	3	50	-40
5	2	-4	51	-49
5	2	-3	44	-28
5	2	-2	30	32
5	2	-1	40	-39
5	2	0	41	-43
5	2	1	<16	24
5	2	2	26	24
5	2	3	67	95
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5	3	-5	64	61
5	3	-4	42	36
5	3	-3	29	-25
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5	3	2	<14	10
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5	4	2	64	67
5	4	3	30	42
5	4	4	25	23
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5	5	-4	35	30
5	5	-3	21	-15
5	5	-2	45	-40
5	5	-1	<16	3
5	5	0	45	50
5	5	1	44	39
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5	5	3	<16	-2
5	5	4	17	-14
5	6	-3	53	-48
5	6	-2	73	-79
5	6	-1	25	-21
5	6	0	21	23
5	6	1	41	43
5	6	2	39	38
5	7	-2	46	41
5	7	-1	50	53
5	7	0	26	27
5	7	1	40	40
5	8	-1	19	-24
5	8	0	20	-21
5	8	1	14	-6
5	8	2	<12	-6
5	8	3	25	27
5	9	-3	24	20
5	9	-2	21	19
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5	9	0	23	28
5	9	1	13	12
5	10	-4	28	24
5	10	-3	17	19
5	10	-2	34	17
5	10	0	20	-23
5	10	1	24	-28
5	11	-4	17	21
5	11	0	7	8
5	13	0	6	-13
6	0	-5	27	-21
6	0	-4	27	-25
6	0	-3	<17	0
6	0	-2	44	-41
6	0	-1	111	-114
6	0	0	29	-36
6	1	-3	19	14
6	1	-2	25	-23
6	1	-1	25	-21
6	2	-3	35	-32
6	2	-2	69	-70
6	2	-1	45	-51
6	2	0	<45	-9
6	2	1	33	28
6	2	2	41	38
6	3	-2	26	-23

h	k	l	10Fo	10Fc
6	3	-1	<16	-14
6	3	0	<45	12
6	3	1	35	32
6	3	2	58	60
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6	4	-3	35	-27
6	4	-2	48	-48
6	4	-1	<16	8
6	4	0	13	18
6	4	1	29	28
6	4	2	29	29
6	5	-3	29	-31
6	5	-2	<13	-2
6	5	-1	<15	14
6	5	0	12	15
6	5	1	38	38
6	6	-4	19	21
6	6	-3	42	41
6	6	-2	24	28
6	6	-1	<16	-7
6	6	0	<43	9
6	6	1	21	18
6	7	-2	16	-17
6	8	-4	20	25
6	8	-3	43	52
6	8	-2	31	37
6	9	-5	25	28
6	9	-4	26	28
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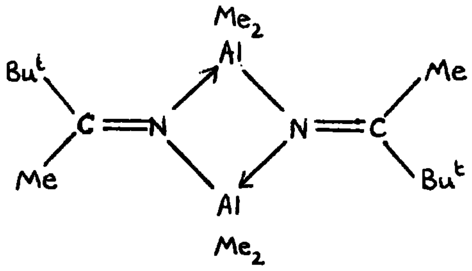
6	9	-2	17	-18
6	9	-1	24	-30
6	9	0	15	-21
6	10	-1	13	16
7	1	-5	26	-28
7	1	-4	28	-32
7	1	-3	19	-21
7	1	-2	39	-43
7	1	-1	34	-36
7	2	-1	22	19
7	2	0	8	11
7	3	-5	17	-18
7	3	-4	37	-37
7	3	-3	26	-30
7	3	-2	15	12
7	4	-3	23	21
7	4	-2	18	17
7	4	-1	<13	4
7	4	0	10	14
7	5	-3	13	8
7	5	-2	18	17
7	6	-4	14	14
7	6	-3	22	25
7	6	-2	10	13
7	7	-4	22	27
7	7	-3	31	-38
8	0	-4	26	-27
8	0	-3	41	-50
8	0	-2	26	-27
8	0	-1	12	11
8	1	-2	19	20
8	2	-4	26	-28
8	2	-3	21	-24
8	4	-3	18	1

The Crystal Structure of 2,2' dimethylbutylidene-3-aminodimethylaluminium dimer $(Bu^tMeCNAlMe_2)_2$.

Introduction.

Trialkylaluminiums react with alkyl cyanides forming adducts which rearrange on heating, giving products thought to contain a nitrogen-aluminium four-membered ring system. Unlike the analagous boron compounds only one product is formed in most cases and this is thought to be exclusively the trans isomer (Wade and Jennings, 1965). These compounds are much more readily hydrolysed than the corresponding ethylideneaminoboranes, but for the compounds in which there is most crowding of the groups round the aluminium the hydrolysis is very slow and $(Bu^tMeCNAlMe_2)_2$ is hydrolysed very slowly indeed. This compound is also unusual in that it does not undergo further rearrangement and is not further attacked by trimethylaluminium. $(Bu^tCMeNAlMe_2)_2$ was studied for comparison with $(MeCHNBMe)_2$ and also to see whether the packing in the crystal would account for its unusual lack of reactivity compared with other aluminium compounds in the series.



Experimental

Plate-like crystals were grown by vacuum sublimation, cut to suitable shapes and mounted in sealed glass capillary tubes, the walls of which were about 0·06 mm. thick. These operations were carried out in a glove box in an atmosphere of oxygen free nitrogen.

Crystal data.

The unit cell dimensions were measured from photographs of the hol and okl nets photographed using Zr- filtered Mo radiation and the precession camera. The statistical errors in the cell dimensions measured from the photographs are 0·004Å in a, 0·006Å in b and 0·003Å in c. The actual error is probably about 0·5% of each dimension and 10' in β.

Orthorhombic a = 11·2Å, b = 14·86Å, c = 12·54Å, V = 2085Å^3 Z = 8 Bu^{t}MeCNAlMe$_2$ formula units. D$_x$ = 0·935 gm.cm^{-3}. μ(λ = 0·7107) = 1·186 cm^{-1}. μ(λ = 1·5418) = 10·5 cm^{-1}.

Reflections observed:-

hkl when h + k = 2n

hko when h = 2n (k = 2n)

hol when l = 2n (h = 2n)

okl when (k = 2n)

These are consistent with the centrosymmetric space group Cmca (International Tables for X-ray Crystallography, Vol. 1, No. 64) or with the non-centrosymmetric C2ca (Aba2, No. 41 if the directions of <u>a</u> and <u>c</u> are interchanged). The density calculated on the basis of eight Bu^{t}MeCNAlMe$_2$ units per unit cell is 0·935 gm.cm^{-3}, in agreement with the experimental value of between 0·91 and 0·96 gm.cm^{-3}.

If the space group is C2ca then the molecule must possess a two-fold axis lying along a. For the trans isomer this must be perpendicular to the plane of the ring. For the space group to be Cmca the molecule must possess, in addition, a mirror plane perpendicular to this two-fold axis. For the trans isomer to fulfill the symmetry requirements of this space group, the plane containing the ring atoms must coincide with the mirror plane and all of the atoms will lie in this plane, except the atoms of the two methyl attached to aluminium and also the atoms of two of the methyl groups forming part of the t-butyl group which will be related by the mirror plane.

Collection of Intensities.

As the absorption coefficient for this compound for Mo radiation is 1·186 cm^{-1} and the crystals were fairly small, no absorption correction was made to any of the data as Mo radiation was used throughout.

The hk0-hk6 nets were recorded using the equi-inclination angle Weissenberg technique and a needle shaped crystal of cross section 0·3 x 0·3 mm^2. A crystal shaped like a triangular plate mounted along its longest side and of height 0·6 mm. and thickness 0·4 mm. and the precession camera were used to record the nets okl-3kl, hol-h6l and some diagonal nets.

The intensities of these reflections were estimated visually using a graduated scale. After the usual Lorentz, polarisation and length corrections (Phillips, 1956) had been applied, the structure factors on the twenty four nets were correlated by a least-squares method.646 independent reflections were recorded, 161 of these appeared on only two nets and a further 185 on at least three.

The Patterson Function

The expression

$$P(uvw) = \frac{8}{V} \sum_{0}^{\infty} \sum_{0}^{\infty} \sum_{0}^{\infty} W_{hkl}^{2} \, |F_{hkl}|^{2} \cos 2\pi hu \cos 2\pi kv \cos 2\pi lw$$

was used to compute the three-dimensional Patterson function, the structure factors being weighted by means of the function $\exp \left\{ 12 \sin^{2}\theta/\lambda^{2} \right\}$. This function was allowed a maximum value of 100 so as not to give too large a weight to the weak high-order reflections.

The Patterson section P(Ovw) showed a large number of pronounced peaks, in agreement with the expected arrangement of the molecules in the cell. An examination of the aluminium-aluminium vectors allowed coordinates to be assigned to the aluminium atom. The x-coordinate of zero is compatible with either space group and can arise from this atom being situated in the mirror plane in the centro-symmetric space group or from the arbitrary position of the origin in the <u>a</u>-axis direction in the non-centrosymmetric one. Direct inspection of the Patterson function, together with the use of superposition methods, revealed the positions of all the atoms except those of the methyl carbons in the t-butyl group. With the omission of these atoms, the molecule was found to be essentially centrosymmetric and structure factors were calculated for these atoms, assuming a centrosymmetrical model. The residual R was 0·38.

An F_o synthesis was then evaluated at the same intervals as the Patterson function using the expression appropriate to the centrosymmetrical case, namely that for Cmca. This is

$$\rho(xyz) = \frac{8}{V}\left\{ \sum_{0} \sum_{0} \sum_{0}^{k + l + 2n} F_{hkl} \cos 2\pi hx \cos 2\pi ky \cos 2\pi lz \right.$$

$$\left. - \sum_{0} \sum_{0} \sum_{0}^{k + l = 2n + 1} F_{\bar{h}kl} \cos 2\pi hx \sin 2\pi ky \sin 2\pi lz \right\}$$

The electron density map showed peaks at positions corresponding to all the atoms whose positions had previously been determined. In addition, peaks corresponding to the methyl carbon atoms in the t-butyl group were also present. These peaks were very drawn out and, in one direction, fell to half their maximum value over a distance of about 2Å. The compound was now established as the trans isomer.

The inability to recognise peaks in the Patterson function arising from vectors involving the methyl carbon atoms in the t-butyl group did not permit a choice of space group to be made at that time. Calculation of the electron density in the centrosymmetrical space group resulted in their being a mirror plane at x = 0. Atoms, which are not related in pairs by the mirror plane, will give rise to peaks of electron density, above and below this plane, of weight one-half. The peaks which were smeared out in the F_o synthesis were thought to have arisen in this way from the overlap of peaks of lesser height. On this basis, coordinates were now given to the methyl carbon atoms in the t-butyl group. The positions of these atoms were not related by a mirror plane and the centre of symmetry in the structure was now removed, permitting systematic methods of refinement to be applied.

Refinement

The atomic parameters of the non-centrosymmetrical model in the space group Aba2 were refined by least-squares methods. With isotropic temperature factors the residual fell to 0·175 and with anisotropic temperature parameters to a value of 0·117. At this stage the temperature factors of two of the methyl carbons in the t-butyl group were very much larger than those of the third and were not consistent with the vibration of the group as a whole. The carbon-carbon distances in the t-butyl group ranged from 1·45 to 1·55A with quoted e.s.d.'s of about 0·03 and the carbon-carbon angles varied considerably amongst themselves. In addition, the molecule showed marked deviations from planarity in a not very systematic manner. At this stage, a difference map showed two peaks of height 0·5eÅ^{-3} close to two of the t-butyl methyl carbons and in positions related by the plane of the molecule, although these atoms had shown no tendency to move to positions related in this way during the refinement.

For these reasons it was thought that the space group might be the centrosymmetric Cmca and atomic coordinates were chosen in accordance with the required molecular symmetry. Of the three methyl carbon atoms in the t-butyl group, one now lay in the mirror plane at $x = 0$ with one above and one below this plane and related by it. The refinement of this model gave thermal parameters more easy to understand and more consistent bond distances and angles. The least-squares refinement was carried out with isotropic thermal parameters until a residual of 0·184 was obtained. Further refinement with anisotropic thermal parameters resulted in the final value of the residual being 0·114, calculated on the 524 observed reflections. A difference synthesis now showed no major features and in particular there were no marked positive or negative regions in the plane of the t-butyl methyl carbons.

It would appear that these atoms are undergoing very large vibrations, apparently as a rigid body, about the bond C3-C4 to the rest of the molecule rather than rotating freely about this bond. The space group was now established as Cmca.

The Final Cycle of Refinement.

No. of planes = 524, $|F_o|$ = 13052, $|F_c|$ = 12684, R = 0·114, R^1 = 0·0351.

In the final cycles of refinement the weighting scheme $W = 1/(a + |F_o| + c|F_o|^2)$ was used. a and c had the values 12 and 0·08 in the last cycle. The real part of the correction for dispersion was applied to the scattering factors for aluminium. The unobserved reflections were given zero weight in the refinement. The final coordinates and their e.s.d.'s are listed in Table VI and the final thermal parameters in Table VII. The average coordinate shift in the final cycle of refinement was 0·0018Å, the shifts ranging up to 0·25 of the corresponding e.s.d. The average shift in thermal parameters was 0·0015Å, the shifts varying from 0 to 0·35 of the corresponding e.s.d. The final values of the structure factors are listed in Table X.

The scattering factors used were those quoted in International Tables for X-ray Crystallography, Vol. 1, page 202.

Table VI. $(\mathrm{Bu^tMeCNAlMe_2})_2$. Atomic Coordinates and their standard deviations

Atom	x	y	z	σx	σy	σz	Å
A1	0	1·260	0·671	0	0·004	0·004	
N	0	-0·600	1·172	0	0·011	0·010	
C1	1·761	2·163	1·028	0·015	0·012	0·013	
C2	1·267	-1·317	4·322	0·028	0·029	0·019	
C3	0	-1·340	2·207	0	0·017	0·016	
C4	0	-0·827	3·664	0	0·016	0·013	
C5	0	-2·879	2·109	0	0·018	0·016	
C6	0	0·678	3·735	0	0·024	0·021	

Table VII. $(\mathrm{Bu^tMeCNAlMe_2})_2$

Thermal parameters in Å^2 and their e.s.d.'s in 10^3 Å^2 in brackets.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
A1	0·067(3)	0·034(2)	0·035(2)	0	0·005(2)	0
N	0·065(8)	0·037(6)	0·019(4)	0	0·010(4)	0
C1	0·082(9)	0·069(7)	0·072(8)	-0·025(7)	-0·008(6)	0·0004(7)
C2	0·209(23)	0·195(22)	0·093(11)	0·105(14)	-0·047(13)	-0·077(14)
C3	0·090(13)	0·058(10)	0·058(10)	0	0·017(9)	0
C4	0·062(10)	0·069(9)	0·026(6)	0	0·003(7)	0
C5	0·175(23)	0·046(9)	0·049(9)	0	0·010(8)	0
C6	0·232(32)	0·079(13)	0·053(10)	0	-0·025(11)	0

Description of the Structure

As expected, the molecule is a dimer and contains a four-membered ring system with a double bond attached to nitrogen. It is the trans isomer.

The bond lengths and angles are listed in Table VIII. The values for the chemically equivalent bonds Al-N and Al-N' (where N' refers to the atom related by the centre at 000) do not differ significantly from one another and their mean value is also quoted. The molecular dimensions are shown in fig. IV.

A value of 1·96Å (Pauling, 1960) is obtained for the length of an aluminium-nitrogen single bond for atoms in sp^3 hybrid states. As the nitrogen is formally sp^2 hybridised, a value of about 1·94Å might be expected. Both these values agree with the mean Al-N distance of 1·942 ± 0·008Å.

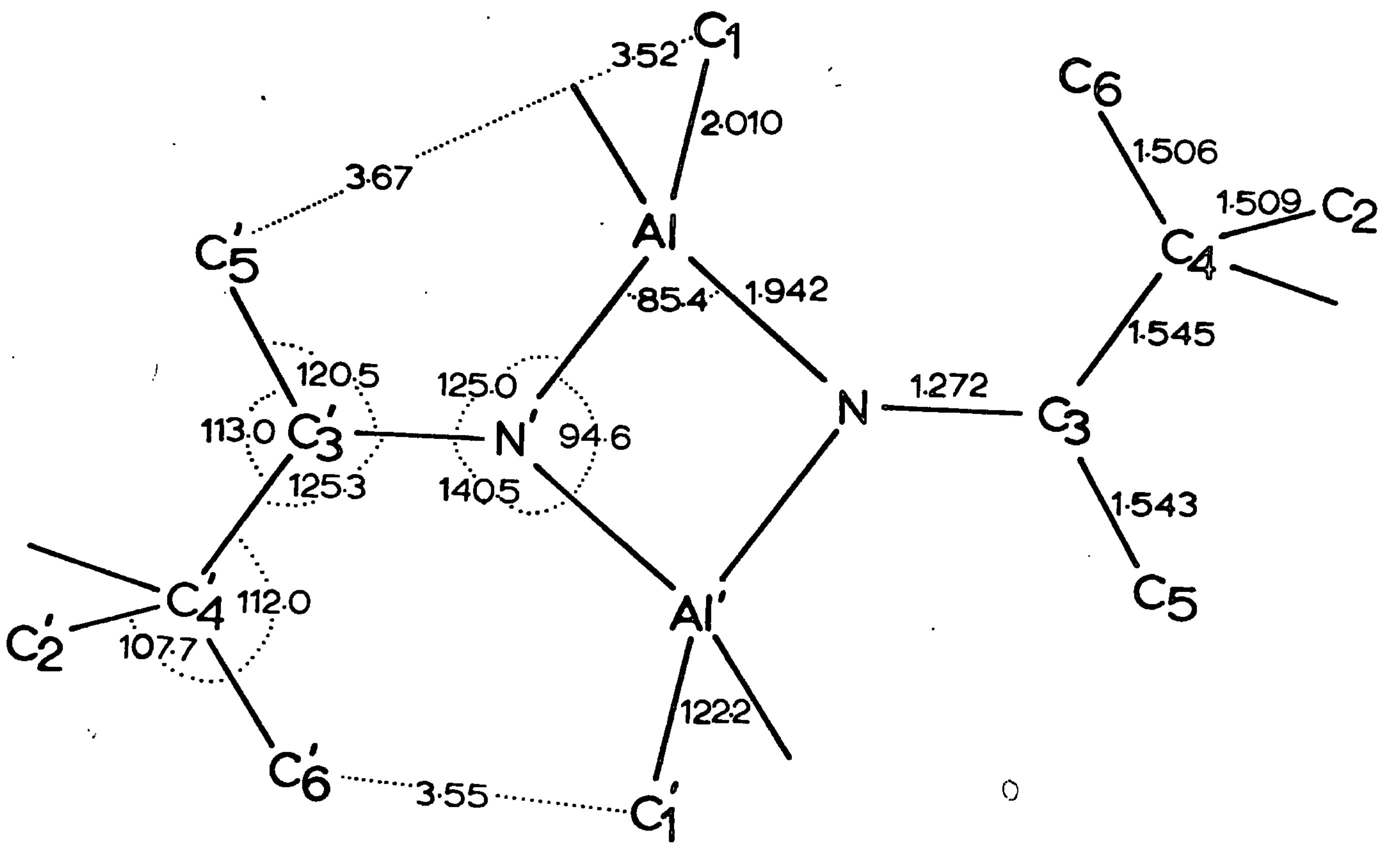
The Al-C1 distance of 2·01 ± 0·014Å is in good agreement with the value of 1·99Å found for the terminal aluminium-carbon bond in trimethylaluminium (Rundle, 1953). This distance is considerably greater than that of a boron-carbon bond and the separation between C1 and the atom related by the mirror plane is increased to 3·52Å, compared with 2·74Å in the boron compound examined previously. This distance is now greater than most of the other intramolecular non-bonding contacts.

The length of the carbon-nitrogen double bond N-C3 is 1·272Å, almost identical with that of the corresponding bond in $(MeHCNBMe)_2$ and of the

Table VIII. $(Bu^{t}MeCNAlMe_{2})_{2}$. Bond lengths and angles.

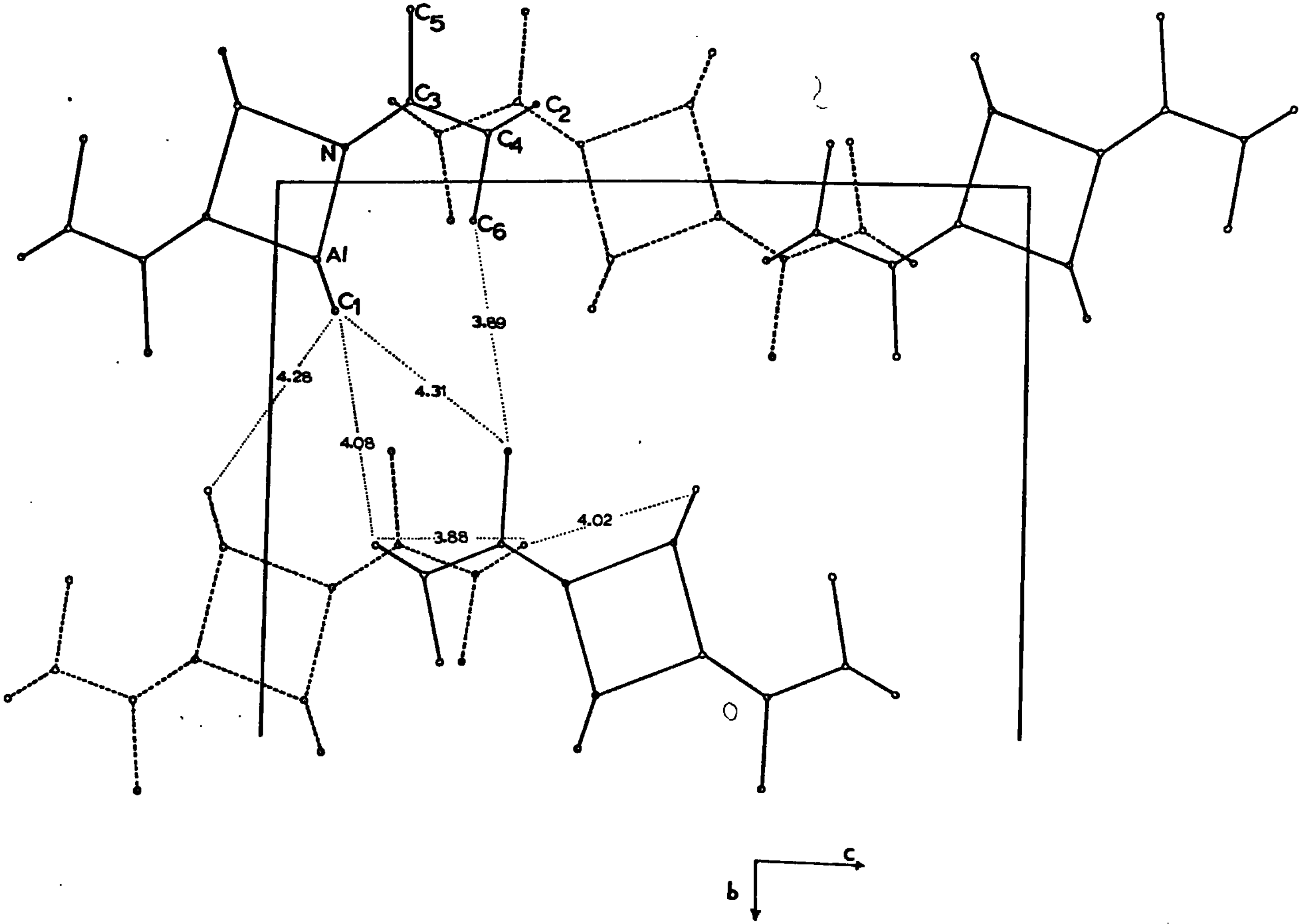
Al-N	1·927Å	0·011Å
Al-N'	1·958	0·011
Al-C1	2·010	0·014
N-C3	1·272	0·020
C3-C5	1·543	0·025
C3-C4	1·545	0·022
C4-C2	1·509	0·027
C4-C6	1·506	0·029
Al-N (mean)	1·942	0·008

N-Al-N'	85·4°	0·5°
Al-N-Al'	94·6	0·5
C1-Al-C1"	122·2	0·6
Al-N-C3	140·5	0·8
Al'-N-C3	125·0	0·8
N-C3-C4	125·3	1·0
N-C3-C5	120·5	1·1
C4-C3-C5	113·0	1·3
C3-C4-C2	107·6	1·1
C3-C4-C6	112·0	1·4
C2-C4-C6	107·7	1·2
C2-C4-C2"	114·2	1·6



$(Bu^tMeCNAlMe_2)_2$

FIG. IV. Molecular Geometry.



$(Bu^tMeCNAlMe_2)_2$ 100 projection

FIG. VI. Molecular packing in the unit cell.

double bond in dimethylglyoxime.

Neither of the carbon-carbon bonds adjacent to the double bond is shortened as in the boron compound. Their lengths of 1·545 ± 0·022Å for C3-C4 and 1·543 ± 0·025Å for C3-C5 do not differ significantly from the value of about 1·52Å, expected for a bond between carbon atoms in sp^2 and sp^3 hybrid states.

In the t-butyl group, the distances involving the methyl carbons are 1·509 ± 0·027Å for C2-C4 and 1·506 ± 0·029Å for C4-C6 and neither is significantly shorter than the standard value of 1·5445Å for diamond. However the space group symmetry requires that the thermal vibration tensor components U_{12} and U_{13} for C6 have zero value and this atom has its major axis of vibration parallel to $\underline{a}$. The correction for thermal oscillation effects (Cruickshank, 1956a) for the bond C4-C6 is 0·017Å giving a corrected length for this bond of 1·523Å. An increase in length of similar magnitude is expected for C2-C4.

As in the boron compound previously examined the ring angle at nitrogen is greater than 90°, presumably because of its formal sp^2 hybrid state and the greater electronegativity of nitrogen compared with aluminium. This angle at 94·6° is greater than in the earlier case, since aluminium forms longer bonds than boron and the bond angle at aluminium would be expected to deform more readily than the one at nitrogen. Corresponding to this reduction in the ring angle at aluminium, the angle C1-Al-C1" (where the C1" refers to the atom related by the mirror plane at x = 0) is increased to 122·2°, considerably greater than the tetrahedral value.

The values other angles seem best discussed in conjunction with the lengths of the non-bonding contacts which arise within the molecule. These together with the intermolecular contacts are listed in Table IX. The arrangement results in pairs of methyl carbons, related by the mirror plane, and methyl carbons lying on the mirror plane being situated round the circumference of the molecule and giving rise to maximum non-bonding contacts.

The distortion of the aluminium-nitrogen-carbon angles to 140° for Al-N-C3 and 125 for Al'-N-C3 increases the C1-C6 separation to 3·55Å making it comparable to the C1-C5 separation of 3·67Å and to corresponding intramolecular contacts in $(Me_2BNCHMe)_2$ of 3·45 and 3·44Å. The value of 112° for the angle C3-C4-C6 is not significantly greater than the tetrahedral value of 109° 28', but the N-C3-C4 angle of 125°, slightly greater than the trigonal value, will help to increase the C1-C6 separation. The value of 3·67 for the distance C1-C5 is in spite of the angle N-C3-C5 of 121° being nearly trigonal and Al'-N-C3 being 125°.

The angle C5-C3-C4 is only 113° which is much less than trigonal and the value for C2-C4-C3 of 108° is not significantly different to tetrahedral. As a result of the molecular geometry the separation between C2 and C5 at 2·99Å is much shorter than other contacts between methyl groups not bonded to the same atom. In hexamethyl benzene

(Robertson, 1939) the methyl contacts round the ring are 2·92 Å.

In the t-butyl group the angle C2-C4-C6 is 108° and close to tetrahedral whereas C2-C4-C2" where this angle is in a plane perpendicular to the plane of the molecule in 114°. The separation between C2 and C6 is 2·44 and that between C2 and C2" is 2·53Å.

All the atoms except C1 and C2 are fixed on the mirror plane by the requirements of the space group symmetry. The best line through N, C3 and the atoms related by the centre of symmetry is

$$x = 0, \ y = -0{\cdot}587z$$

N is 0·55Å from this and C3 - 0·038Å and the four atoms are not co-linear. The equation of the mean plane through Al, C1 and the atoms related by the centre of symmetry is

$$0{\cdot}0719x - 0{\cdot}4088y + 0{\cdot}90872z = 0$$

where x, y and z are parallel to the crystal axes. The angle between the normal to this plane and the mirror plane is 7°.

The intermolecular contacts are listed in Table IX. The only contacts of less than 4Å are between C2 and C2' of the next molecule at ($\frac{1}{2}$, 0, $\frac{1}{2}$) and C5 with C6 of the molecule at ($\frac{1}{2}$, $\frac{1}{2}$, 0).

The molecular packing is shown in fig. VL

The lack of reactivity of this compound compared with similar compounds of aluminium is explained by the molecular structure. The aluminium has two nitrogens and four methyl groups around it in a very distorted tetrahedral arrangement. In addition it has two methyl groups as more distant neighbours at 3·21 and 3·12Å and another aluminium atom at a distance of 2·8Å.

Table IX. $(Bu^tMeCNAlMe_2)_2$. Non-bonding contacts.

Intramolecular contacts.

C5'-C1	3·67Å
C1-C6	3·55
Al-C6	3·12
N-C6	2·86
Al-C5'	3·21
N-C5'	2·46
C6-C2	2·44
C2-C2"	2·53
C1-C1"	3·52
C2-C5	2·99

Intermolecular contacts.

C2-C2	$\frac{1}{2} - x, y, \frac{1}{2} - z$	3·878Å
C5-C6	$0, y - \frac{1}{2}, \frac{1}{2} - z$	3·891
C1-C2	$\frac{1}{2} - x, \bar{y}, z - \frac{1}{2}$	4·022
C1-C2	$x, \frac{1}{2} + y, \frac{1}{2} - z$	4·083
C1-C1	$\frac{1}{2} - x, \frac{1}{2} - y, \bar{z}$	4·262
C1-C5	$0, \frac{1}{2} + y, \frac{1}{2} - z$	4·313
C2-C3	$\frac{1}{2}, y, \frac{1}{2} - z$	4·341
C1-C2	$\frac{1}{2} - x, y, \frac{1}{2} - z$	4·424

TABLE X. $(Bu^tMeCNAlMe_2)_2$.

Observed and calculated structure factors.

h	k	l	10Fo	10Fc
0	0	2	209	-137
0	0	4	934	-762
0	0	6	248	-156
0	0	8	844	-894
0	0	10	143	-101
0	2	0	1751	1617
0	2	1	737	687
0	2	2	323	-227
0	2	3	1075	-983
0	2	4	<117	31
0	2	5	1350	-1341
0	2	6	231	-148
0	2	7	<109	16
0	2	8	326	-318
0	2	9	<134	51
0	2	10	114	86
0	2	11	143	108
0	2	12	173	-139
0	2	13	202	243
0	2	14	<124	11
0	2	15	156	132
0	4	0	1080	-1085
0	4	1	306	472
0	4	2	450	-462
0	4	3	<141	35
0	4	4	255	233
0	4	5	445	-460
0	4	6	105	121
0	4	7	382	-424
0	4	8	250	260
0	4	9	212	-246
0	4	10	297	292
0	4	11	129	123
0	4	12	<161	-1
0	4	13	192	210
0	4	14	<161	-42
0	4	15	136	199
0	6	0	1070	-870
0	6	1	535	424
0	6	2	<88	48
0	6	3	642	518
0	6	4	190	-167
0	6	5	221	160
0	6	6	122	-114
0	6	7	180	-146
0	6	8	340	363
0	6	9	224	-255
0	6	10	306	322
0	6	11	<109	-42
0	6	12	207	191
0	8	0	771	-658
0	8	1	195	-195
0	8	2	212	167
0	8	3	372	360
0	8	4	<61	-117
0	8	5	598	554
0	8	6	158	-99
0	8	7	<83	10
0	8	8	250	275
0	8	10	<107	23
0	8	11	<107	0
0	8	12	<107	74
0	8	13	117	-118
0	10	0	<83	2
0	10	1	<107	-52
0	10	2	117	81
0	10	3	353	380
0	10	4	<114	7
0	10	5	377	380
0	10	6	221	263
0	10	7	<114	24
0	10	8	<107	-76
0	10	9	<107	89
0	10	10	309	-334
0	10	11	<107	-47
0	10	12	<107	-11
0	10	13	122	-94
0	12	0	180	195
0	12	1	122	119
0	12	2	246	259
0	12	3	97	116
0	12	4	141	125
0	12	5	<102	-76
0	12	6	<102	-8
0	12	7	<109	-9
0	12	8	216	-194
0	12	9	<112	-3
0	12	10	260	-277
0	14	0	109	71
0	14	1	114	-122
0	14	2	114	110
0	14	3	231	-249
0	14	4	<129	69
0	14	5	226	-231
0	14	6	<129	-46
0	14	7	122	-112
0	16	0	148	-169
0	16	1	109	-60
0	16	2	134	-137
0	16	3	231	-220

h	k	l	10Fo	10Fc
0	16	4	<122	36
0	16	5	156	-189
0	18	0	182	-199
0	18	1	<122	-4
0	18	2	190	-109
1	1	1	1131	1145
1	1	2	406	-285
1	1	3	907	781
1	1	4	849	-736
1	1	5	788	-789
1	1	6	199	-206
1	1	7	336	-350
1	1	8	<122	2
1	1	9	460	-418
1	1	10	<151	-49
1	1	11	<136	17
1	1	12	197	173
1	1	13	<139	-4
1	1	14	146	130
1	1	15	134	-113
1	3	1	464	-316
1	3	2	669	-636
1	3	3	491	434
1	3	4	109	-456
1	3	5	474	-422
1	3	6	426	-452
1	3	7	197	158
1	3	8	297	-359
1	3	9	131	138
1	3	10	<134	-7
1	3	11	<139	-10
1	3	12	331	313
1	3	13	<139	1
1	3	14	195	209
1	5	1	263	-345
1	5	2	457	303
1	5	3	640	-554
1	5	4	110	157
1	5	5	<90	-14
1	5	6	348	-302
1	5	7	464	392
1	5	8	311	-330
1	5	9	360	316
1	5	10	<134	-99
1	5	11	151	172
1	5	12	173	158
1	5	13	109	103
1	5	14	134	156
1	7	1	396	-355
1	7	2	598	563
1	7	3	229	-247
1	7	4	382	322
1	7	5	<150	30
1	7	6	105	96
1	7	7	<124	64
1	7	8	<112	6
1	7	9	336	376
1	7	10	<105	-99
1	7	11	131	113
1	9	1	<105	-65
1	9	2	187	225
1	9	3	148	-131
1	9	4	574	526
1	9	5	282	286
1	9	6	272	273
1	9	7	90	-74
1	9	8	<134	24
1	9	9	<134	4
1	9	10	<143	34
1	9	11	<143	-73
1	9	12	119	-102
1	11	1	248	262
1	11	2	258	271
1	11	3	<122	-7
1	11	4	100	104
1	11	5	321	293
1	11	6	119	130
1	11	7	175	-173
1	11	8	<122	39
1	11	9	272	-261
1	11	10	<122	-48
1	11	11	146	-158
1	13	1	182	180
1	13	2	<131	-60
1	13	3	122	158
1	13	4	231	-220
1	13	5	<131	68
1	13	6	<134	-86
1	13	7	182	-153
1	13	8	<134	-48
1	13	9	146	-139
1	15	1	<122	-55
1	15	2	182	-203
1	15	3	<122	-15
1	15	4	241	-266
1	15	5	<122	60
1	15	6	146	-145
1	17	1	178	-204
2	0	0	2562	2722
2	0	2	438	-284

h	k	l	10Fo	10Fc
2	0	4	163	-75
2	0	6	<107	20
2	0	8	596	-620
2	0	10	117	-109
2	0	12	180	-154
2	2	0	1362	1306
2	2	1	632	635
2	2	2	151	93
2	2	3	150	-157
2	2	4	<71	53
2	2	5	749	-685
2	2	6	336	-368
2	2	7	243	-260
2	2	8	326	-298
2	2	9	153	-188
2	2	10	<136	108
2	2	11	109	91
2	2	12	131	-129
2	2	13	204	240
2	2	14	<122	26
2	2	15	129	160
2	4	0	<109	-70
2	4	1	204	-56
2	4	2	122	-139
2	4	3	309	-310
2	4	4	<124	-125
2	4	5	343	-377
2	4	6	131	-137
2	4	7	409	-444
2	4	8	122	146
2	4	9	143	-159
2	4	10	304	298
2	4	11	185	202
2	4	12	122	94
2	4	13	175	168
2	4	14	<131	-6
2	4	15	161	168
2	6	0	1021	-940
2	6	1	156	154
2	6	2	336	-345
2	6	3	122	136
2	6	4	170	-140
2	6	5	<92	27
2	6	6	209	20
2	6	7	80	-74
2	6	8	370	406
2	6	9	<131	-104
2	6	10	248	239
2	6	11	<119	5
2	6	12	136	155
2	8	0	824	-726
2	8	1	<83	71
2	8	2	<88	-2
2	8	3	640	625
2	8	4	<95	-42
2	8	5	554	570
2	8	6	<105	85
2	8	7	<112	-17
2	8	8	265	265
2	10	0	219	223
2	10	1	<95	49
2	10	2	190	195
2	10	3	413	434
2	10	4	<105	-53
2	10	5	345	342
2	10	6	<112	82
2	10	7	<112	20
2	10	8	141	-149
2	10	9	<112	48
2	10	10	238	-271
2	12	0	185	185
2	12	1	<107	29
2	12	2	243	254
2	12	3	<80	-47
2	12	4	129	115
2	12	5	146	-139
2	12	6	<119	-34
2	12	7	<119	40
2	12	8	209	-177
2	12	9	<119	61
2	12	10	226	-240
2	14	0	<97	-47
2	14	1	117	-116
2	14	2	<117	51
2	14	3	195	-222
2	14	4	212	112
2	14	5	185	-201
2	16	0	114	-133
2	16	1	<117	-29
2	16	2	129	-113
2	16	3	129	-145
2	16	4	<117	27
2	16	5	153	-150
2	18	0	156	-149
3	1	1	691	732
3	1	2	893	647
3	1	3	<117	84
3	1	4	302	-284
3	1	5	224	-233
3	1	6	212	-229

h	k	l	10Fo	10Fc
3	1	7	<131	13
3	1	8	92	-88
3	1	9	433	-475
3	1	10	175	-185
3	1	11	136	-48
3	1	12	<136	121
3	1	13	<146	-14
3	1	14	156	171
3	3	1	625	446
3	3	2	338	221
3	3	3	328	306
3	3	4	399	-507
3	3	5	671	-654
3	3	6	445	-498
3	3	7	114	-152
3	3	8	212	-219
3	3	9	100	86
3	3	10	136	-120
3	3	11	114	108
3	3	12	260	248
3	3	14	212	247
3	5	1	409	-439
3	5	2	97	-133
3	5	3	178	-190
3	5	4	275	-392
3	5	5	165	-103
3	5	6	302	-295
3	5	7	216	201
3	5	8	<173	-43
3	5	9	377	374
3	5	10	<117	-6
3	5	11	161	181
3	5	12	161	151
3	7	1	795	-792
3	7	2	406	394
3	7	3	<85	-75
3	7	4	379	405
3	7	5	236	223
3	7	6	107	138
3	7	7	219	203
3	7	8	<97	-50
3	7	9	336	396
3	9	1	<92	-53
3	9	2	345	347
3	9	3	75	-90
3	9	4	761	724
3	9	5	161	155
3	9	6	260	262
3	9	7	88	-105
3	9	8	114	-128
3	9	9	<134	-10
3	9	10	<134	-30
3	9	11	<134	-65
3	9	12	92	-84
3	11	1	384	396
3	11	2	90	111
3	11	3	<112	-30
3	11	4	<88	24
3	11	5	141	141
3	11	6	<124	93
3	11	7	117	-206
3	11	8	<124	63
3	11	9	253	-245
3	13	1	105	73
3	13	2	122	-114
3	13	3	122	114
3	13	4	253	-263
3	13	5	129	136
3	15	1	<105	-83
3	15	2	107	-100
3	15	3	<105	-2
3	15	4	185	-183
3	15	5	<97	82
3	15	6	136	-121
3	17	1	141	-132
4	0	0	1228	1169
4	0	2	<51	9
4	0	4	265	242
4	0	6	107	-148
4	0	8	464	-486
4	0	10	<153	-28
4	0	12	173	-178
4	2	0	803	806
4	2	1	178	178
4	2	2	195	197
4	2	3	163	-154
4	2	4	80	85
4	2	5	272	-279
4	2	6	311	-380
4	2	7	263	-306
4	2	8	268	-255
4	2	9	233	-262
4	2	10	107	112
4	2	11	119	131
4	2	12	112	-106
4	2	13	204	203
4	4	0	173	175
4	4	1	265	-205
4	4	2	122	-135
4	4	3	530	-408/

h	k	l	10Fo	10Fc
4	4	4	<263	-242
4	4	5	248	-232
4	4	6	100	-60
4	4	7	355	-373
4	4	8	126	137
4	4	9	143	-160
4	4	10	243	210
4	4	11	216	228
4	4	12	<165	101
4	4	13	168	134
4	6	0	657	-665
4	6	1	302	166
4	6	2	365	-401
4	6	3	<85	88
4	6	4	170	-177
4	6	5	<85	-8
4	6	6	287	309
4	6	7	<114	-52
4	6	8	357	373
4	6	9	<136	-72
4	6	10	136	147
4	6	11	<148	17
4	6	12	117	131
4	8	0	464	-520
4	8	1	146	217
4	8	2	<97	-36
4	8	3	552	592
4	8	4	80	-39
4	8	5	409	418
4	8	6	100	91
4	8	7	<97	9
4	8	8	190	196
4	10	0	212	189
4	10	1	<88	66
4	10	2	231	202
4	10	3	377	334
4	10	4	<88	-22
4	10	5	277	244
4	10	6	<97	-3
4	10	7	<97	47
4	10	8	<97	-146
4	10	9	<97	49
4	10	10	265	-196
4	12	0	139	112
4	12	1	<97	-17
4	12	2	178	198
4	12	3	73	-70
4	12	4	105	121
4	12	5	126	-112
4	12	6	<117	-17
4	12	7	<117	39
4	12	8	163	-141
4	12	9	<117	60
4	12	10	168	-198
4	14	0	<100	-46
4	14	1	<100	-93
4	14	2	<100	34
4	14	3	156	-157
4	14	4	<97	100
4	14	5	190	-153
5	1	1	931	807
5	1	2	105	99
5	1	3	88	74
5	1	4	396	-408
5	1	5	370	-363
5	1	6	243	-247
5	1	7	105	-82
5	1	8	<117	44
5	1	9	309	-353
5	1	10	<117	-42
5	1	11	<117	-33
5	1	12	126	81
5	3	1	<73	-47
5	3	2	<75	-21
5	3	3	204	204
5	3	4	460	-475
5	3	5	250	-242
5	3	6	457	-480
5	3	7	<129	11
5	3	8	<122	-93
5	3	9	<122	78
5	3	10	<122	-27
5	3	11	<122	40
5	3	12	182	163
5	3	13	<122	4
5	3	1	143	193
5	5	1	503	-471
5	5	2	112	83
5	5	3	78	-88
5	5	4	<102	-6
5	5	5	<102	4
5	5	6	268	-251
5	5	7	163	144
5	5	8	124	-136
5	5	9	297	300
5	5	10	<161	-71
5	5	11	163	151
5	5	12	107	104
5	5	13	<146	24
5	5	14	124	130

h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc
5	7	1	365	-359	6	4	0	270	-271
5	7	2	209	220	6	4	1	131	103
5	7	3	119	-98	6	4	2	209	-243
5	7	4	321	382	6	4	3	163	-158
5	7	5	<146	42	6	4	4	<107	-51
5	7	6	126	107	6	4	5	214	-188
5	7	7	80	48	6	4	6	92	136
5	7	8	<146	-71	6	4	7	216	-226
5	7	9	255	286	6	4	8	221	201
5	9	1	<113	41	6	4	9	178	-206
5	9	2	129	123	6	4	10	109	114
5	9	3	102	-111	6	4	11	109	120
5	9	4	409	426	6	4	12	<107	7
5	9	5	112	131	6	4	13	129	132
5	9	6	192	209	6	6	0	316	-342
5	11	1	238	207	6	6	1	229	271
5	11	2	112	137	6	6	2	129	-144
5	11	3	<109	-19	6	6	3	209	240
5	11	4	151	51	6	6	4	170	-173
5	11	5	136	180	6	6	5	<97	48
5	11	6	<112	84	6	6	6	119	30
5	11	7	<112	-87	6	6	7	126	-80
5	11	8	<112	36	6	6	8	250	251
5	11	9	197	-197	6	6	9	112	-140
5	13	1	<112	102	6	6	10	134	146
5	13	2	<109	-10	6	8	0	253	-294
5	13	3	<109	100	6	8	1	<100	61
5	13	4	163	-165	6	8	2	<100	31
5	15	1	<73	-36	6	8	3	229	244
5	15	2	95	-112	6	8	4	<100	-55
5	15	3	<109	11	6	8	5	238	233
6	0	0	1311	1293	6	8	6	<100	-33
6	0	2	231	252	6	8	7	<100	49
6	0	4	<73	-28	6	8	8	105	128
6	0	6	282	-301	6	10	0	<100	-43
6	0	8	484	-498	6	10	1	<100	2
6	2	0	486	490	6	10	2	<100	69
6	2	1	<73	-37	6	10	3	385	207
6	2	2	<73	-37	6	10	4	<100	64
6	2	3	574	-536	6	10	5	185	197
6	2	4	<78	50	6	10	6	<90	97
6	2	5	404	-404	6	10	7	<90	47
6	2	6	122	-132	6	10	8	<90	-90
6	2	7	<129	-74	6	10	9	<90	48
6	2	8	216	-184	6	10	10	161	-166
6	2	9	<129	-81	6	12	0	<105	115
6	2	10	<129	52	6	12	1	<105	21
6	2	11	151	135	6	12	2	102	141
6	2	12	<129	-68	6	12	3	134	65
6	2	13	165	151	6	12	4	<100	88

h	k	l	10Fo	10Fc
6	12	5	<100	-16
6	12	6	<100	2
6	12	7	<100	-18
6	12	8	153	-123
6	12	9	<100	-9
6	12	10	151	-163
6	14	0	<100	67
6	14	1	<100	-79
6	14	2	<100	57
6	14	3	129	-137
6	18	0	141	-119
6	18	1	<100	-7
6	18	2	95	-75
7	1	1	433	502
7	1	2	126	-125
7	1	3	170	177
7	1	4	263	-266
7	1	5	280	-292
7	1	6	165	-176
7	1	7	158	-154
7	1	8	<146	21
7	1	9	175	-189
7	3	1	143	-113
7	3	2	161	-170
7	3	3	112	95
7	3	4	88	-240
7	3	5	<92	-65
7	3	6	326	-331
7	3	7	<102	54
7	3	8	<100	-100
7	3	9	<100	51
7	3	10	<100	12
7	3	11	<100	16
7	3	12	148	129
7	5	1	270	-257
7	5	2	58	61
7	5	3	122	-135
7	5	4	<163	105
7	5	5	150	12
7	5	6	156	-174
7	5	7	126	115
7	5	8	148	-153
7	5	9	173	178
7	5	10	<120	-72
7	5	11	109	118
7	7	1	146	-149
7	7	2	119	113
7	7	3	129	-143
7	7	4	229	216
7	7	5	<90	3
7	7	6	<90	59
7	7	7	<90	37
7	7	8	<90	-11
7	7	9	151	169
7	9	1	<73	-28
7	9	2	<73	110
7	9	3	<75	-78
7	9	4	209	234
7	9	5	119	127
7	9	6	124	141
7	11	1	105	120
7	11	2	136	157
7	11	3	<70	26
7	11	4	92	77
7	11	5	129	121
7	11	6	<70	62
7	11	7	70	-67
7	11	8	<70	0
7	11	9	143	-133
7	13	1	<100	109
7	13	2	<117	-17
7	13	3	<70	83
7	13	4	107	-125
7	15	1	<100	-45
7	15	2	117	-112
7	15	3	<90	3
7	15	4	146	-165
8	0	0	679	649
8	0	2	126	105
8	0	4	<100	-3
8	0	6	<100	-72
8	0	8	282	-263
8	2	0	326	338
8	2	1	<117	87
8	2	2	<107	56
8	2	3	209	-195
8	2	4	<100	-3
8	2	5	285	-254
8	2	6	<124	-80
8	2	7	124	-79
8	2	8	143	-115
8	4	0	119	-100
8	4	1	88	90
8	4	2	88	-71
8	4	3	146	-137
8	4	4	<120	-55
8	4	5	221	-191
8	4	6	<141	-29
8	4	7	122	-129
8	4	8	131	104

h	k	l	10Fo	10Fc
8	6	0	287	-330
8	6	1	97	97
8	6	2	112	-113
8	6	3	<112	48
8	6	4	<100	-58
8	6	5	<100	13
8	6	6	<120	20
8	6	7	<120	-39
8	6	8	178	180
8	6	9	<120	-57
8	6	10	129	120
8	8	0	226	-260
8	8	1	<120	46
8	8	2	<120	-35
8	8	3	197	202
8	8	4	<120	2
8	8	5	209	211
8	10	0	<130	50
8	10	1	<130	27
8	10	2	<130	67
8	10	3	163	187
8	10	4	<130	16
8	10	5	158	162
8	12	0	114	135
8	12	1	<130	-10
8	12	2	112	104
9	1	1	212	195
9	1	2	<139	14
9	1	3	178	115
9	1	4	<140	-43
9	1	5	<140	-84
9	1	6	97	-93
9	1	7	<148	-66
9	1	8	<150	-59
9	1	9	<150	-120
9	1	10	163	-33
9	3	1	85	89
9	3	2	<140	-73
9	3	3	<140	29
9	3	4	170	-105
9	3	5	122	-126
9	3	6	180	-191
9	5	1	168	-132
9	5	2	95	-83
9	5	3	95	-104
9	5	4	<140	-63
9	5	5	<140	-18
9	5	6	100	-117
9	5	7	<140	84
9	5	8	<180	-21
9	5	9	146	118
9	7	1	192	-206
9	7	2	85	101
9	7	3	85	-91
9	7	4	<140	144
9	7	5	<140	76
9	7	6	<140	27
9	7	7	112	101
9	9	1	<140	3
9	9	2	136	165
9	9	3	<140	-21
9	9	4	231	220
9	11	1	114	124
10	0	0	233	280
10	0	2	<140	53
10	0	4	<140	28
10	0	6	<140	-24
10	0	8	114	-116
10	2	0	231	211
10	2	1	<134	56
10	2	2	<134	57
10	2	3	<134	-56
10	2	4	<134	-9
10	2	5	141	-119
10	4	0	<71	-25
10	4	1	<120	20
10	4	2	<120	-25
10	4	3	136	-129
10	4	4	<141	-41
10	4	5	146	-125
10	6	0	219	-245
10	6	1	<131	37
10	6	2	114	-107
10	6	3	<130	2
10	6	4	<130	-13
10	6	5	<130	20
10	6	6	<130	64
10	6	8	105	116
10	8	0	236	-129
10	8	1	<130	64
10	8	2	<130	-29
10	8	3	158	166
10	8	4	<130	-10
10	8	5	153	150
11	1	1	141	141
11	3	1	<130	26
11	3	2	<130	-55
11	3	3	<130	10
11	3	4	85	-89
11	7	1	105	-93

h	k	1	10Fo	10Fc
11	7	2	<130	73
11	7	3	130	-43
11	7	4	105	110
11	9	1	<130	13
11	9	2	<130	60
11	9	3	<130	-11
11	9	4	146	107

h	k	1	10Fo	10Fc
12	0	0	204	210
12	2	0	102	99
12	2	1	<130	-2
12	2	2	<130	21
12	2	3	129	-92
13	1	1	105	87

Dimethylphosphinatodimethylgallium dimer $(Me_2GaO_2PMe_2)_2$.

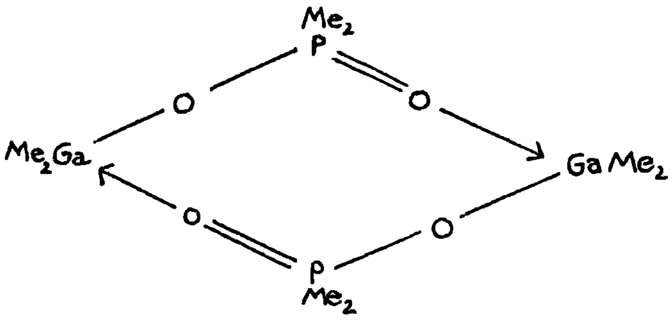
Introduction.

Phosphinic acids react with a variety of metals. Some of these compounds have been shown to be polymeric and others dimeric. In all known cases the metal atoms are linked by two bridging phosphinate groups.

Cobalt and zinc phosphinates are thought to have a polymeric structure (Coates, 1962).

Recent work (Danielsen, 1963) has shown that $Mn(CH_3COOC_2H_5)_2(O_2PCl_2)_2\,n$ is polymeric with two phosphinate bridges between the metal atoms. Wilkes, 1965, has shown that the molecule $(CH_3OCHOCH_3)_2Cr(OP(C_6H_5)_2O)_2Cr(CH_3OCHOCH_3)_2$ contains an eight membered chromium phosphinate ring system.

Trimethylaluminium and trimethylgallium react with phosphinic acids giving products whose infrared spectra and molecular weights suggest that they are dimeric with phosphinate bridges. (Coates, 1964). A crystal structure analysis of dimethylgallium dimethylphosphinate has confirmed that the dimer contains an eight membered phosphinate ring system.



Experimental

The crystals are extremely soluble in organic solvents. Sublimation in vacuo gives needle-shaped crystals elongated along b. Crystals of 0·1 x 0·1 mm^2 crossection were sealed in thin walled lithium borate capillary tubes. The substance is air sensitive but crystals mounted in the air were sufficiently stable for data collection purposes.

Crystal data.

The unit cell dimensions were measured from photographs of the zero nets using the precession method and Zr-filtered Mo radiation.

The calculated statistical standard deviations in the cell dimensions are 0·003Å in a, 0·014Å in b and 0·003Å in c, but the actual errors are thought to be about 0·005 of the unit cell lengths and 20' in β.

Monoclinic a = 15·23Å, b = 6·78Å, c = 16·31Å, β = 105° 23'.

Absorption μ(Mo Kα) = 36·28 cm^{-1}, μ(Cu Kα) = 61·34 cm^{-1}.

Dx = 1·55 gm. cm^{-3}, z = 8, V = 1652Å^3.

Observed reflections:-

hkl when h + k = 2n.

hol when l = 2n, (h = 2n).

oko when (k = 2n).

These are consistent with the two space groups Cc and C2/c (Numbers 9 and 15 in International Tables for X-ray Crystallography, Vol. 1).

The calculated density, assuming eight $Me_2GaO_2PMe_2$ units per unit cell, is 1·55 gm. cm^{-3}. The density of the crystals is found to lie between that of water and carbon tetrachloride (1·6 gm. cm^{-3}). If the space group is C2/c then the dimer must possess a twofold axis or be centrosymmetric.

Collection of Intensities

Zr-filtered Mo radiation was used to record photographically the nets hol - h6l using the equiinclination angle Weissenberg technique and the okl - 2kl and the hko - hk2 nets using the precession method.

The intensities were estimated visually using a calibrated scale. The usual Lorentz and polarisation corrections were applied to the data. The length correction, (Phillips, 1956) was made to the data from the upper level Weissenberg photographs. No correction for absorption was made.

The structure factors were correlated using a least squares method. They were 726 in number, 188 appearing on more than one net.

Structure Determination

The Patterson function

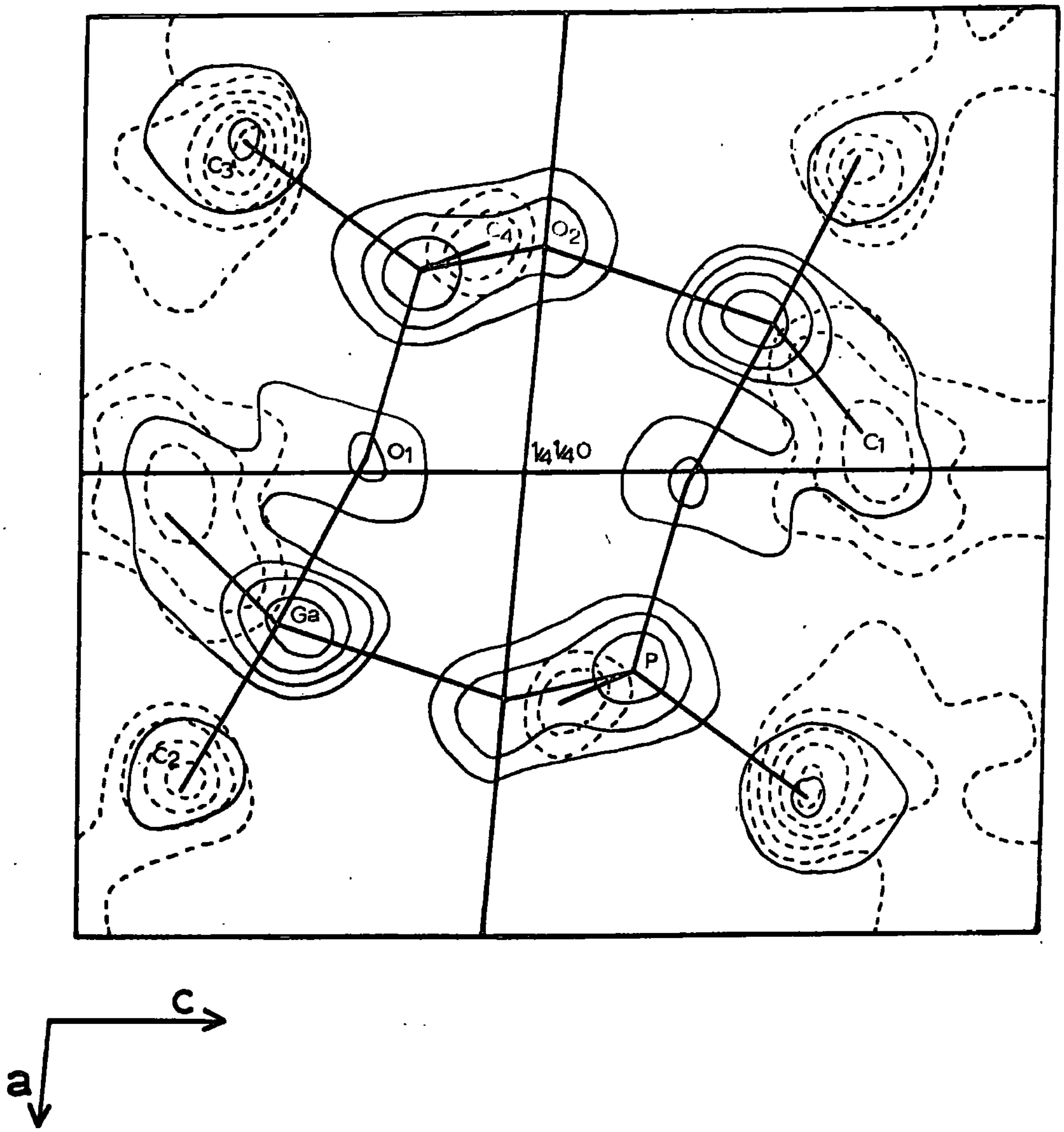
The expression evaluated was

$$P(uvw) = \frac{4}{Vc} \sum_{0}^{\infty} \sum_{0}^{\infty} \sum_{0}^{\infty} \left\{ W_{hkl} |F_{hkl}|^2 \cos 2\pi(hu + lw) + W_{\bar{h}kl} |F_{\bar{h}kl}|^2 \cos 2\pi(-hu + lw) \right\} \cos 2\pi kv$$

in intervals in u of 0·2538Å, in v of 0·2718Å and 0·2823Å in w. The coefficients were sharpened by weighting them using the expression $\exp(2B\sin^2\theta/\lambda^2)$ with B taking the value of 6. The maximum value this expression was allowed to take was 100 to reduce the weighting for the weak high order reflections.

While the data collection was in progress, the Patterson function was computed in projection along the three crystal axes and showed the space group to be C2/c. In the 010 projection, three peaks of similar height appeared, two of which arise from double-weight phosphorus-gallium vectors and the third from the gallium-gallium single weight vector. The situation was resolved since an estimate of the gallium z-coordinate, with respect to the cell origin, was obtained from the projection along a. In the 010 projection a single application of superposition methods, based on the gallium-gallium single-weight peak, revealed a centrosymmetric eight-membered ring. Structure factors, based on the ring atoms alone, gave a residual of 0·32 after one cycle of least-squares refinement. A difference map then revealed the positions of the methyl carbon atoms in this projection (Fig. VII).

The space group C2/c possesses centres of symmetry at 0,0,0, and $\frac{1}{4},\frac{1}{4}$,0 and two-fold axes. Examination of the Patterson function suggested that the molecule is grouped around the centre of symmetry at $\frac{1}{4},\frac{1}{4}$,0. The hko structure factors, calculated on the gallium and phosphorus atoms alone, gave a residual of 0·42.



$(Me_2GaO_2PMe_2)_2$ 010 projection

— Fo synthesis

--- Fo-Fc synthesis

(Fc's based on the ring atoms only)

FIG. VII. Solution in projection.

As a check on the two dimensional results the three dimensional Patterson function was evaluated. This allowed atomic coordinates to be assigned to the gallium and phosphorus atoms. R(hkl) was 0·27.

Fo synthesis

A three dimensional Fo synthesis was computed at the same intervals as the Patterson function using the signs of structure factors based on the phosphorus and gallium atoms only. This showed peaks corresponding to all the atoms other than hydrogen and allowed coordinates to be assigned to them. The reliability index was now 0·12.

The expression evaluated was

$$\rho(xyz) = \frac{4}{Vc}\Big(\sum_{0}^{\infty}\sum_{0}^{\infty}\sum_{0}^{\infty}(F_{hkl}\cos 2\pi(hx + lz) + F_{\bar{h}kl}\cos 2\pi(hx + lz))\cos 2\pi ky.$$

$$-\sum_{0}^{\infty}\sum_{0}^{\infty}\sum_{0}^{\infty}(F_{hkl}\sin 2\pi(hx + lz) + F_{\bar{h}kl}\sin 2\pi(hx + lz))\sin 2\pi ky\Big)$$

Structure refinement

The atomic parameters of all eight atoms were refined by one cycle of least squares calculations using isotropic thermal parameters to a residual of 0·116. Introduction of anisotropic thermal parameters for all the atoms reduced the residual to 0·085, its final value, over the 726 reflections.

An $F_o - F_c$ synthesis computed at this stage showed only one pronounced feature, a peak of height 1 e.A.$^{-3}$ near the site of the gallium atom. Many of the other peaks were close to carbon atoms, but could not readily be explained as due to hydrogen atoms.

Structure factors for the unobserved reflections were not included in the refinement. None of these were found to be significantly greater than their minimum observable value.

The scattering curves used were those in International Tables for X-ray Crystallography, Vol. III, p. 202, to which the real part of the correction for dispersion (ibid, p.213) was applied for gallium and phosphorus, but not the imaginary part.

The final cycle of refinement

No. of planes = 726, $\sum|F_o| = 39{,}977$, $\sum|F_c| = 39{,}102$, $R = 0{\cdot}0856$, $R' = 0{\cdot}0188$.

The values of the constants A and C in the expression used for the weighting w, where $w = 1/(A + |F_o| + C|F_o|^2)$, were 80 and 0·1 in the final cycle. At this stage the average coordinate shift was 0·0028Å the shifts varying up to 0·35 of the corresponding e.s.d. The average shift in thermal parameters was 0·0023Å^2, the shifts ranging up to 0·50 of the corresponding e.s.d.

The coordinates and thermal parameters are listed in Tables XI and XII and the final values of the structure factors in Table XV.

Table XI. $(Me_2GaO_2PMe_2)_2$. Atomic Coordinates and their standard deviations.

Atom	x	y	zÅ	σ_x	σ_y	σ_z	Å
Ga	5·017	1·495	-1·820	0·002	0·002	0·002	
P	5·406	3·086	0·957	0·004	0·005	0·005	
01	3·670	0·262	-1·287	0·011	0·015	0·012	
02	1·875	1·310	0·064	0·011	0·013	0·012	
C1	3·466	0·330	2·736	0·023	0·025	0·023	
C2	6·421	0·351	-2·524	0·022	0·028	0·023	
C3	1·143	0·615	-2·505	0·023	0·025	0·019	
C4	1·830	-1·366	-0·370	0·024	0·023	0·025	

Table XII. $(Me_2GaO_2PMe_2)_2$. Thermal parameters in Å^2 with e.s.d.'s in 10^3 Å^2 in brackets.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Ga	0·048(1)	0·064(1)	0·050(1)	0·001(1)	−0·006(1)	0·013(1)
P	0·039(2)	0·057(3)	0·054(2)	0·004(2)	−0·010(5)	0·006(2)
O1	0·042(7)	0·082(10)	0·072(8)	0·004(7)	−0·008(7)	0·019(6)
O2	0·043(6)	0·074(9)	0·047(6)	0·004(6)	−0·006(6)	−0·004(5)
C1	0·085(15)	0·072(16)	0·095(16)	0·005(13)	0·027(13)	0·004(12)
C2	0·064(13)	0·103(20)	0·081(15)	0·064(13)	−0·018(14)	0·004(11)
C3	0·079(15)	0·104(18)	0·053(11)	0·014(13)	0·013(12)	−0·016(10)
C4	0·075(14)	0·068(16)	0·101(17)	0·006(12)	−0·005(13)	0·019(12)

Description of the Structure.

The molecular dimensions are listed in Table XIII and are shown in Fig. VIII. The lengths of the two phosphorus-oxygen bonds, $P'-O_1$ and $P'-O_2$, are $1{\cdot}522 \pm 0{\cdot}012$ and $1{\cdot}492 \pm 0{\cdot}013$Å respectively and do not differ significantly from one another. Their mean value is also quoted in Table XIII. Similarly the mean values of $Ga-O_1$ and $Ga-O_2'$, of $Ga-C_1'$ and $Ga-C_2$, of $P'-C_3$ and $P'-C_4$ and also of the angles $Ga-O_1-P'$ and $Ga'-O_2-P'$ are also listed. However the variations in the four carbon-phosphorus-oxygen angles and in the four oxygen-gallium-carbon angles are significant.

The mean gallium-oxygen distance of $1{\cdot}934 \pm 0{\cdot}009$Å is not significantly shorter than that of $1{\cdot}96 \pm 0{\cdot}03$. Å in $(Me_2GaOH)_4$ (Smith and Hoard, 1959). For a single covalent bond, a length of 1·92Å (Pauling, 1960) is expected.

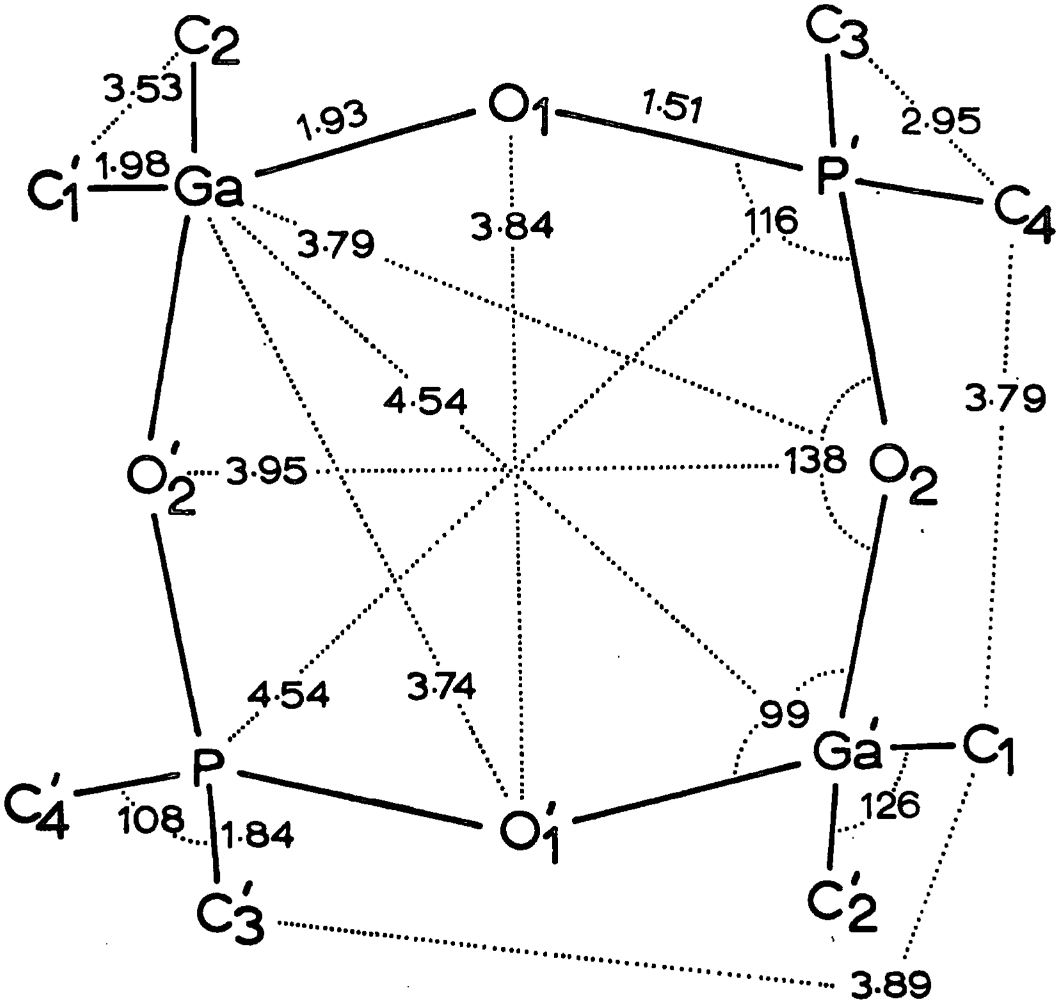
The mean phosphorus-oxygen length of $1{\cdot}505 \pm 0{\cdot}008$Å is the same as the average value of that in the chromium(III)phosphinate, $(CH_3COCHCOCH_3)_2Cr(OP(C_6H_5)_2O)_2Cr(CH_3COCHCOCH_3)_2$ (Wilkes and Jacobson, 1965). The expected value for a phosphorus-oxygen single bond is 1·71Å (Schomaker and Stevenson, 1941) so that, in the present case, there is considerable shortening due to $d\pi - p\pi$ bonding.

The average gallium-carbon distance of $1{\cdot}980 \pm 0{\cdot}016$Å is the same as that in $(Me_2GaOH)_4$. Similarly the mean phosphorus-carbon length of

Table XIII. $(Me_2GaO_2PMe_2)_2$. Intramolecular distances and angles.

Bonding		e.s.d.
Ga-O1	1·932Å	0·013Å
Ga-O2'	1·936	0·011
P'-O1	1·522	0·012
P'-O2	1·492	0·013
Ga-C1'	1·978	0·024
Ga-C2	1·982	0·024
P'-C3	1·837	0·020
P'-C4	1·815	0·024
Ga-O mean	1·934	0·009
Ga-C mean	1·980	0·016
P-O mean	1·505	0·008
P-C mean	1·826	0·016
C1'-Ga-C2	126·1°	0·9°
O1-Ga-O2'	99·3	0·5
O2-P'-O1	115·9	0·7
C3-P'-C4	107·8	1·1
O1-Ga-C1	110·0	0·8
O1-Ga-C2	105·0	0·9
O2'-Ga-C1	107·5	0·8
O2'-Ga-C2	105·7	0·7
Ga-O1-P'	138·1	0·9
Ga'-O2-P'	137·4	0·8
C3-P'-O1	108·9	0·8
C3-P'-O2	108·2	0·8
C4-P'-O1	106·0	1·0
C4-P'-O2	109·5	0·9

Ga-O-P mean	137·7°
O-Ga-C mean	107·0
C-P-O mean	108·1



$(Me_2GaO_2PMe_2)_2$

FIG. VIII. Molecular geometry.

1·826 ± 0·016Å is very similar to the value of 1·84 ± 0·02Å found in trimethylphosphine (Lide and Mann, 1958).

The O_1-Ga-O_2' angle of 99·3° is much less than the tetrahedral value and is the same as in $(Me_2GaOH)_4$. Resulting from this, the angle C_1'-Ga-C_2 is increased to 126·1°, giving a separation C_1'-C_2 of 3·52Å. However the ring angle O_1-P'-O_2, at 115·9°, is greater than tetrahedral and the angle C_3-P'-C_4 of 107·8° gives a C_3-C_4 separation of 2·95Å.

The mean angle at oxygen of 137·7° is similar to the value of 133° in $(Me_2GaOH)_4$ and comparable values have been reported for other phosphinates. In the chromium(III) phosphinate, the angles at oxygen range from 141 to 161° and in the polymeric $(Mn(PO_2Cl_2)_2(CH_3COOC_2H_5)_2)_n$ the angles are 141 and 173°. In the former case the effect is attributed to the non-bonding contacts involving atoms of the phenyl groups.

The non-bonding contacts of less than 4·4Å are listed in Table XIV. There are two carbon-carbon contacts around the ring of less than 4Å, the separations C_1 - C_4 and C_1 - C_3' being 3·79 and 3·89Å respectively. These distances are normal and are similar to the shorter contacts of 3·74 and 3·79Å across the ring and it would appear that the ring conformation and the distortions at the ring angles is chiefly determined by the nature of these contacts. The shortest intermolecular contact of 3·45Å between O_1 and an atom related to C_4 and at the equivalent position $\frac{1}{2}-x$, $y-\frac{1}{2}$, $\bar{z}$, is less than any of the intramolecular contacts already described. A perspective view of the atoms in the

Table XIV. $(Me_2GaO_2PMe_2)_2$. Non-bonding Contacts.

Intermolecular Contacts

Ga	C4	$\frac{1}{2}-x, y-\frac{1}{2}, \bar{z}$	4·182
P	C4	$x, 1+y, z$	4·381
O1	C4	$\frac{1}{2}-x, y-\frac{1}{2}, \bar{z}$	3·45
C3	C3	$\bar{x}, y, -\frac{1}{2}-z$	3·74
C2	C4	$\frac{1}{2}-x, -\frac{1}{2}-y, \bar{z}$	3·83
C2	C3	$x+\frac{1}{2}, y-\frac{1}{2}, z$	3·90
C2	C4	$x+\frac{1}{2}, y+\frac{1}{2}, z$	3·94
C1	C3	$x, \bar{y}, \frac{1}{2}+z$	3·981
C4	C4	$\frac{1}{2}-x, y-\frac{1}{2}, \bar{z}$	4·02
C1	C2	$x, \bar{y}, \frac{1}{2}-z$	4·027
C2	C2	$1-x, y, -\frac{1}{2}-z$	4·07
C1	C4	$\frac{1}{2}-x, y-\frac{1}{2}, \bar{z}$	4·169
C2	C3	$x-\frac{1}{2}, y+\frac{1}{2}, z$	4·34
C3	C4	$\bar{x}, \bar{y}, \bar{z}$	4·36

Intramolecular contacts

C3	C4	2·95Å
C1'	C2	3·53
Ga	O1'	3·74
Ga	O2	3·79
P	O1	3·93
P	O2	3·99
Ga	Ga'	4·54
P	P'	4·54
O1	O1'	3·85
O2	O2'	3·95
C4	C1	3·79
C1	C3'	3·89

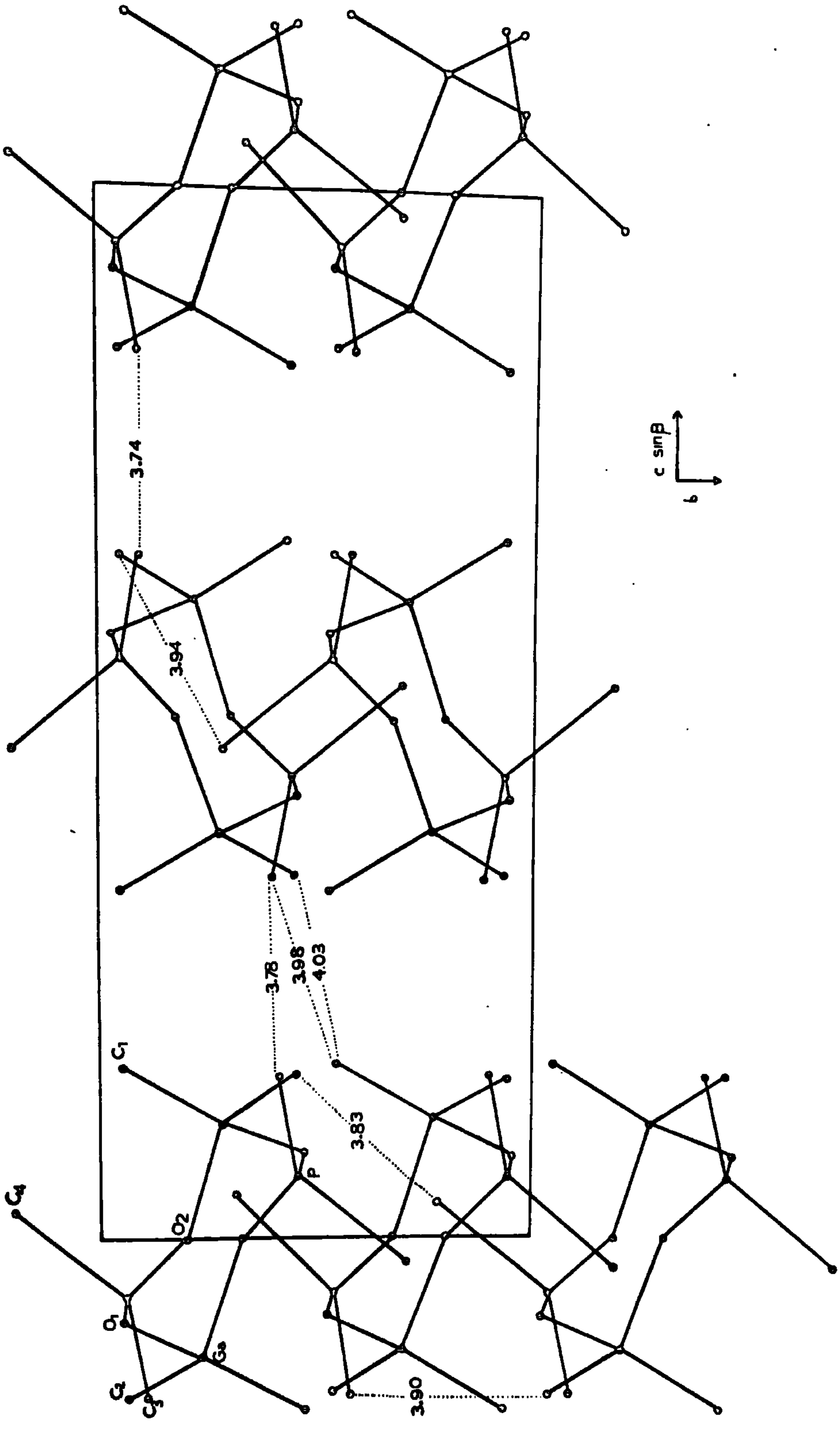
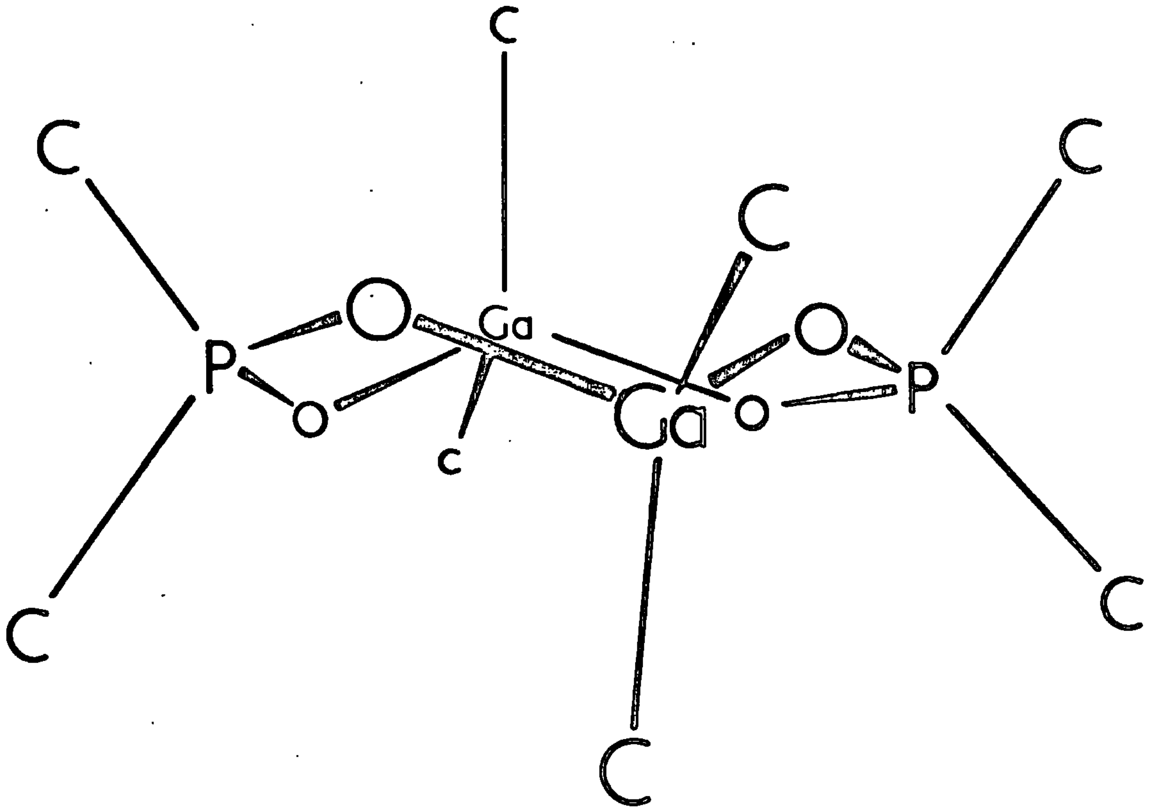


FIG. IX.

(Me$_2$GaO$_2$PMe$_2$)$_2$ 100 projection



$(Me_2GaO_2PMe_2)_2$

FIG. X. Perspective view of the ring.

ring is shown in figure X.

The equation of the mean plane through the ring atoms Ga, P, O_1, O_2 and the atoms related by the centre of symmetry at $\frac{1}{4}$, $\frac{1}{4}$, 0 is

$$-0{\cdot}3496x' + 0{\cdot}7556y - 0{\cdot}5541z' = -0{\cdot}0381$$

where the coordinates are referred to orthogonal axes parallel to a, b and c*. The distances of the atoms from the plane are as follows:

Ga	0·39Å	C_1	-2·35Å
P	0·00	C_2	-0·60
O_1	-0·36	C_3	1·42
O_2	0·35	C_4	-1·44

TABLE XV. $(Me_2GaO_2PMe_2)_2$.

Observed and calculated structure factors.

h	k	l	10Fo	10Fc
0	0	2	2097	2043
0	0	4	1928	-1988
0	0	6	306	-452
0	0	8	685	701
0	0	10	417	488
0	0	12	222	-170
0	0	14	316	-321
0	0	16	281	260
0	0	18	396	502
0	2	0	598	-685
0	2	1	899	887
0	2	2	501	-367
0	2	3	1049	1148
0	2	4	544	699
0	2	5	<213	-80
0	2	6	<280	120
0	2	7	507	-478
0	2	8	1702	-1713
0	2	9	<252	-143
0	2	10	1094	-1235
0	2	11	<273	-46
0	2	12	320	396
0	2	13	<292	-91
0	2	14	549	578
0	4	0	1059	1216
0	4	1	197	-186
0	4	2	382	405
0	4	3	<259	-27
0	4	4	564	-658
0	4	5	556	634
0	4	6	358	-395
0	4	7	631	765
0	4	8	298	325
0	4	9	<145	28
0	4	10	277	232
0	4	11	503	-566
0	4	12	254	-238
0	4	13	282	-254
0	6	0	270	-250
0	6	1	360	370
0	6	2	351	38
0	6	7	309	-313
1	1	-17	453	-447
1	1	-16	<145	178
1	1	-15	<255	-70
1	1	-14	336	309
1	1	-13	707	715
1	1	-12	299	237
1	1	-11	414	412
1	1	-10	<321	-83
1	1	-9	1069	-938
1	1	-8	<287	-121
1	1	-7	1011	-941
1	1	-6	231	-231
1	1	-5	1332	1191
1	1	-4	1036	-923
1	1	-3	2138	1747
1	1	-1	1613	-1473
1	1	0	663	719
1	1	1	2654	-2697
1	1	3	<198	140
1	1	4	1648	1620
1	1	5	1526	1604
1	1	6	158	147
1	1	7	314	309
1	1	8	651	-570
1	1	9	1128	-1136
1	1	10	458	-440
1	1	11	801	-824
1	1	12	<124	-182
1	1	13	288	238
1	1	14	<134	-5
1	1	15	363	305
1	1	16	<146	27
1	1	17	263	-246
1	3	-13	492	-455
1	3	-12	256	261
1	3	-11	<377	-83
1	3	-10	416	371
1	3	-9	1141	1049
1	3	-8	385	-384
1	3	-7	929	795
1	3	-6	1361	-1208
1	3	-5	792	-790
1	3	-4	797	-725
1	3	-3	1262	-1221
1	3	-2	323	372
1	3	-1	356	-316
1	3	0	179	247
1	3	1	681	736
1	3	2	379	-381
1	3	3	373	381
1	3	4	192	-206
1	3	5	562	-649
1	3	6	190	183
1	3	7	201	167
1	3	8	<357	107
1	3	9	1001	1084
1	3	10	367	359
1	3	11	360	300

h	k	l	10Fo	10Fc
1	3	12	520	-564
1	3	13	457	-499
1	3	14	<172	-188
1	3	15	326	-321
1	5	-11	338	239
1	5	-10	341	-302
1	5	-9	<190	48
1	5	-8	<181	125
1	5	-7	<172	-121
1	5	-6	513	476
1	5	-5	<395	136
1	5	-4	<392	133
1	5	-3	231	222
1	5	-2	450	-427
1	5	-1	547	-562
1	5	0	<387	-156
1	5	1	715	-770
1	5	2	657	678
1	5	3	221	199
1	5	4	645	692
1	5	5	704	711
1	5	6	<165	-93
1	5	7	374	351
1	5	8	470	-363
2	0	-16	486	-492
2	0	-14	348	334
2	0	-12	1195	1177
2	0	-10	403	329
2	0	-8	1094	-1097
2	0	-6	1011	-992
2	0	-4	461	545
2	0	0	2398	-2047
2	0	4	1641	1611
2	0	6	2829	2803
2	0	8	734	692
2	0	10	1361	-1268
2	0	12	797	-781
2	0	14	248	264
2	0	16	220	174
2	2	-16	358	407
2	2	-15	344	-335
2	2	-14	<159	70
2	2	-13	263	-311
2	2	-12	611	-579
2	2	-11	254	265
2	2	-9	341	327
2	2	-8	1627	1443
2	2	-7	311	-278
2	2	-6	619	593
2	2	-5	<279	-145
2	2	-4	1876	-1797
2	2	-3	<250	97
2	2	-2	1734	-1840
2	2	-1	186	-102
2	2	0	299	345
2	2	1	<231	-195
2	2	2	1475	1521
2	2	3	997	-979
2	2	4	307	298
2	2	5	841	-785
2	2	6	744	-703
2	2	7	486	493
2	2	8	<329	140
2	2	9	589	597
2	2	10	640	678
2	2	11	<141	-96
2	2	12	<191	-30
2	2	13	282	-310
2	2	14	547	-622
2	4	-12	346	377
2	4	-11	<160	-127
2	4	-10	176	180
2	4	-9	188	-154
2	4	-8	500	-491
2	4	-7	583	523
2	4	-6	496	-520
2	4	-5	1157	1120
2	4	-4	389	388
2	4	-3	<103	86
2	4	-2	452	477
2	4	-1	1024	-1098
2	4	0	626	-635
2	4	1	469	-457
2	4	2	662	-717
2	4	3	265	342
2	4	4	418	502
2	4	5	259	296
2	4	6	794	876
2	4	7	<139	103
2	4	8	<141	105
2	4	9	<148	65
2	4	10	346	-387
2	4	11	295	311
2	4	12	218	-172
2	4	13	320	357
2	6	-1	243	241
3	1	-17	277	217
3	1	-16	<146	-86
3	1	-15	371	357
3	1	-14	<134	-210

h	k	l	10Fo	10Fc
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3	1	-12	<126	164
3	1	-11	1266	-1158
3	1	-10	497	511
3	1	-9	<107	-117
3	1	-8	<101	23
3	1	-7	1155	1158
3	1	-6	<89	47
3	1	-5	418	420
3	1	-4	322	136
3	1	-3	1777	-1612
3	1	-2	1614	-1308
3	1	-1	1411	-1395
3	1	0	839	-846
3	1	1	1264	1201
3	1	2	<211	-85
3	1	3	1533	1417
3	1	4	1092	-994
3	1	5	1051	-966
3	1	6	<92	100
3	1	7	1637	-1517
3	1	8	1115	1124
3	1	9	190	196
3	1	10	375	352
3	1	11	962	963
3	1	12	252	-222
3	1	13	<131	134
3	1	14	194	-237
3	1	15	430	-444
3	1	16	258	-219
3	1	17	253	-206
3	3	-15	341	-381
3	3	-14	313	294
3	3	-13	<165	-6
3	3	-12	289	291
3	3	-11	661	666
3	3	-10	<145	-106
3	3	-9	<139	134
3	3	-8	<132	-161
3	3	-7	927	-879
3	3	-6	740	674
3	3	-5	<113	69
3	3	-4	939	979
3	3	-3	1484	1553
3	3	-2	253	-280
3	3	-1	755	752
3	3	0	836	-925
3	3	1	943	-1032
3	3	2	<97	-37
3	3	3	1087	-1200
3	3	4	641	695
3	3	5	<116	27
3	3	6	538	598
3	3	7	562	615
3	3	8	<135	126
3	3	9	183	125
3	3	10	<149	-42
3	3	11	254	-244
3	5	-11	341	-278
3	5	-10	328	267
3	5	-9	<193	17
3	5	-8	300	242
3	5	-7	476	470
3	5	-6	465	-420
3	5	-5	442	430
3	5	-4	746	-670
3	5	-3	<154	-124
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3	5	1	193	206
3	5	2	<142	-141
3	5	3	<149	35
3	5	4	555	-556
3	5	5	473	-444
3	5	6	281	-246
3	5	7	375	-373
3	5	8	327	290
3	5	9	<197	177
3	5	10	290	284
3	5	11	390	404
4	0	-14	233	241
4	0	-12	613	-594
4	0	-10	967	-974
4	0	-8	195	226
4	0	-6	1529	1502
4	0	-4	182	-122
4	0	-2	3723	-2905
4	0	0	2096	-1963
4	0	2	281	284
4	0	4	226	-164
4	0	6	1441	-1519
4	0	8	1009	-1053
4	0	10	572	554
4	0	12	937	900
4	0	16	477	-534
4	2	-16	400	-416
4	2	-15	<167	-20
4	2	-14	491	-491
4	2	-13	<155	109

h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc
4	2	-12	469	502	4	4	9	<154	152
4	2	-10	1234	1197	4	4	10	207	210
4	2	-9	595	-556	4	4	11	236	258
4	2	-8	<124	135	4	4	12	374	415
4	2	-7	304	-267	5	1	-17	281	187
4	2	-6	529	-804	5	1	-16	284	-271
4	2	-5	336	305	5	1	-15	412	-429
4	2	-4	482	427	5	1	-14	251	-270
4	2	-3	594	591	5	1	-13	437	-465
4	2	-2	1866	1957	5	1	-12	<127	32
4	2	-1	<157	135	5	1	-11	665	595
4	2	0	1089	979	5	1	-10	<116	-105
4	2	1	567	-589	5	1	-9	934	935
4	2	2	1341	-1293	5	1	-8	173	-143
4	2	3	<99	52	5	1	-7	753	-742
4	2	4	1140	-1090	5	1	-6	486	449
4	2	5	497	491	5	1	-5	1716	-1610
4	2	6	897	883	5	1	-4	399	383
4	2	7	223	-202	5	1	-3	582	491
4	2	8	1155	1228	5	1	-2	<83	-22
4	2	9	363	-351	5	1	-1	1993	1939
4	2	10	228	180	5	1	0	<175	-176
4	2	11	<146	33	5	1	1	452	477
4	2	12	249	-247	5	1	2	638	-610
4	2	13	290	244	5	1	3	1013	-1037
4	2	14	<213	103	5	1	4	621	-535
4	2	15	280	243	5	1	5	510	-484
4	2	16	291	248	5	1	6	307	-260
4	4	-13	335	-356	5	1	7	1030	920
4	4	-12	<169	-162	5	1	8	221	-191
4	4	-11	229	-207	5	1	9	994	863
4	4	-10	393	-387	5	1	10	<156	-51
4	4	-9	376	372	5	1	11	126	-228
4	4	-8	203	191	5	1	12	186	147
4	4	-7	475	470	5	1	13	378	-423
4	4	-6	647	660	5	1	14	343	267
4	4	-5	339	-301	5	1	15	241	192
4	4	-4	<121	21	5	1	16	353	134
4	4	-3	291	-287	5	3	-15	363	414
4	4	-2	685	-756	5	3	-14	287	-197
4	4	-1	668	719	5	3	-13	292	212
4	4	0	398	-416	5	3	-12	363	-359
4	4	1	627	683	5	3	-11	563	-593
4	4	2	306	332	5	3	-10	<140	38
4	4	3	<119	-246	5	3	-9	767	-742
4	4	4	236	243	5	3	-8	794	766
4	4	5	768	-793	5	3	-7	<132	140
4	4	6	358	-386	5	3	-6	676	637
4	4	7	503	-540	5	3	-5	861	877
4	4	8	340	-402	5	3	-4	272	-317

h	k	l	10Fo	10Fc
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5	3	-2	<111	-174
5	3	-1	991	-946
5	3	0	739	783
5	3	1	228	-238
5	3	2	615	628
5	3	3	1079	1185
5	3	4	198	-209
5	3	5	342	336
5	3	6	450	-468
5	3	7	809	-966
5	3	8	<143	-32
5	3	9	558	-661
5	3	10	380	417
5	3	11	161	105
5	3	12	306	320
5	3	13	284	252
5	5	-8	399	-352
5	5	-7	337	-268
5	5	-6	260	-187
5	5	-5	409	-388
5	5	-4	360	307
5	5	-3	264	222
5	5	-2	317	262
5	5	-1	531	561
5	5	0	418	-420
5	5	1	251	218
5	5	2	583	-631
5	5	3	<166	-171
5	5	4	<171	-21
5	5	5	270	-239
5	5	6	352	320
5	5	7	<191	-3
5	5	8	<199	-88
5	5	9	<206	30
5	5	10	369	-349
6	0	-18	405	475
6	0	-14	1215	-833
6	0	-12	720	-825
6	0	-10	622	703
6	0	-8	944	923
6	0	-6	908	-891
6	0	-4	683	-639
6	0	-2	1342	1294
6	0	0	1142	1192
6	0	4	1421	-1355
6	0	6	1199	-1141
6	0	8	497	530
6	0	10	531	537
6	0	12	382	-441
6	0	14	279	-235
6	0	16	342	343
6	2	-15	312	348
6	2	-14	330	363
6	2	-13	<159	21
6	2	-12	<153	-82
6	2	-11	269	-303
6	2	-10	1058	-928
6	2	-9	<136	110
6	2	-8	829	-729
6	2	-7	262	292
6	2	-6	844	734
6	2	-5	191	-189
6	2	-4	1677	1627
6	2	-3	270	-251
6	2	-2	<108	82
6	2	-1	<107	79
6	2	0	1567	-1469
6	2	1	496	506
6	2	2	<111	22
6	2	3	635	672
6	2	4	1272	1246
6	2	5	<122	121
6	2	6	<127	4
6	2	7	294	-304
6	2	8	877	-905
6	2	9	<142	-32
6	2	10	399	-395
6	2	11	<153	226
6	2	12	318	323
6	2	13	<135	35
6	2	14	356	414
6	4	-14	357	-317
6	4	-13	312	227
6	4	-12	301	-279
6	4	-11	274	206
6	4	-10	281	279
6	4	-9	271	-260
6	4	-8	399	422
6	4	-7	781	-832
6	4	-6	244	-216
6	4	-5	401	-436
6	4	-4	419	-438
6	4	-3	579	571
6	4	-2	366	317
6	4	-1	378	419
6	4	0	636	684
6	4	1	324	-354
6	4	2	<129	-56
6	4	3	265	-260

h	k	l	10Fo	10Fc
6	4	4	546	-617
6	4	5	244	265
6	4	6	253	-229
6	4	7	261	248
6	4	8	261	241
6	4	9	<163	-248
6	4	10	<168	117
6	4	11	389	-462
6	6	1	365	426
7	1	-17	288	-327
7	1	-16	278	292
7	1	-15	<147	170
7	1	-14	239	234
7	1	-13	917	869
7	1	-12	252	-249
7	1	-11	421	428
7	1	-10	509	-542
7	1	-9	847	-801
7	1	-8	307	-320
7	1	-7	593	-574
7	1	-6	<106	44
7	1	-5	1147	1052
7	1	-4	407	412
7	1	-3	1125	1095
7	1	-2	470	448
7	1	-1	612	-630
7	1	0	397	379
7	1	1	1166	-1156
7	1	2	569	581
7	1	3	342	343
7	1	4	215	202
7	1	5	1394	1336
7	1	6	455	-339
7	1	7	343	267
7	1	8	349	-301
7	1	9	766	-747
7	1	10	<129	-98
7	1	11	242	-253
7	1	13	330	364
7	3	-9	602	582
7	3	-8	516	-517
7	3	-7	142	165
7	3	-6	721	-708
7	3	-5	1032	-939
7	3	-4	<131	18
7	3	-3	1055	-1072
7	3	-2	649	669
7	3	-1	365	393
7	3	0	321	278
7	3	1	1058	1067
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7	3	3	<131	-14
7	3	4	426	-475
7	3	5	506	-518
7	3	6	<143	62
7	3	7	<148	54
7	3	8	<153	149
7	3	9	316	371
7	3	10	<164	-258
7	3	11	<169	81
7	3	12	320	-329
7	5	-13	363	315
7	5	-12	265	-202
7	5	-11	288	257
7	5	-10	330	-289
7	5	-9	270	-249
7	5	-8	<203	178
7	5	-7	360	-369
7	5	-6	564	524
7	5	-5	<187	19
7	5	-4	<183	118
7	5	-3	<180	4
7	5	-2	355	-324
7	5	-1	264	-276
7	5	0	<176	-9
7	5	1	<171	-158
7	5	2	442	450
7	5	3	237	209
7	5	4	242	285
7	5	5	416	408
7	5	6	<199	-167
7	5	7	<204	127
7	5	8	272	-221
8	0	-14	394	466
8	0	-12	1010	1095
8	0	-10	228	282
8	0	-8	1590	-1496
8	0	-6	995	-922
8	0	-4	1414	1423
8	0	-2	1479	1380
8	0	0	<171	-88
8	0	2	<35	9
8	0	4	1108	1072
8	0	6	1114	1156
8	0	10	720	-683
8	0	12	284	-214
8	0	14	276	274
8	2	-16	379	454
8	2	-15	<176	167
8	2	-14	<171	-23

h	k	l	10Fo	10Fc
8	2	-13	<166	7
8	2	-12	461	-468
8	2	-11	389	398
8	2	-10	<150	-74
8	2	-9	529	551
8	2	-8	334	267
8	2	-7	<136	45
8	2	-6	366	-365
8	2	-5	533	-542
8	2	-4	1404	-1328
8	2	-3	215	-182
8	2	-2	982	-977
8	2	-1	334	345
8	2	0	807	806
8	2	1	<124	-129
8	2	2	1124	1172
8	2	3	374	-381
8	2	4	694	-374
8	2	5	<134	113
8	2	6	863	-964
8	2	7	306	298
8	2	8	<147	-156
8	2	9	<152	135
8	2	10	299	283
8	2	11	<162	-56
8	2	12	<167	-98
8	2	13	<173	-180
8	2	14	371	-363
8	4	-12	377	404
8	4	-11	<176	-142
8	4	-10	<170	-6
8	4	-9	<166	-42
8	4	-8	564	-596
8	4	-7	349	352
8	4	-6	278	-280
8	4	-5	258	186
8	4	-4	422	441
8	4	-3	455	-480
8	4	-2	418	392
8	4	-1	693	-719
8	4	0	<142	-150
8	4	1	207	-231
8	4	2	250	-219
8	4	3	449	502
8	4	4	245	233
8	4	5	452	519
8	4	6	341	408
8	4	7	<163	-64
8	4	8	<167	-9
8	4	9	<172	-132
8	4	10	307	-327
9	1	-15	304	273
9	1	-14	<145	105
9	1	-13	360	-325
9	1	-12	253	276
9	1	-11	819	-714
9	1	-10	540	467
9	1	-9	262	235
9	1	-8	339	371
9	1	-7	1280	1269
9	1	-6	505	-451
9	1	-5	307	251
9	1	-4	990	-961
9	1	-3	1345	-1269
9	1	-2	241	-193
9	1	-1	719	-691
9	1	0	355	331
9	1	1	684	651
9	1	2	266	229
9	1	3	550	482
9	1	4	522	469
9	1	5	592	-591
9	1	6	435	407
9	1	7	792	-725
9	1	8	<132	73
9	1	9	<136	34
9	1	10	<145	-118
9	1	11	381	402
9	1	12	<145	-118
9	1	13	<150	-21
9	1	14	<155	-214
9	1	15	333	-325
9	3	-11	383	429
9	3	-10	<166	-205
9	3	-9	<162	44
9	3	-8	<158	-217
9	3	-7	<154	-231
9	3	-6	<150	16
9	3	-5	<147	70
9	3	-4	<144	-160
9	3	-3	545	568
9	3	-2	550	-581
9	3	-1	<141	180
9	3	0	600	-572
9	3	1	819	-875
9	3	2	<143	24
9	3	3	623	-663
9	3	4	445	489
9	3	5	429	479
9	3	6	269	199

h	k	l	10Fo	10Fc
9	3	7	560	662
9	3	8	267	-279
9	3	9	<169	49
9	3	10	284	-235
9	5	-10	357	285
9	5	-9	217	153
9	5	-8	<217	172
9	5	-7	572	535
9	5	-6	358	-257
9	5	-5	237	194
9	5	-4	327	-296
9	5	-3	456	-342
9	5	-2	<196	108
9	5	-1	363	-319
9	5	0	436	480
9	5	1	<197	-51
9	5	2	<199	132
9	5	3	<202	37
9	5	4	264	-235
9	5	5	<209	-73
9	5	6	<214	3
9	5	7	<219	-53
9	5	8	290	286
10	0	-14	260	212
10	0	-12	273	-320
10	0	-10	382	-366
10	0	-8	785	819
10	0	-6	1324	1297
10	0	-4	387	-324
10	0	-2	1650	-1659
10	0	0	845	-865
10	0	2	615	678
10	0	4	933	864
10	0	6	<132	-84
10	0	8	<140	-235
10	0	10	354	376
10	0	12	329	332
10	2	-16	345	-397
10	2	-15	<184	3
10	2	-14	308	-323
10	2	-13	<173	12
10	2	-12	412	465
10	2	-11	<164	-183
10	2	-10	740	787
10	2	-9	334	-317
10	2	-8	<151	63
10	2	-7	<148	-52
10	2	-6	527	-582
10	2	-5	477	489
10	2	-4	<140	-15

h	k	l	10Fo	10Fc
10	2	-3	484	451
10	2	-2	419	429
10	2	-1	265	-260
10	2	0	245	-245
10	2	1	491	-535
10	2	2	875	-966
10	2	3	244	-241
10	2	4	262	-259
10	2	5	<147	-4
10	2	6	713	688
10	2	7	<154	-8
10	2	8	553	584
10	4	-13	356	-349
10	4	-12	<190	-96
10	4	-11	<185	-109
10	4	-10	312	-206
10	4	-9	321	357
10	4	-8	222	200
10	4	-7	322	289
10	4	-6	415	445
10	4	-5	<162	-11
10	4	-4	<160	-90
10	4	-3	<159	64
10	4	-2	615	-623
10	4	-1	271	267
10	4	0	288	-259
10	4	1	<158	175
10	4	2	331	351
10	4	3	263	-272
10	4	4	267	265
10	4	5	431	-443
10	4	6	220	-133
10	4	7	<172	18
10	4	8	<179	-95
10	4	9	334	361
11	1	-15	400	-418
11	1	-14	<155	-65
11	1	-13	274	-285
11	1	-12	239	-140
11	1	-11	339	342
11	1	-10	<139	2
11	1	-9	340	318
11	1	-8	<132	199
11	1	-7	646	-575
11	1	-6	254	233
11	1	-5	911	-832
11	1	-4	437	439
11	1	-3	223	252
11	1	-2	197	160
11	1	-1	972	1009

h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc
11	1	0	685	-679	12	0	0	753	778
11	1	1	<211	114	12	0	2	538	-555
11	1	2	763	-727	12	0	4	1252	-1337
11	1	3	1015	-923	12	0	6	323	-463
11	1	4	206	-166	12	0	8	290	305
11	1	5	459	-444	12	0	10	<160	188
11	1	6	<132	128	12	0	14	290	-85
11	1	7	389	396	12	2	-13	332	-113
11	1	8	<138	169	12	2	-12	229	70
11	1	9	231	230	12	2	-11	<173	-152
11	3	-11	376	-436	12	2	-10	508	-544
11	3	-10	<177	168	12	2	-9	<166	-91
11	3	-9	545	-532	12	2	-8	281	-290
11	3	-8	525	544	12	2	-7	<160	16
11	3	-7	287	256	12	2	-6	712	773
11	3	-6	311	299	12	2	-5	<155	-68
11	3	-5	634	659	12	2	-4	896	959
11	3	-4	<159	-72	12	2	-3	195	-307
11	3	-3	<157	69	12	2	-2	<151	49
11	3	-2	<156	-110	12	2	-1	<151	23
11	3	-1	<275	-279	12	2	0	372	-394
11	3	0	<156	45	12	2	1	453	488
11	3	1	<157	132	12	2	2	<153	5
11	3	2	<158	70	12	2	3	283	242
11	3	3	292	307	12	2	4	287	284
11	3	4	<166	-171	12	2	5	<160	-184
11	3	5	<166	-68	12	2	6	<163	-19
11	3	6	<168	-205	12	2	7	<166	-217
11	3	7	358	-400	12	2	8	309	-300
11	3	8	<176	171	12	2	9	<173	-68
11	3	9	312	-250	12	2	10	<178	-17
11	5	-8	376	-283	12	2	11	<182	36
11	5	-7	<227	-119	12	2	12	341	346
11	5	-6	<223	-75	12	4	-14	382	-219
11	5	-5	<220	-100	12	4	-13	<204	171
11	5	-4	<217	259	12	4	-12	<200	-127
11	5	-3	329	250	12	4	-11	<196	232
11	5	-2	<214	71	12	4	-10	<191	186
11	5	-1	444	451	12	4	-9	<187	-217
11	5	0	370	-324	12	4	-8	<182	186
11	5	1	215	118	12	4	-7	417	-429
11	5	2	354	-286	12	4	-6	229	-166
11	5	3	399	-304	12	4	-5	<176	-18
12	0	-14	422	-543	12	4	-4	174	-190
12	0	-12	291	-302	12	4	-3	345	338
12	0	-10	247	264	12	4	-2	222	191
12	0	-8	250	212	12	4	-1	292	295
12	0	-6	376	-446	12	4	0	280	289
12	0	-4	501	-502	12	4	1	<172	27
12	0	-2	438	482	12	4	2	<173	-116

h	k	l	10Fo	10Fc
12	4	3	<175	-105
12	4	4	370	-392
13	1	-13	529	438
13	1	-12	<179	-186
13	1	-11	<175	28
13	1	-10	<171	-182
13	1	-9	619	-565
13	1	-8	<165	-134
13	1	-7	336	-277
13	1	-6	<160	9
13	1	-5	580	491
13	1	-4	<155	60
13	1	-3	463	414
13	1	-2	<154	90
13	1	-1	416	-386
13	1	0	311	269
13	1	1	447	-446
13	1	2	336	181
13	1	3	435	356
13	1	4	206	-131
13	1	5	694	620
13	1	6	357	-313
13	1	7	<168	68
13	1	8	358	-306
13	3	-5	511	-546
13	3	-4	281	222
13	3	-3	395	-443
13	3	-2	469	505
13	3	-1	285	276
13	3	0	311	280
13	3	1	401	458
13	3	2	398	-86
13	5	-2	329	-256
14	0	-12	276	372
14	0	-10	248	-270
14	0	-8	526	-648
14	0	-6	195	-195
14	0	-4	353	388
14	0	-2	311	372
14	0	2	285	-259
14	0	4	278	341
14	0	6	287	357
14	0	8	283	-261
14	0	10	418	-444
14	2	-12	343	-358
14	2	-11	<184	242
14	2	-10	<181	-101
14	2	-9	<177	120
14	2	-8	391	364
14	2	-7	<167	-135
14	2	-6	<170	33
14	2	-5	<167	-165
14	2	-4	543	-574
14	2	-3	<166	-5
14	2	-2	213	-157
14	2	-1	<165	83
14	2	0	547	597
14	2	1	<166	-20
14	2	2	481	497
14	2	3	<168	-20
14	2	4	<170	-76
14	2	5	<173	65
14	2	6	304	-289
14	4	-3	305	-242
14	4	-2	<188	190
14	4	-1	340	-375
15	1	-7	579	503
15	1	-6	<173	-199
15	1	-5	<171	25
15	1	-4	<169	-126
15	1	-3	505	-468
15	1	-2	<167	-9
15	1	-1	200	-195
15	1	0	274	127
15	1	1	349	387
15	1	2	310	174
15	1	3	297	287
16	0	-6	286	330
16	0	-4	<127	-178
16	0	-2	434	-471
16	0	0	<97	-21
16	0	2	438	502
16	0	4	270	313
16	2	-5	406	209
16	2	-4	<168	-118
16	2	-3	<167	66
16	2	-2	293	203

COMPUTER PROGRAMMES

The computations were carried out on an Elliott 803 computer using programmes prepared in this laboratory.

The following programmes have been written by myself in Algol.

1. A programme to correct the intensities of reflections, obtained by Weissenberg or precession methods, for Lorentz and polarisation factors. If desired, corrections for spot extension (Phillips, 1956) may also be applied to upper level Weissenberg data.

2. A programme to calculate bond distances and their e.s.d.'s using the formula put forward by Cruickshank, 1953.

$$\sigma^2 = (\sigma(x)_p^2 + \sigma(x)_q^2)l^2 + (\sigma(y)_p^2 + \sigma(y)_q^2)m^2 + (\sigma(z)_p^2 + \sigma(z)_q^2)n^2$$

where l, m and n are the direction cosines referred to orthogonal axes for the bond between p and q.

This programme also calculates the e.s.d., dθ in an angle as follows:

$$d\theta^2 = l_3^2\ (\mathrm{Cos}\alpha_3 - \mathrm{Cos}\theta\mathrm{Cos}\alpha_1)^2\sigma(x)_u^2$$

$$+ \ (l_1(\mathrm{Cos}\alpha_1 - \mathrm{Cos}\theta\mathrm{Cos}\alpha_3) + l_3(\mathrm{Cos}\alpha_3 - \mathrm{Cos}\theta\mathrm{Cos}\alpha_1)^2\sigma(x)_v^2$$

$$+ \ l_1^2(\mathrm{Cos}\alpha_1 - \mathrm{Cos}\theta\mathrm{Cos}\alpha_3)^2\sigma(x)_w^2$$

plus similar terms for $\sigma(y)_{u,v,w}$, and $\sigma(z)_{u,v,w}$, where $\mathrm{Cos}\alpha_1$, $\mathrm{Cos}\beta_1$, $\mathrm{Cos}\gamma_1$ are the direction cosines for the bond l_1 between atoms u and v and $\cos\alpha_3$, $\cos\beta_3$ and $\cos\gamma_3$ are the direction cosines for the bond l_3 between v and w referred to orthogonal axes. (Darlow, 1960).

3. A programme to compute van der Waals contacts between atoms of adjacent molecules. This generates the coordinates for each atom in all the equivalent positions within any combinations of translations of half a cell edge in any direction from one complete unit cell for monoclinic and orthorhombic space groups. The programme then calculates the distance between each atom in the asymmetric unit and each of the stored sets of coordinates for all the atoms, out-putting those less than a pre-set limit.

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