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The Molecular Structures of Trimethylindium and Trimethylthallium Determined by Gas Electron Diffraction

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The gas electron diffraction patterns of trimethylindium and trimethylthallium have been recorded with nozzle temperatures of 50 to 60 °C and 30 to 45 °C, respectively. The diffraction patterns are consistent with molecular models with planar MC_3 skeletons and freely rotating methyl groups. The M–C bond distances (r_a) are In–C = 2.161(3) Å and Tl–C = 2.206(3) Å. The variation of M–C bond distances among methyl derivatives of group IIA, IIB and IIIB elements is discussed.

Trimethylindium and trimethylthallium are monomeric in the gas phase and in hydrocarbon solution.[1] A relatively recent (1974) gas electron diffraction (GED) study of $(CH_3)_3In$ yielded an In–C bond distance of 2.093(6) Å.[2] As pointed out by the authors,[2] this value is significantly smaller than that obtained in an early (1941) GED study,[3] 2.16 ± 0.04 Å. It is also considerably smaller than the values obtained for single In–C bond distances by X-ray studies of several organoindium compounds.[2] We have recently completed a GED study of dimeric dimethyl(propynyl)indium where the terminal In–C (methyl) bond distance was found to be 2.18(2) Å.[4] We suggested, therefore, that the 1974 GED study of $(CH_3)_3In$ is marred by a scale error, and that the correct value for the In–C bond distance in this compound is around 2.16 Å.[4]

The molecular structures of $(CH_3)_3B$,[5] $(CH_3)_3Al$[6] and $(CH_3)_3Ga$[7] have all been determined by GED. And in the article describing their study of $(CH_3)_3Ga$, Beagley and coworkers[7] refer to an unpublished GED study of $(CH_3)_3Tl$ (Beagley, Robiette and Sheldrick, 1967) yielding a Tl–C bond distance of 2.218(3) Å.

In this paper we report the results of reinvestigations of trimethyl-indium and -thallium by GED.

EXPERIMENTAL

The electron scattering patterns of $(CH_3)_3In$ and $(CH_3)_3Tl$ were recorded on Balzers Eldigraph KDG-2 with nozzle temperatures of 50–60 °C (In) and 30–45 °C (Tl). Exposures were made with nozzle-to-photographic plate distances of 50 and 25 cm. This study is based on four 50 cm and three 25 cm plates for In and four 50 cm and four 25 cm plates for Tl. The data were processed by standard methods.[8]

The complex atomic scattering factors, $f'(s) = |f'(s)| \exp i\eta(s)$, were calculated from analytical representations of the atomic potentials[9] using a program written by Yates.[10] The molecular intensities were modified through multiplication with $s/|f'_M(s)||f'_C(s)|$ where M = In or Tl. The molecular intensity curves obtained for each nozzle-to-plate distance were averaged and connected. The final molecular intensity curves extended from $s = 2.00$ Å^{-1} to 19.75 Å^{-1} for M = In and from $s = 2.00$ Å^{-1} to 25.50 Å^{-1} for M = Tl. For M = In the "beat out", corresponding to $\Delta\eta_{MC}(s) = \eta_M(s) - \eta_C(s) = \pi/2$ occurs between $s = 19$ and 20 Å^{-1}. The factor cos $[\Delta\eta_{MC}(s)]$ clearly increases too slowly to allow the diffraction pattern to be detected at larger angles. For M = Tl the MC "beat out" occurs at about $s = 14$ Å^{-1} and the interference pattern could be detected out to 25 Å^{-1}.

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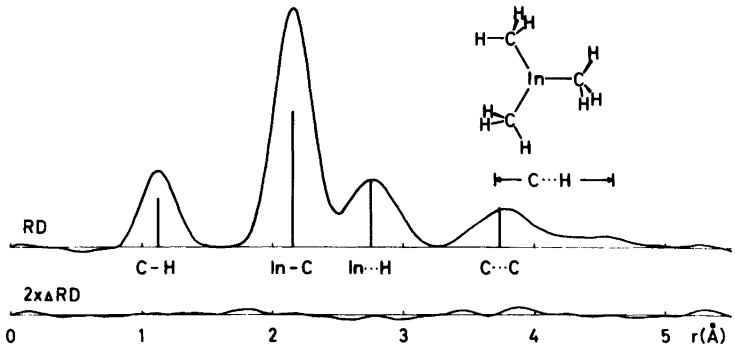

Fig. 1. Above: Experimental radial distribution curve for $(CH_3)_3In$. Artificial damping constant $k = 0.003$ Å^2. Major interatomic distances are indicated by bars of height proportional to the area under the corresponding peak. *Below:* Difference between the experimental curve and the theoretical curve calculated for the best model.

STRUCTURE ANALYSIS

Both $(CH_3)_3In$ and $(CH_3)_3Tl$ were assumed to have planar MC_3 skeletons with all $\angle CMC = 120°$. The methyl groups were assumed to have C_{3v} symmetry with the threefold axes coinciding with the M–C bonds. The methyl groups are expected to undergo virtually non-hindered internal rotation about the M–C axes, but the structure refinements were carried out on models of overall symmetry C_3 in which one C–H bond in each methyl group is lying in the MC_3 plane as indicated in Figs. 1 and 2. The molecular structure of each compound is then determined by only three parameters, the M–C and C–H bond distances and the valence angle $\angle MCH$.

Simple valence force fields of the two molecules were adjusted[11] to reproduce the vibrational frequencies assigned for the two molecules.[12] Since the out-of-plane MC_3 deformation frequency of $(CH_3)_3Tl$ has not been assigned, the corresponding force constant was transferred from $(CH_3)_3In$. Root mean square vibrational amplitudes, l, and perpendicular amplitude correction coefficients, K, were calculated using a program written by Hilderbrandt.[11]

The molecular structures were refined by least squares calculations with diagonal weight matrices under the constraints of geometrically consistent r_α structures.[13] Those vibrational amplitudes which could not be refined were fixed at their calculated values. The refinements converged to yield the structure parameters listed in Table 1. The estimated standard deviations have been multiplied by a factor

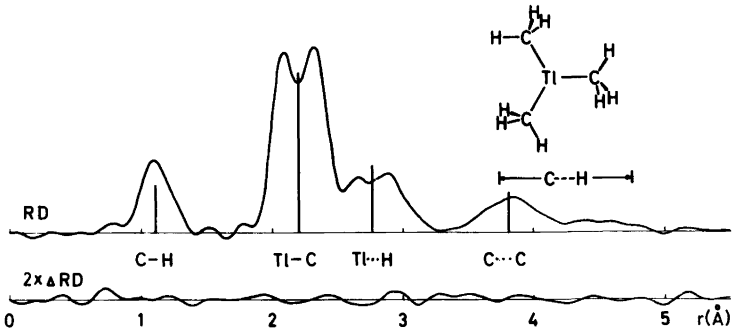

Fig. 2. Above: Experimental radial distribution curve for $(CH_3)_3Tl$. Artificial damping constant $k = 0.002$ Å^2. Major interatomic distances are indicated by bars of height proportional to the area under the corresponding (double) peak. *Below:* Difference between the experimental curve and the theoretical curve calculated for the best model.

Table 1. Internuclear distances (r_a), valence angles and root mean square vibrational amplitudes (l) of $(CH_3)_3In$ and $(CH_3)_3Tl$ obtained by least square refinement on gas electron diffraction (GED) data. (Estimated standard deviations in parentheses in units of the last digit.) Root mean square vibrational amplitudes and perpendicular amplitude correction coefficients (K) calculated from a molecular force field (FF).

	r_a (Å)	l (Å) (GED)	l (Å) (FF)	K (Å) (FF)
$(CH_3)_3In$				
In–C	2.161(3)	0.056(4)	0.058	0.005
C–H	1.124(4)	0.080(5)	0.078	0.060
In---H	2.755(6)	0.136(6)	0.133	0.060
C---C	3.735(2)	0.153(13)	0.102	0.001
C---H	3.69 to 4.61	0.22 to 0.13	0.22 to 0.13	
∠CInC (°)	120 (ass)			
∠InCH (°)	109.8(4)			
$(CH_3)_3Tl$				
Tl–C	2.206(3)	0.053(3)	0.059	0.005
C–H	1.108(7)	0.066(5)	0.078	0.059
Tl---H	2.767(9)	0.150(10)	0.133	0.060
C---C	3.815(4)	0.162(21)	0.103	0.001
C---H	3.78 to 4.76	0.22 to 0.13	0.22 to 0.13	
∠CTlC (°)	120 (ass)			
∠TlCH (°)	107.5(9)			

of two to compensate for the error introduced by the connection of intensity curves and the neglect of data correlation and expanded to include an estimated scale uncertainty of 0.1 %.

Experimental radial distribution curves calculated by Fourier inversion of experimental modified molecular intensity curves, are shown in Figs. 1 and 2 along with the difference between the experimental RD curves and their theoretical counterparts calculated for the best models. We consider the agreement satisfactory.

DISCUSSION

The experimental radial distribution curve of $(CH_3)_3In$ shown in Fig. 1 has the normal appearance: each internuclear distance, R_{ij}, in the molecule is represented by an approximately Gaussian peak centered around $r=R_{ij}$. The area under each peak is roughly proportional to $n_{ij}Z_iZ_j/R_{ij}$ where Z_i and Z_j are the atomic numbers and n_{ij} the number of times the distance occurs in the molecule, *e.g.* $n=3$ for the M–C bond distance; $Z_{In}=49$. Because of the high atomic number of Tl ($Z_{Tl}=81$), the factor in the intensity expression depending on the phase shift,[8] $\cos[\eta_{Tl}(s)-\eta_i(s)]$, varies greatly with s for i=C and H, and the Tl–C and Tl–H distances are consequently represented in the RD-curve (Fig. 2) by double peaks centered around the average value.

The close agreement between experimental and calculated RD curves in the ranges containing the C–C distance peaks, confirms the assumption that ∠CMC = 120° in both compounds. The appearance of the experimental RD curves in the ranges containing the nonbonded C–H distances suggests that the methyl groups undergo virtually nonhindered internal rotation. A molecular model as shown in Fig. 1 and 2 is clearly able to simulate this internal rotation if the C–H vibrational amplitudes are sufficiently large, $l=0.13$ to 0.22 Å.

The value obtained for the Tl–C bond distance in the present study is not significantly smaller than that obtained in the unpublished study by Beagley, Robiette and Sheldrick.[7]

The value obtained for the In–C bond distance is, however, significantly larger than that obtained in the 1974 study[2] and in better agreement with the values obtained for single In–C bond distances in other molecules. The 1974 study was based on three plates obtained with *one* nozzle to plate distance. Since our study is based on two independent sets of plates, the probability of a systematic scale error is greatly reduced, and we believe that our value should be regarded as more reliable. In the solid

Table 2. M – C bond distances in methyl derivatives of Group IIA, IIB and IIIB metals (M) determined by gas-electron diffraction (GED) or rotational Raman spectroscopy (RR).

Group IIA $(CH_3)_2M$	Group IIB $(CH_3)_2M$	Group IIIB $(CH_3)_3M$
$n=2$		
Be – C		B – C
1.698(2) GED [16]		1.578(1) GED [5]
$n=3$		
Mg – C [a]		Al – C
2.126(6) GED [17]		1.957(3) GED [6]
$n=4$		
Ca – C	Zn – C	Ga – C
	1.930(2) GED [18]	1.967(2) GED [7]
	1.929(4) RR [19]	
$n=5$		
Sr – C	Cd – C	In – C
	2.112(4) RR [19]	2.160(3) GED [b]
$n=6$		
Ba – C	Hg – C	Tl – C
	2.083(5) GED [20]	2.206(3) GED [b]
	2.094(5) RR [19]	

[a] In bisneopentylmagnesium. [b] This work.

state $(CH_3)_3In$ and $(CH_3)_3Tl$ are associated through the formation of very asymmetric $M-CH_3-M$ bridges.[14,15]

In Table 2 we compare M – C bond distances in monomeric di- or trimethyl derivatives of group IIA, IIB and IIIB metals. The radius of a hydrogen atom or hydrogen-like ion increases with the principal quantum number n of the filled atomic orbital and decreases with increasing nuclear charge Z. In accordance with this, the covalent radii, or the ionic radii of ions carrying the same net charge, are generally found to increase with increasing principal quantum number of the valence electrons down a group of *s*- or *p*-block elements in the periodic Table. Similarly, the decrease in the covalent radii with increasing atomic number generally found within the same period (n), has been explained as the effect of an increasing effective nuclear charge, Z_{eff}. The data collected in Table 2, however, show three apparent anomalies. Firstly, even though the covalent radii are expected to increase with n within the group, the Hg – C bond distance is significantly shorter than the Cd – C distance. The smaller covalent radius of Hg is probably a relativistic effect: Pyykkö and Desclaux [21] have shown that introduction of relativistic terms in the Schrödinger equation leads to a contraction of the atomic orbitals. The relativistic contraction shows a general increase with Z, but the increase is not monotonic; it appears to be particularly large for Au and the neighbouring elements Pt and Hg. Thus non-relativistic *ab initio* calculations on CdH_2 and HgH_2 predict that the Cd – H is shorter than the Hg – H bond distance, while relativistic calculations reverse the trend.[22]

Secondly the Ga – C is only 0.01 Å longer than the Al – C bond distance. This anomaly is probably due to the increase of the effective nuclear charge accompanying the filling in of ten 3*d* electrons between Ca and Zn.[7]

Finally, in each of the periods $n=4$, 5 and 6 the M(IIB) – C bond distance is *smaller* than the M(IIIB) – C bond distance. This difference might be rationalized as a hybridization effect. But since no such difference is visible between the M(IIA) – C and M(IIIB) – C bond distances in the $n=2$ and 3 series, we prefer to rationalize the larger covalent radii of Ga, In and Tl as an effect of the contracting $(n-1)d$ electron shells: In Group IB these electrons are valence electrons, but as we move to the right along the period they sink into the atomic core and thus become increasingly effective in shielding the nucleus.

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