

## The Molecular Structure of Trimethylamine–Gallane in the Gas Phase as determined by Electron Diffraction †

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The structure of the gaseous trimethylamine–gallane molecule,  $\text{Me}_3\text{N}\cdot\text{GaH}_3$ , has been determined by electron diffraction. Salient structural parameters ( $r_s$ ) are:  $r(\text{Ga}-\text{H})$  149.7(1.5),  $r(\text{Ga}-\text{N})$  212.4(0.7),  $r(\text{N}-\text{C})$  148.2(0.5),  $r(\text{C}-\text{H})$  111.2(0.4) pm,  $\text{Ga}-\text{N}-\text{C}$  109.9(0.5), and  $\text{N}-\text{C}-\text{H}$  112.7(2.2)°. The main features of the structure are compared with those of other molecules including either aluminium or gallium bound to hydrogen and/or a nitrogen atom.

Trimethylamine–gallane,  $\text{Me}_3\text{N}\cdot\text{GaH}_3$ , has been studied more extensively than any other gallium hydride derivative.<sup>1</sup> In part this reflects its thermal stability, in part its use as a synthetic intermediate. It is also one of the few gallium hydrides whose molecular structure has been investigated. Thus, X-ray crystallography has confirmed the  $C_{3v}$  symmetry of the molecular skeleton and indicated a Ga–N bond distance of  $197 \pm 9$  pm while failing to locate the hydrogen atoms.<sup>2</sup> In addition, there has been a microwave study of the gaseous molecule and the rotational constants thus derived have been used to calculate a Ga–N distance of  $211.1 \pm 0.2$  pm but are relatively insensitive to the location of the hydrogen atoms.<sup>3</sup>

We have investigated the structure of the gaseous trimethylamine–gallane molecule by electron diffraction. In this we have had two principal aims: (i) the accurate definition of the positions of as many atoms as possible, and (ii) the independent determination of not only dimensions but also amplitudes of vibration to establish realistic bench-marks for the structural characterization of other gallium hydrides. In connection with the second of these aims we have in mind the molecule  $\text{Ga}(\text{BH}_2)_2\text{H}$  in particular; here the electron-diffraction pattern suggests the presence of unsymmetrical  $\text{Ga}(\mu\text{-H})_2\text{B}$  bridges but correlation between parameters makes it deficient on information about vibrational amplitudes.<sup>4</sup> By contrast, any difficulties caused by similar correlation of the molecular parameters of  $\text{Me}_3\text{N}\cdot\text{GaH}_3$  could be countered in principle by using the rotational constants calculated from the microwave spectrum as additional data in the structure refinement. This sort of strategy we have successfully applied for example in redetermining the structure of tetraborane(10).<sup>5</sup> In practice, our refinement calculations on  $\text{Me}_3\text{N}\cdot\text{GaH}_3$  have converged satisfactorily without the need for any additional constraints and we have been able to determine quite independently the structure of the gaseous molecule. This has afforded the first realistic estimates of the length and vibrational amplitude of the Ga–H bonds.

### Experimental

The synthesis and manipulation of trimethylamine–gallane were achieved using conventional vacuum-line techniques. Gallium(III) chloride was prepared by the direct interaction of gallium (Alcoa Chemicals) with chlorine. Lithium tetrahydrogallate,  $\text{Li}[\text{GaH}_4]$ , was prepared by the reaction of lithium hydride (Aldrich Chemicals) with gallium(III) chloride in diethyl ether.<sup>6</sup> The reaction of  $\text{Li}[\text{GaH}_4]$  with  $\text{NHMe}_3\text{Cl}$

(Aldrich Chemicals) in diethyl ether was then used as the source of trimethylamine–gallane,<sup>6</sup> which was purified by sublimation *in vacuo*. The purity of the product was judged by the i.r. spectrum of its vapour.<sup>7</sup> It was stored *in vacuo* at 77 K.

Electron-scattering patterns were recorded photographically on Kodak Electron Image plates using the Edinburgh gas-diffraction apparatus.<sup>8</sup> The sample was held at ambient temperature (corresponding to an equilibrium vapour pressure of ca. 2 mmHg<sup>7</sup>) in an ampoule closed by a greased stopcock and gained access to the nozzle of the diffraction apparatus via a greased glass taper joint and a stainless steel needle valve. The patterns were recorded at nozzle-to-plate distances of 285.7 and 128.3 mm. The electron wavelength, which was calibrated with reference to the scattering pattern of benzene vapour, was 5.685–5.686 pm.

The plates were left in air for 16 h before developing to reduce the effects of reaction between the vapour and the emulsion of the plates.<sup>4</sup> Despite this, some fogging could not be avoided, especially with the shorter nozzle-to-plate distance which entailed longer exposure times.

Data were accumulated in digital form using a Joyce-Loebl MDM6 microdensitometer.<sup>9</sup> Calculations, performed on an ICL 2970 computer at the Edinburgh Regional Computing Centre, used the programs for data reduction<sup>8</sup> and least-squares refinement<sup>10</sup> described elsewhere with the complex scattering factors listed by Schafer *et al.*<sup>11</sup> The weighting functions used to set up the off-diagonal weight matrix are given in Table 1 together with the correlation parameters and final scale factors.

### Results

**Structure Analysis.**—The vibrational spectra of trimethylamine–gallane,  $\text{Me}_3\text{N}\cdot\text{GaH}_3$ , in the solid and gas phases have been interpreted on the basis of a molecular skeleton with  $C_{3v}$  symmetry.<sup>3,7</sup> We have therefore adopted a structural model consistent with this symmetry with the  $\text{GaH}_3$  and  $\text{NC}_3$  units in a staggered conformation. Such a model entails ten independent geometrical parameters. With reference to Figure 1, these parameters are the four internuclear distances Ga–H, Ga–N, N–C, and C–H<sub>Me</sub> (where H<sub>Me</sub> denotes a hydrogen atom of the methyl groups), and six angles H–Ga–N, Ga–N–C, N–C–H<sub>Me</sub>,  $\alpha$  defining the twisting of the  $\text{GaH}_3$  and  $\text{NC}_3$  rotors from the staggered conformation,  $\beta$  defining the twisting of the  $\text{CH}_3$  rotors from the staggered conformation with respect to the  $\text{GaNC}_2$  moiety, and  $\gamma$  defining the tilting of the  $\text{CH}_3$  units with respect to the N–C bonds.

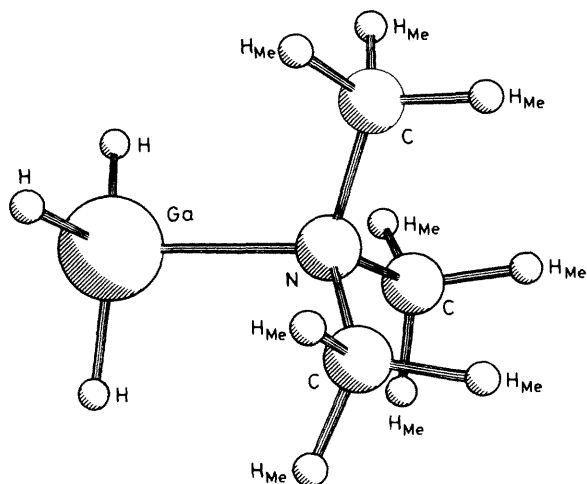
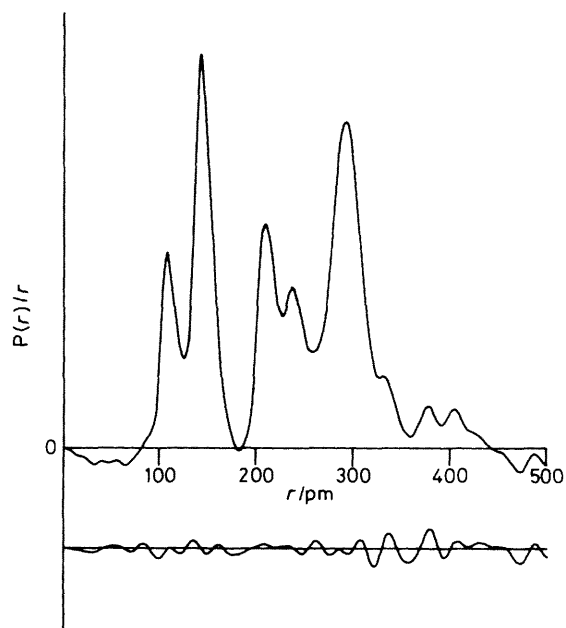
Molecular-scattering intensities have been calculated by

† *Non-S.I. unit employed*: mmHg  $\approx 13.6 \times 9.8$  Pa.

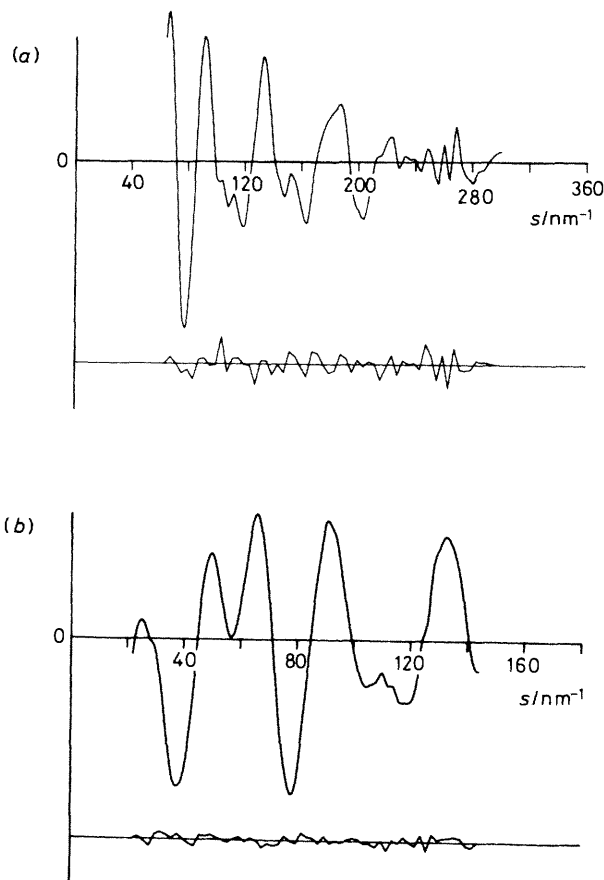
**Table 1.** Nozzle-to-plate distances, weighting functions, correlation parameters, and scale factors

| Nozzle-to-plate distance/mm | $\Delta s$ | $s_{min.}$ | $sw_1$<br>nm <sup>-1</sup> | $sw_2$ | $s_{max.}$ | Correlation,<br>$p/h$ | Scale factor,<br>$k^*$ |
|-----------------------------|------------|------------|----------------------------|--------|------------|-----------------------|------------------------|
| 285.7                       | 2          | 22         | 40                         | 120    | 144        | 0.0456                | 0.900(23)              |
| 128.3                       | 4          | 64         | 84                         | 240    | 300        | -0.2304               | 0.591(23)              |

\* Figures in parentheses are the estimated standard deviations of the last digits.

**Figure 1.** Perspective view of the molecule  $\text{Me}_3\text{N}\cdot\text{GaH}_3$ **Figure 2.** Observed and difference radial-distribution curves,  $P(r)/r$  versus  $r$ , for  $\text{Me}_3\text{N}\cdot\text{GaH}_3$ . Before Fourier transformation the data were multiplied by  $s \cdot \exp[(-0.00002 s^2)/(Z_{\text{Ga}} - f_{\text{Ga}})(Z_{\text{N}} - f_{\text{N}})]$ 

established procedures and the molecular structure has been refined on this basis by full-matrix least-squares analysis. We have not applied shrinkage corrections in our refinements but there is no reason to suppose that shrinkage effects will make any significant difference to the estimated molecular parameters derived from the least-squares analysis, within the

**Figure 3.** Experimental and final-difference molecular-scattering intensities for  $\text{Me}_3\text{N}\cdot\text{GaH}_3$ ; nozzle-to-plate distances (a) 128.3 and (b) 285.7 mm

limits of error stipulated by the estimated standard deviations. Such deviations take into account the effects of correlation, whether involving data points or the molecular parameters themselves, and have been increased to allow for systematic errors in the electron wavelength, nozzle-to-plate distance, etc.

Figure 2 depicts the radial-distribution curve,  $P(r)/r$  vs.  $r$ , derived from the experimental data sets after scaling, combination, and Fourier transformation. Of the prominent peaks, that at ca. 110 pm is identified with scattering from directly bound C-H<sub>Me</sub> atom pairs, while that at ca. 145 pm is due to scattering from directly bound Ga-H and N-C atom pairs. The peak at ca. 210 pm originates in scattering from directly bound Ga-N with a small contribution from non-bonded N...H<sub>Me</sub> atom pairs. The conspicuous peak at ca. 295 pm is attributable to scattering from non-bonded Ga...C atom pairs. The weaker features between 300 and 450 pm represent scattering from other non-bonded atom pairs, e.g. Ga...H<sub>Me</sub> and C...H.

**Table 2.** Molecular parameters <sup>a</sup> for Me<sub>3</sub>N·GaH<sub>3</sub>

| Parameter   | Distance/pm or angle/° | Amplitude/pm      |
|---|------------------------|-------------------|
| <b>(a) Independent distances and amplitudes</b>           |                        |                   |
| <i>r</i> <sub>1</sub> (Ga-H)                              | 149.7(1.5)             | 7.9(0.8)          |
| <i>r</i> <sub>2</sub> (Ga-N)                              | 212.4(0.7)             | 6.1(1.1)          |
| <i>r</i> <sub>3</sub> (N-C)                               | 148.2(0.5)             | 3.9 <sup>b</sup>  |
| <i>r</i> <sub>4</sub> (C-H <sub>Me</sub> )                | 111.2(0.4)             | 5.0(0.8)          |
| <b>(b) Dependent distances and amplitudes<sup>c</sup></b> |                        |                   |
| <i>d</i> <sub>5</sub> (Ga···C)                            | 297.5(0.7)             | 10.5(0.7)         |
| <i>d</i> <sub>6</sub> (N···H <sub>Me</sub> )              | 217.0(2.4)             | 15.4(3.0)         |
| <i>d</i> <sub>7</sub> (C···C)                             | 241.4(1.0)             | 6.7(1.2)          |
| <i>d</i> <sub>8</sub> (C···H)                             | 327.0(1.0)             | 30.0 <sup>d</sup> |
| <i>d</i> <sub>9</sub> (C···H)                             | 410.0(1.4)             | } 14.3(2.3)       |
| <i>d</i> <sub>10</sub> (Ga···H <sub>Me</sub> )            | 400.3(2.2)             |                   |
| <i>d</i> <sub>11</sub> (Ga···H <sub>Me</sub> )            | 325.3(8.1)             |                   |
| <i>d</i> <sub>12</sub> (Ga···H <sub>Me</sub> )            | 305.9(8.5)             |                   |
| <b>(c) Independent angles</b>                             |                        |                   |
| H-Ga-N  | 102 <sup>d</sup>       |                   |
| Ga-N-C  | 109.9(0.5)             |                   |
| N-C-H <sub>Me</sub>                                       | 112.7(2.2)             |                   |
| α, H <sub>3</sub> Ga-NC <sub>3</sub> twist                | 0 <sup>d</sup>         |                   |
| β, H <sub>3</sub> C-NC <sub>2</sub> Ga twist              | 50(10)                 |                   |
| γ, CH <sub>3</sub> tilt                                   | 0 <sup>d</sup>         |                   |

<sup>a</sup> Figures in parentheses are the estimated standard deviations of the last digits. <sup>b</sup> Constrained to equal one-half the Ga-H amplitude of vibration. <sup>c</sup> Other non-bonded C···H, N···H, and H···H distances were included in the refinement, but are not listed here. <sup>d</sup> Fixed.

Seven of the ten independent geometrical parameters used to define the model (the distances Ga-H, Ga-N, N-C, and C-H<sub>Me</sub> and the angles Ga-N-C, N-C-H<sub>Me</sub>, and β defining twisting about the C-N bond) are amenable to simultaneous refinement. Independent refinement is also possible for five amplitudes of vibration; these relate to the Ga-N, C-H<sub>Me</sub>, Ga···C, N···H<sub>Me</sub>, and C···C atom pairs. In addition, the N-C and Ga-H amplitudes of vibration were refined as a single parameter with a ratio 1:2, and the two amplitudes of vibration associated with the proximal Ga···H<sub>Me</sub> atom pairs have been refined as a single parameter, as have those associated with C···H and the distal Ga···H<sub>Me</sub> atom pairs.

Since it is not possible to refine the H-Ga-N bond angle, we have performed a series of calculations to explore the dependence of the *R* factor on this parameter. The *R* factor is at a minimum for H-Ga-N = *ca.* 102° and the angle has been fixed at this value in the final refinement calculations. The angle α defining the mutual orientation of the H<sub>3</sub>Ga and NC<sub>3</sub> rotors has been fixed at 0° following similar calculations, although there is very little variation in the *R* factor as this parameter is varied. The angle γ specifying tilting of the CH<sub>3</sub> groups about the N-C axes has likewise been fixed at 0°, on similar grounds.

It has not been possible to refine the amplitudes of vibration other than those already detailed. Accordingly we have fixed the remaining amplitudes at values in line with those determined for related molecules or derived from spectroscopic data.

The final least-squares correlation matrix shows no major problems of correlation between the refining parameters, apart from the Ga-H and C-N distances. The success of the refinement may be judged by reference to the difference between the experimental radial-distribution curve and that calculated on the basis of the optimum model (Figure 2). Figure 3 offers a similar comparison between the experimental

and calculated molecular scattering. The structural details and vibrational amplitudes of the optimum refinement, corresponding to *R*<sub>G</sub> = 0.092, are listed in Table 2, together with the estimated standard deviations.

## Discussion

A notable feature of the final refinement is the comparative shortness of the Ga-H bonds at 149.7 pm. This is appreciably shorter than the value assumed (159 pm) in the analysis of the microwave spectrum of the gaseous Me<sub>3</sub>N·GaH<sub>3</sub> molecule; that it is shorter than the terminal Ga-H bond in Ga(BH<sub>4</sub>)<sub>2</sub>H (156.5 ± 2.4 pm)<sup>4</sup> is perhaps less surprising than that it should be shorter than the Al-H bond in the analogous complex Me<sub>3</sub>N·AlH<sub>3</sub> (156.0 ± 1.1 pm).<sup>12</sup> Although the difference between the Ga-H and Al-H distances is not much greater than three standard deviations, it is paralleled by the vibrational properties of the molecules Me<sub>3</sub>N·GaH<sub>3</sub><sup>3,7</sup> and Me<sub>3</sub>N·AlH<sub>3</sub>,<sup>13</sup> the M-H stretching fundamentals of which (M = Ga or Al) occur near 1 853 and 1 792 cm<sup>-1</sup> respectively. Furthermore, the Ga-H stretching force constant of the GaH<sub>4</sub><sup>-</sup> anion exceeds the Al-H stretching force constant of the AlH<sub>4</sub><sup>-</sup> anion.<sup>14</sup> An explanation of this effect may be found in the nature of the metal-hydrogen bond and the different electronegativities (χ) of aluminium (1.5) and gallium (1.8).<sup>15</sup> The better energy match between the valence orbitals of gallium and those of the hydrogen atoms (χ 2.1)<sup>15</sup> results in bonds which are not only less polar but also stronger than those between aluminium and hydrogen. With carbon, a somewhat more electronegative substituent (χ 2.5), there is little to choose between the lengths of bonds to aluminium and gallium, as witnessed by the Al-C distance of 195.9 pm in the gaseous AlMe<sub>3</sub> monomer<sup>16</sup> and the Ga-C distance of 196.7 pm in GaMe<sub>3</sub>.<sup>17</sup> On the other hand, with nitrogen (χ 3.0)<sup>15</sup> as the substituent, we note that aluminium forms the shorter bonds, as exemplified by the metal-nitrogen distances in the molecules Me<sub>3</sub>N·AlH<sub>3</sub> (206.3 pm)<sup>12</sup> and Me<sub>3</sub>N·GaH<sub>3</sub> (212.4 pm).

A comparison with the dimensions of other related molecules, displayed by Table 3, shows that the Ga-N bond is somewhat shorter in Me<sub>3</sub>N·GaH<sub>3</sub> than in the corresponding adduct of trimethylgallane, Me<sub>3</sub>N·GaMe<sub>3</sub> (220 ± 3 pm).<sup>18</sup> This is presumably a sign of the superior electron-releasing properties of the methyl substituents which reduce the acidity of the gallane unit (*i.e.* raise the energy of the lowest unoccupied molecular orbital). A similar effect has been observed with the Al-N bond lengths in the molecules Me<sub>3</sub>N·AlH<sub>3</sub> (206.3 pm)<sup>12</sup> and Me<sub>3</sub>N·AlMe<sub>3</sub> (209.9 pm);<sup>19</sup> the Al-N bond length in Me<sub>3</sub>N·AlCl<sub>3</sub> is appreciably shorter (194.5 ± 3.5 pm).<sup>20</sup>

Unfortunately the N-Ga-H bond angle in Me<sub>3</sub>N·GaH<sub>3</sub> does not lend itself to refinement although the value which affords the minimum *R* factor (102°) is appreciably less than the tetrahedral angle (109.5°). This seems to be a feature of adducts of the type X<sub>3</sub>N·MY<sub>3</sub> (X = H or Me; M = Al or Ga; Y = H, Me, or halogen) in which the N-M-Y bond angle is consistently found to occur in the range 101–105° (see Table 3).

The dimensions of the co-ordinated trimethylamine moiety are not very different from those of the free trimethylamine molecule.<sup>21</sup> However, the N-C bonds suffer some attenuation with co-ordination, the length increasing from 145.4 ± 0.2 pm in free NMe<sub>3</sub><sup>21</sup> to 148.2 ± 0.5 pm in Me<sub>3</sub>N·GaH<sub>3</sub>. A similar effect has been observed in the molecules Me<sub>3</sub>N·AlH<sub>3</sub>,<sup>12</sup> Me<sub>3</sub>N·AlMe<sub>3</sub>,<sup>19</sup> and Me<sub>3</sub>N·AlCl<sub>3</sub><sup>20</sup> with N-C bond lengths of 147.6 ± 0.3, 147.5 ± 0.3, and 151.6 ± 1.2 pm respectively. This is to be expected in view of the mixing between the formally non-bonding orbital which is the highest occupied

**Table 3.** A comparison of the molecular parameters of trimethylamine-gallane with those of related molecules, mainly of the type  $X_3N \cdot MY_3$  (M = Al or Ga)<sup>a</sup>

| Compound   | Phase/method <sup>b</sup> | Distances/pm |                  | N-M-Y bond angle/ <sup>o</sup> | Ref.      |
|--|---------------------------|--------------|------------------|--------------------------------|-----------|
|  |                           | M-N          | M-H              |                                |           |
| Me <sub>3</sub> N·GaH <sub>3</sub>                                       | Vapour/ED                 | 212.4(0.7)   | 149.7(1.5)       | 102 <sup>c</sup>               | This work |
|  | Vapour/M                  | 211.1(0.2)   | 159 <sup>d</sup> | 102 <sup>d</sup>               | 3         |
|  | Solid/X                   | 197(9)       | —                | —                              | 2         |
| Me <sub>3</sub> N·GaMe <sub>3</sub>                                      | Vapour/ED                 | 220(3)       | —                | 101                            | 18        |
| H <sub>3</sub> N·GaCl <sub>3</sub>                                       | Vapour/ED                 | 205.7(1.1)   | —                | 101.1                          | e         |
| H <sub>3</sub> N·GaBr <sub>3</sub>                                       | Vapour/ED                 | 208.1(2.3)   | —                | 100.8                          | f         |
| Me <sub>3</sub> N·AlH <sub>3</sub>                                       | Vapour/ED                 | 206.3(0.8)   | 156.0(1.1)       | 104.3(1.1)                     | 12        |
| Me <sub>3</sub> N·AlMe <sub>3</sub>                                      | Vapour/ED                 | 209.9(1.0)   | —                | 102.3(0.3)                     | 19        |
| Me <sub>3</sub> N·AlCl <sub>3</sub>                                      | Vapour/ED                 | 194.5(3.5)   | —                | 104.9(0.7)                     | 20        |
| H <sub>3</sub> N·AlCl <sub>3</sub>                                       | Vapour/ED                 | 199.6(1.9)   | —                | 101.2                          | g         |
| H <sub>3</sub> N·AlBr <sub>3</sub>                                       | Vapour/ED                 | 199.7(1.9)   | —                | 101.5                          | f         |
| bipy·GaCl <sub>3</sub>   | Solid/X                   | 210.5        | —                | —                              | h         |
| [(GaH <sub>2</sub> (μ-NCH <sub>2</sub> CH <sub>2</sub> )) <sub>3</sub> ] | Solid/X                   | 197(1)       | —                | —                              | i         |
| [(GaD <sub>2</sub> (μ-NCHCHCHN)) <sub>2</sub> ]                          | Solid/X                   | 197.4(0.5)   | 156 <sup>c</sup> | —                              | j         |
| Ga(BH <sub>4</sub> ) <sub>2</sub> H                                      | Vapour/ED                 | —            | 156.5(2.4)       | —                              | 4         |

<sup>a</sup> Estimated standard deviations are given in parentheses where values are available. <sup>b</sup> ED = Electron diffraction; M = microwave spectroscopy; X = X-ray diffraction. <sup>c</sup> Not included in the final refinement (see text). <sup>d</sup> Assumed value. <sup>e</sup> M. Hargittai, I. Hargittai, and V. P. Spiridonov, *J. Mol. Struct.*, 1976, **30**, 31. <sup>f</sup> M. Hargittai, I. Hargittai, V. P. Spiridonov, and A. A. Ivanov, *J. Mol. Struct.*, 1977, **39**, 225. <sup>g</sup> M. Hargittai, I. Hargittai, V. P. Spiridonov, M. Pelissier, and J. F. Labarre, *J. Mol. Struct.*, 1975, **24**, 27. <sup>h</sup> R. Restivo and G. J. Palenik, *Chem. Commun.*, 1969, 867. Data refer to the cation [GaCl<sub>2</sub>(bipy)<sub>2</sub>]<sup>+</sup> (bipy = 2,2'-bipyridyl). <sup>i</sup> W. Harrison, A. Storr, and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1972, 1554. <sup>j</sup> D. F. Rendle, A. Storr, and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1973, 2252.

molecular orbital of the NMe<sub>3</sub> molecule and the lower-energy bonding orbital (of predominantly *s* character) having the same irreducible representation (*a*<sub>1</sub>).

This is the first time that an amplitude of vibration has been determined independently for a Ga-H bond in a derivative of gallane. In fact the amplitude determined in this study (7.9 pm) is close to values calculated from spectroscopic data for Ge-H bonds in various derivatives of germane.<sup>22</sup> In our analysis of the electron-diffraction pattern of the molecule Ga(BH<sub>4</sub>)<sub>2</sub>H we were obliged to assume amplitudes for the Ga-H bonds;<sup>4</sup> in the event the values of 6.0 and 9.5 pm we chose for the terminal and bridging bonds respectively seem to have been reasonably close to the mark, giving us added confidence in the structural inferences we have drawn from the electron-diffraction pattern of Ga(BH<sub>4</sub>)<sub>2</sub>H.<sup>4</sup> The other vibrational parameters calculated for Me<sub>3</sub>N·GaH<sub>3</sub> are in sensible agreement with those determined by similar means for free trimethylamine<sup>21</sup> and for other adducts of trimethylamine.<sup>19,20</sup>

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