The Crystal Structures of Triphenylgallium and Triphenylindium

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Summary The crystal structures of triphenylgallium and triphenylindium have been determined, and show the presence of trigonal molecules linked in chains by weak intermolecular bonds.

X-RAY crystallographic studies have shown that the trimethyls of aluminium[1,2] and indium[3] are associated in the solid state. For the aluminium compound the association is strong, giving dimeric molecules, and our earlier work[4] has shown that triphenylaluminium has a similar structure. Trimethylindium, however, consists in the solid of nearly trigonal planar molecules, with additional long intermolecular bonds on either side of the molecular plane.

We have now determined the crystal structures of triphenylgallium and triphenylindium, and find that they, too, show evidence of weak bonds between molecules, similar to those found in trimethylindium.

Crystallographic data for the two compounds are given in the Table. Photographic data were estimated visually, and each structure has been refined by least-squares. For the gallium compound the refinement is complete, with allowance for anisotropic vibrations and hydrogen positions. Refinement of the triphenylindium structure is continuing, and the present results are based on isotropic refinement.

Crystallographic data

	Ph_3Ga	Ph_3In
a	18·36	14·86
b	10·62	11·13
c	7·43	8·86
Space group	*Pbcn*	*Pbcn*
No. of reflections	840	625
R factor	5·2%	8·9%
Z	4	4

Although the two compounds crystallise in the same space group, and in each case the Ph_3M molecule lies on a crystallographic two-fold axis, their structures are markedly different. For triphenylgallium the shortest intermolecular Ga–C distance (3·42 Å) is to a *meta*-carbon atom of a phenyl group lying on the two-fold axis, and each ring of this type contacts two gallium atoms, one above and one below the plane of the ring. The molecules seem to be linked in chains parallel to the *c*-axis, as shown in Figure 1. In the triphenylindium structure (Figure 2) the shortest intermolecular In–C distance (3·07 Å) is to an *ortho*-carbon atom of a phenyl group which is not on the two-fold axis, and two such rings of any molecule each contact an indium atom of different neighbouring molecules. The molecules are again linked in chains parallel to the *c*-axis.

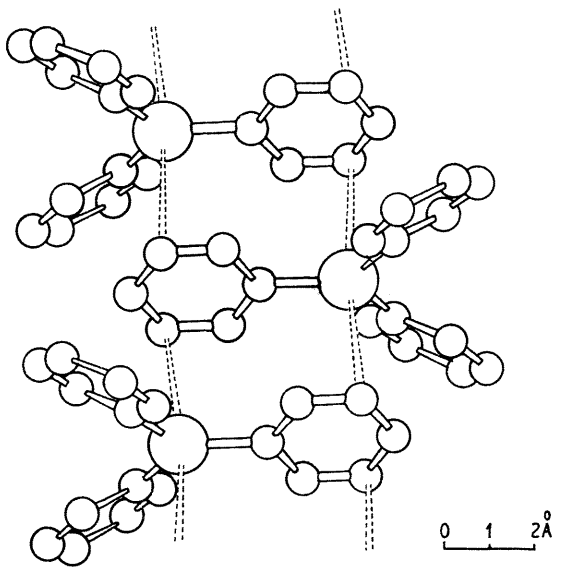

FIGURE 1. *Triphenylgallium*

In triphenylgallium the two independent Ga–C distances are 1·946(7) Å and 1·968(4) Å and the angles within the rings at these carbons are 116·2°(0·6) and 117·5°(0·4). For

triphenylindium the corresponding dimensions are 2·11(2) Å and 2·15(2) Å for In–C, 116·5°(2·8) and 118·4°(2·3) for the angles. Similar ring distortions were found in triphenylaluminium.[4]

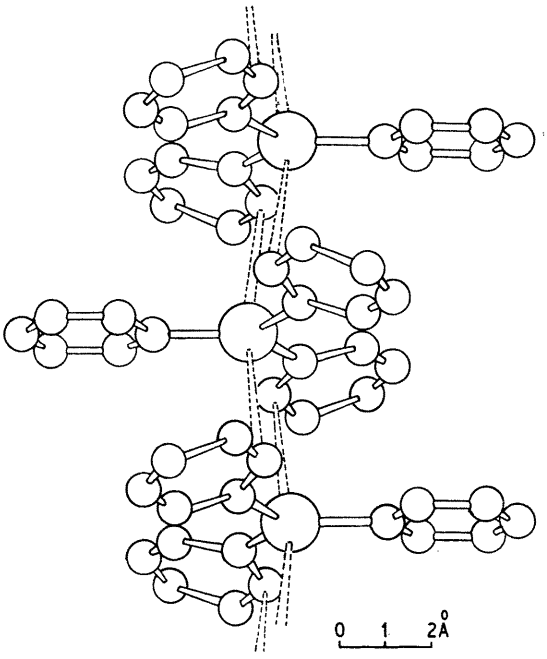

FIGURE 2. *Triphenylindium*

The significance of the intermolecular Ga–C distance of 3·42 Å is not clear. Pauling[5] gives Van der Waals radii for As and Se of 2·0 Å, and if we assume a similar value for Ga, the contact is about 0·3 Å less than the expected distance for a Van der Waals contact, and would indicate weak intermolecular bonding. However, it might be that the appropriate Van der Waals radius of a trigonal covalent gallium atom, for a contact in a direction normal to the trigonal plane, is appreciably less than 2·0 Å. If it were as low as 1·7 Å then the distance found is no more than a Van der Waals contact.

For triphenylindium the situation is clearer. The covalent and metallic radii of indium are each about 0·2 Å greater than those of gallium, and Pauling gives Van der Waals radii for Sb, Te, and I, each 0·2 Å greater than the corresponding value in the previous row. A similar intermolecular interaction to that in triphenylgallium would therefore be expected to give an intermolecular In–C distance of 3·6 Å. The observed distance is 0·5 Å less than this, and is the same as the intermolecular distance found in trimethylindium.[3] It would seem, therefore, that in triphenylindium, at least, and perhaps also in triphenylgallium, there is significant intermolecular bonding other than of the Van der Waals type.

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