Synthesis and Structural Characterisation of R_3AsX_2 Compounds (R = Me, Ph, *p*-FC_6H_4 or *p*-$MeOC_6H_4$; X_2 = Br_2, I_2 or IBr); Dependency of Structure on R, X and the Solvent of Preparation†

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Compounds of stoichiometry R_3AsX_2 (R = *p*-$MeOC_6H_4$, Ph or Me; X = Br or I; R = *p*-FC_6H_4, X = I), R_3AsI_4 (R = *p*-FC_6H_4 or Ph) and Ph_3AsIBr have been synthesised in anhydrous diethyl ether and characterised by elemental analysis and Raman spectroscopy. Single-crystal X-ray diffraction studies of Ph_3AsBr_2 showed it to possess a molecular trigonal-bipyramidal structure, in contrast to Ph_3AsI_2 which adopts the molecular four-co-ordinate structure Ph_3As–I–I. Both Me_3AsI_2 and Me_3AsBr_2 have the molecular four-co-ordinate structure, Me_3As–X–X, thus illustrating that the structure of R_3AsX_2 compounds isolated from diethyl ether is dependent on R and X. The structure of Ph_3AsIBr also revealed four-co-ordinate molecular geometry in contrast to Ph_3AsBr_2. The compound Ph_3AsIBr showed no dual occupancy of the halogen sites, and the heavier halogen is bound directly to the arsenic. The X-ray powder diffraction patterns of Ph_3AsX_2 (X_2 = Br_2, I_2 or IBr) have been recorded and are compared. Solution studies on R_3AsI_2 (R = *p*-FC_6H_4, Ph or *p*-$MeOC_6H_4$) again showed the sensitivity of these molecules to the nature of R. For example, (*p*-$FC_6H_4)_3AsI_2$ was not formed in any solvent employed; instead, equimolar quantities of (*p*-$FC_6H_4)_3AsI_4$ and (*p*-$FC_6H_4)_3As$ were isolated; Ph_3AsI_2 was only formed in non-polar solvents upon dropwise addition of a light petroleum solution of I_2 to a saturated solution of Ph_3As in the same solvent. The compound (*p*-$MeOC_6H_4)_3AsI_2$ was the quantitative product from the direct reaction of the tertiary arsine with I_2 in diethyl ether. Its stability constant in CCl_4 is approximately 2.5 times greater than that calculated for Ph_3AsI_2.

Compounds of stoichiometry R_3AsX_2 (X_2 = F_2, Cl_2, Br_2 or IBr) have not been the subject of extensive study, but have received sporadic attention over the past century. Several crystal structures are available including the trigonal-bipyramidal Ph_3AsF_2,[1] Me_3AsCl_2[2] and $(Me_3CCH_2)_3AsBr_2$.[3] However, Me_3AsBr_2[2] was assigned an ionic structure from a preliminary X-ray study, despite a significant anion–cation interaction of 3.38 Å (the van der Waals radius of dibromine is 3.9 Å).[4] Additionally, extensive conductimetric and spectroscopic studies on Ph_3AsX_2 (X = Cl or Br)[5–12] have supported regular trigonal-bipyramidal geometry and one study of Et_3AsBr_2[13] concluded ionic tetrahedral geometry, $[Et_3AsBr]Br$, for the arsenic atom. More recently, X-ray crystallographic studies of Ph_3AsI_2 compounds isolated from diethyl ether revealed a novel four-co-ordinate molecular 'spoke' structure, Ph_3As–I–I.[14,15] Clearly, the precise structural nature of R_3AsX_2 compounds is dependent not only on the halide ion but also the nature of the R groups.

The stability of Ph_3AsI_2 in various solvents has also been investigated by Klaboe and co-workers,[16] who concluded that it was only formed in non-polar solvents such as hexane. In highly polar solvents such as MeCN no evidence for its formation was noted; instead, equimolar quantities of Ph_3AsI_4 and Ph_3As were formed. This observation was in agreement with the results of Beveridge and Harris[12] and those of Bhat and Rao[17,18] who postulated a mechanism for the conversion of Ph_3AsI_2 into Ph_3AsI_4 and Ph_3As. The latter carried out spectroscopic and kinetic studies into the donor properties of Ph_3As towards I_2 in CH_2Cl_2 solution, and concluded that a 1 : 1 charge-transfer complex is formed. In the UV spectrum the intensity of this charge-transfer band at 320 nm decreased markedly with time, whilst a concurrent intensification of bands due to I_3^- was observed.[17] These observations were described in terms of an 'outer' and 'inner' sphere complex (Scheme 1). The activation energy of the process decreased appreciably with increasing relative permittivity of the solvent.

$$Ph_3As + I_2 \longrightarrow \underset{\text{outer}}{Ph_3AsI_2} \longrightarrow \underset{\text{inner}}{[Ph_3AsI]I}$$

$$[Ph_3AsI]I + I_2 \longrightarrow [Ph_3AsI]I_3$$

Scheme 1

We have recently reported the structural characterisation of a number of compounds of stoichiometry Ph_3EX_2 (E = P[19–22] or Sb;[23] X_2 = Br_2 I_2 or IBr) synthesised in diethyl ether and have found that the phosphorus compounds adopt a novel four-co-ordinate molecular 'spoke' structure, Ph_3P–X–X, whereas the antimony compounds are all trigonal-bipyramidal Ph_3SbX_2. We therefore decided to investigate a series of compounds of stoichiometry R_3AsX_2 (X_2 = Br_2, I_2 or IBr) in the solid state. In particular we were interested in the structural study of Ph_3AsIBr for two reasons; first, no compound of this stoichiometry has previously been isolated in the solid state and, secondly, and more importantly, since Ph_3AsI_2 is a four-co-ordinate charge-transfer species and Ph_3AsBr_2 has been reported[6–12] to be trigonal bipyramidal, the structure of Ph_3AsIBr could be either of these two forms. We have also structurally characterised Me_3AsI_2, Ph_3AsBr_2, and reinvestigated Me_3AsBr_2 which was previously reported by Hursthouse and Steer[2] and said to be disordered. The high final residuals

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Analytical and spectroscopic data for R_3AsX_2 and R_3AsX_4 compounds

Compound	Colour	Analysis (%)[a] C	H	I	Br	$\tilde{\nu}$(As–X)/cm^{-1}
$(p\text{-}FC_6H_4)_3AsBr_2$	White	41.6 (41.5)	2.1 (2.3)		30.3 (30.8)	125
Ph_3AsBr_2	White	46.2 (46.4)	3.2 (3.2)		34.4 (34.3)	151
$(p\text{-}MeOC_6H_4)_3AsBr_2$	White	45.0 (45.3)	3.7 (3.6)		29.2 (28.8)	184
Me_3AsBr_2	White	13.0 (12.8)	3.4 (3.2)	57.7 (57.1)		289
$(p\text{-}FC_6H_4)_3AsI_4$	Brown	25.3 (25.4)	1.4 (1.4)	59.4 (59.8)		70, 113, 150[b]
Ph_3AsI_4	Brown	28.3 (28.1)	2.0 (1.9)	65.5 (66.0)		65, 104, 145[b]
Ph_3AsI_2	Yellow	39.6 (39.6)	2.7 (2.7)	45.0 (45.4)		122
$(p\text{-}MeOC_6H_4)_3AsI_2$	Orange	45.0 (45.3)	3.7 (3.6)	29.2 (28.8)		156
Me_3AsI_2	Cream	9.7 (9.6)	2.4 (2.4)	67.4 (67.9)		185
Ph_3AsIBr	Yellow	42.1 (41.9)	2.9 (3.2)	15.4 (15.6)	24.3 (24.6)	143

[a] Calculated values in parentheses. [b] Raman bands resulting from I_3^- ion, not ν(As–X).

given previously for the last compound meant a reinvestigation was worthwhile.

We also investigated the effect on the stability of R_3AsI_2 (R = p-FC_6H_4, Ph or p-$MeOC_6H_4$) compounds with respect to R_3AsI_4 and R_3As in diethyl ether upon variation of the R groups in the present study.

Results and Discussion

The compounds R_3AsX_2 (R = Me or p-$MeOC_6H_4$), X = Br or I were simply prepared by the direct reaction of the tertiary arsine with the dihalogen in diethyl ether under anhydrous and anaerobic conditions, equation (1). Synthesis of Ph_3AsIBr was

$$R_3As + X_2 \xrightarrow[Et_2O]{N_2,\, ca.\, 4\, d} R_3AsX_2 \qquad (1)$$

similarly achieved by direct reaction of Ph_3As with IBr in diethyl ether. The compound Ph_3AsI_2 cannot be synthesised by the above method, the reaction yielding equimolar quantities of Ph_3AsI_4 and Ph_3As. Consequently synthesis was carried out according to the published[12] method (see Experimental section). The instability of Ph_3AsI_2 in diethyl ether has been studied using electronic spectroscopy [17,18] and will be discussed later. Both $(p\text{-}FC_6H_4)_3AsI_4$ and Ph_3AsI_4 were synthesised by the direct reaction of the tertiary arsine with 2 mol equivalents of diiodine in diethyl ether.

All the triorganoarsenic di- and tetra-halides synthesised in this study are listed in Table 1, together with analytical data and the ν(As–X) (X = Br or I) frequency in the Raman spectra. The ν(As–X) band for both the bromide and iodide compounds shifts to higher wavenumbers with increasing basicity of the tertiary arsine, as expected. This phenomenon was also observed for analogous phosphorus compounds, R_3PX_2.[22] Of the compounds described herein, only Ph_3AsI_2[24] and Me_3AsBr_2[25] have previously been the subject of Raman spectroscopic study; the bands previously recorded for ν(As–X) are in excellent agreement with ours. The compound Ph_3AsBr_2 was investigated using Raman spectroscopy[6] but no ν(As–Br) bands were reported because of experimental limitations. A previous Raman spectroscopic study[13] on Et_3AsBr_2 exhibited a ν(As–Br) band at 290 cm^{-1} a value not inconsistent with that reported for Me_3AsBr_2 here, Table 1.

In order to gain further insight into the solid-state structures of compounds of stoichiometry Ph_3AsX_2 (X_2 = Br_2 or IBr) we grew crystals from diethyl ether solution at 0 °C. The compound Ph_3AsI_2 adopts the novel molecular 'spoke' structure, Ph_3As–I–I,[14,15] similar to Ph_3PX_2 (X = Br_2, I_2 or IBr).[19–21] We were thus intrigued to know if Ph_3AsX_2 (X_2 = Br or IBr) also adopted this structure and, in the case of Ph_3AsIBr, which halogen would be bound to the arsenic atom. Additionally, previous studies[22] have shown that Ph_3PIBr is a complicated molecule containing dual occupancy of the halogen sites, and we were interested to know if Ph_3AsIBr also exhibited this phenomenon.

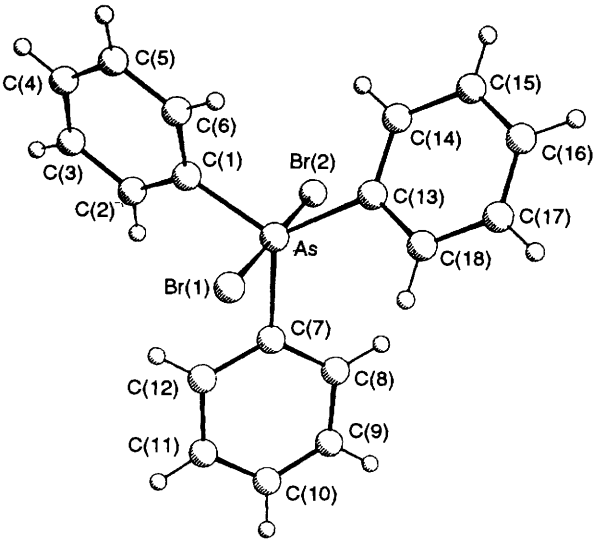


Fig. 1 Crystal structure of Ph_3AsBr_2

The crystal structure of Ph_3AsBr_2 is illustrated in Fig. 1; bond lengths and angles and fractional atomic coordinates are listed in Tables 2 and 3, respectively. The structure shows Ph_3AsBr_2 to be a simple trigonal-bipyramidal molecule. This is in agreement with previous spectroscopic studies[5–10] but in direct contrast to the analogous diiodine compound, Ph_3AsI_2. Clearly, the nature of the halogen in R_3AsX_2 compounds is critical in determining the geometry of the compound formed.

The arsenic compounds represent a transition between the two structural types found previously for P and Sb, Ph_3AsBr_2 being trigonal bipyramidal and Ph_3AsI_2 having the molecular four-co-ordinate 'spoke' structure. Additionally, an approximate structural characterisation of Me_3AsBr_2 has been reported[2] and tetrahedral geometry was found for the arsenic atom. Thus, the geometry of R_3AsX_2 compounds is dependent not only on the X atom but also the nature of the R group.

We thus reinvestigated the crystal structure of Me_3AsBr_2 and also determined that of Me_3AsI_2. The structure of Me_3AsBr_2 is shown in Fig. 2, and selected bond lengths and angles and fractional atomic coordinates are listed in Tables 4 and 5, respectively. In agreement with a previous study by Hursthouse and Steer,[2] the arsenic atom adopts tetrahedral geometry; however, unlike their structure determination, the present structure has no disorder and much reduced final residuals. More importantly, this result confirms Me_3AsBr_2 as a further

Table 2 Selected bond lengths (Å) and angles (°) for Ph_3AsBr_2

Br(1)–As	2.552(5)	As–C(7)	1.94(2)
Br(2)–As	2.441(5)	As–C(13)	1.92(2)
As–C(1)	1.88(2)		
Br(1)–As–Br(2)	119.1(2)	Br(2)–As–C(1)	89.2(8)
Br(1)–As–C(1)	90.5(8)	Br(2)–As–C(7)	89.0(6)
Br(1)–As–C(7)	90.4(6)	Br(2)–As–C(13)	88.9(8)
Br(1)–As–C(13)	92.0(8)		

Table 3 Fractional atomic coordinates for the non-hydrogen atoms in Ph_3AsBr_2

Atom	*x*	*y*	*z*
Br(1)	0.4949(3)	0.4368(2)	0.1732(2)
Br(2)	0.5343(2)	0.5674(2)	0.6205(2)
As	0.5133(2)	0.5031(3)	0.3966(3)
C(1)	0.646(2)	0.566(2)	0.355(2)
C(2)	0.746(2)	0.537(2)	0.408(2)
C(3)	0.842(2)	0.591(2)	0.377(2)
C(4)	0.832(3)	0.669(2)	0.291(3)
C(5)	0.736(3)	0.699(2)	0.230(3)
C(6)	0.644(3)	0.645(3)	0.266(3)
C(7)	0.516(2)	0.366(2)	0.460(2)
C(8)	0.435(2)	0.333(2)	0.542(3)
C(9)	0.440(3)	0.232(3)	0.578(3)
C(10)	0.514(2)	0.169(2)	0.533(2)
C(11)	0.594(2)	0.200(2)	0.455(3)
C(12)	0.597(2)	0.302(2)	0.415(3)
C(13)	0.377(2)	0.573(2)	0.386(2)
C(14)	0.365(2)	0.675(2)	0.407(3)
C(15)	0.265(3)	0.723(2)	0.401(3)
C(16)	0.177(2)	0.666(2)	0.368(3)
C(17)	0.184(2)	0.566(3)	0.338(3)
C(18)	0.285(2)	0.518(2)	0.248(2)

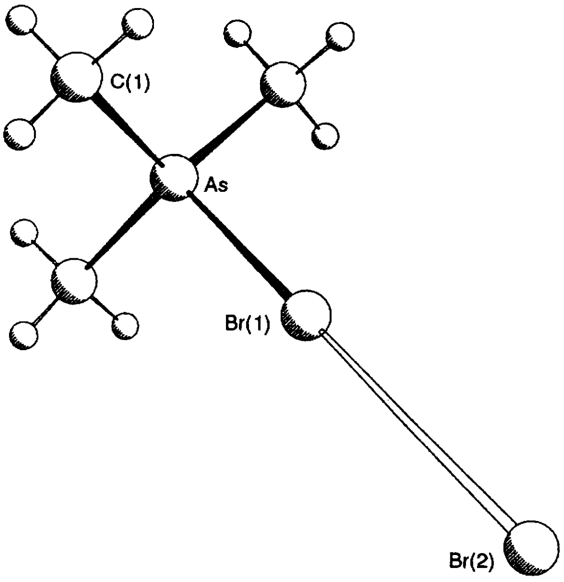


Fig. 2 Crystal structure of Me_3AsBr_2

Table 4 Selected bond lengths (Å) and angles (°) for Me_3AsBr_2

Br(1)–Br(2)	3.363(4)	As–C(1)	1.89(1)
Br(1)–As	2.275(4)		
Br(1)–As–C(1)	105.3(4)	C(1)–As(1)–C(2)	113.3(3)

Table 5 Fractional atomic co-ordinates for the non-hydrogen atoms in Me_3AsBr_2

Atom	*x*	*y*	*z*
Br(1)	0.67	0.33	0.4710(3)
Br(2)	0.67	0.33	0.8323(3)
As	0.67	0.33	0.2266(3)
C(1)	0.369(2)	0.1843(2)	0.173(1)

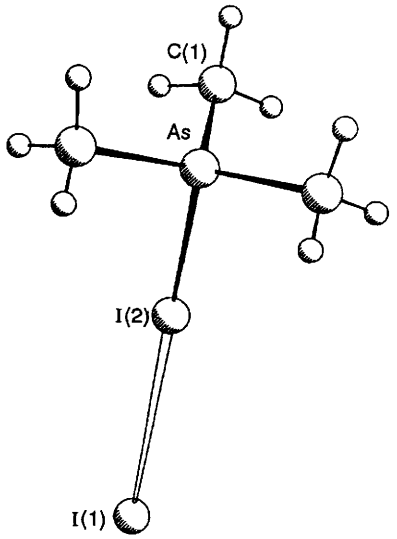


Fig. 3 Crystal structure of Me_3AsI_2

example of the molecular four-co-ordinate 'spoke' structure, in direct contrast to the trigonal-bipyramidal Ph_3AsBr_2, and further illustrates the geometrical dependence on R as well as X for compounds of stoichiometry R_3AsX_2.

The crystal structure of Me_3AsI_2 is illustrated in Fig. 3, and selected bond lengths and angles and fractional atomic coordinates are listed in Tables 6 and 7, respectively. As expected, and in accord with the structure of Ph_3AsI_2,[14,15] Me_3AsI_2 is also an example of the four-co-ordinate molecular structure, $Me_3As–I–I$. The I–I bond in Me_3AsI_2, 3.39 Å, is considerably lengthened with respect to molecular iodine (2.67 Å)[4] and Ph_3AsI_2 (3.05 Å),[15] but is still within bonding distance when compared to the van der Waals radius of di-iodine (4.3 Å).[4] Also, as expected, increased lengthening of the I–I bond occurs upon increasing basicity of the tertiary arsine. We have previously observed this phenomenon with analogous phosphorus compounds, *e.g.* Ph_3PI_2 [*d*(I–I) 3.14 Å][19] and $PhMe_2PI_2$ (3.41 Å).[26]

The crystal structure of Ph_3AsIBr has been described elsewhere.[27] No compound of this stoichiometry had previously been isolated in the solid state. The molecule exists as a molecular four-co-ordinate structure analogous to Ph_3AsI_2 and Ph_3PX_2 ($X_2 = Br_2$, I_2 or IBr) and contrasts with trigonal-bipyramidal Ph_3AsBr_2. One surprising difference between Ph_3AsIBr and Ph_3PIBr, prepared in an identical way by us from diethyl ether, is in the nature of the bonded halogen sites. In Ph_3PIBr there is dual occupancy of the sites, *i.e.* although the molecule exists predominantly as $Ph_3P–I–Br$, evidence of the species Ph_3PI_2, Ph_3PBr_2 and Ph_3PBrI was also observed within the unit cell.[22] In contrast, Ph_3AsIBr exists as 100% Ph_3AsIBr with no dual occupancy of the halogen sites. We have also recorded the X-ray powder-diffraction patterns of the compounds Ph_3AsX_2 ($X_2 = Br_2$, I_2 or IBr) for comparative purposes, Fig. 4. The patterns of these bulk samples clearly establish Ph_3AsIBr as a unique species and not simply a statistical mixture of Ph_3AsBr_2 and Ph_3AsI_2.

Table 6 Selected bond lengths (Å) and angles (°) for Me_3AsI_2

I(1)–I(2)	3.3912(7)	I(2)–As	2.272(6)
I(1)–As	3.695(6)	As–C(1)	1.83(3)
I(2)–I(1)–As	180.00	I(2)–As–C(1)	103.1(6)
I(1)–As–I(2)	180.00	C(1)–As–C(2)	115.0(4)
I(1)–As–C(1)	76.9(6)		

Table 7 Fractional atomic coordinates for the non-hydrogen atoms in Me_3AsI_2

Atom	*x*	*y*	*z*
I(1)	0.33	−0.33	0.2210(6)
I(2)	0.33	−0.33	0.5834(5)
As	0.33	−0.33	0.8261(6)
C(1)	0.189(2)	−0.1892(2)	0.870(2)

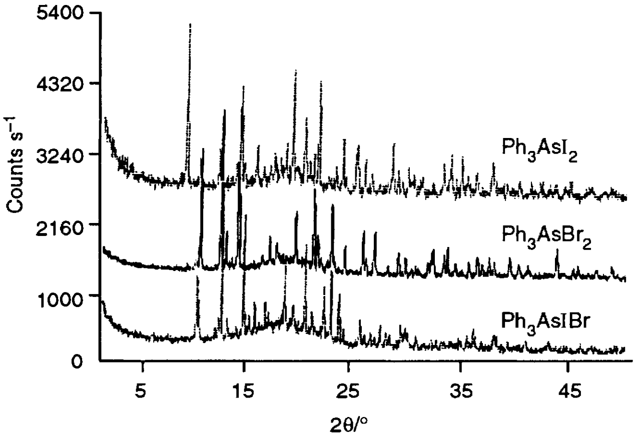


Fig. 4 Comparison of the X-ray powder-diffraction patterns of Ph_3AsX_2 (X_2 = Br_2, I_2 or IBr)

An Overview.—At this point we wish to attempt some explanation of the structures adopted. A summary of all the crystallographically determined structures of R_3EX_2 compounds (E = P, As or Sb; X_2 = F_2, Cl_2, Br_2 or IBr) is presented in Table 8. Clearly, these results indicate that for R_3AsX_2 compounds, the structure adopted, *i.e.* tetrahedral or trigonal bipyramidal, depends on both R and X; Me_3AsBr_2 containing the arsenic in tetrahedral geometry, Me_3As–Br–Br and Ph_3AsBr_2 containing the arsenic in trigonal-bipyramidal geometry. Additionally, Ph_3AsI_2 is also tetrahedral, Ph_3As–I–I.[14,15] Steric factors are unimportant, since the arsenic atom can accommodate three bulky triphenylarsine groups in trigonal-bipyramidal geometry but prefers tetrahedral geometry even with the much less sterically demanding trimethylarsine groups. If we extend this argument further, our recent discoveries have shown from X-ray crystallographic data that Ph_3PX_2 (X_2 = Br_2,[19] I_2[20] or IBr[22]) and $PhMe_2PI_2$[26] are all molecular four-co-ordinate with the phosphorus in tetrahedral geometry. The trimethylstibine compounds Me_3SbX_2 (X = F, Cl, Br or I)[33] and Ph_3SbI_2[23] have a trigonal-bipyramidal structure. Additionally, other workers have shown from X-ray crystallographically that Ph_3PF_2[28] is trigonal bipyramidal, as are $(Me_3CCH_2)_3AsBr_2$[3] and Ph_3AsF_2.[1] On the other hand, Me_3NI_2 is a further example of the molecular four-co-ordinate structure, Me_3N–I–I, containing tetrahedral nitrogen.[33] The initial interaction of R_3E (E = N, P, As or Sb) with X_2 (X_2 = F_2, Cl_2, Br_2, I_2 or IBr) depends on the basicity of the R_3E species. The more acidic is the E atom in R_3EX_2, the more likely is the trigonal-bypyramidal structure, *i.e.* N < P < As < Sb and I < Br < Cl < F.

Table 8 Crystallographically determined structures of R_3EX_2 compounds (E = P, As or Sb; X_2 = Br_2, I_2 or IBr)

Compound	Structure[a]	Ref.
R_3PF_2 (R = Ph or C_6F_5)	TBPY	28
R_3PCl_2	*b*	—
R_3PBr_2 (R = Ph or *p*-FC_6H_4)	c.t.	20,26,29
R_3PI_2 (R_3 = Ph_3, $PhMe_2$ or $Bu^t{}_3$)	c.t.	19,26,30
Ph_3PIBr	c.t.	22
Ph_3AsF_2	TBPY	1
R_3AsCl_2	*c*	—
R_3AsBr_2 (R = Ph or Me_3CCH_2)	TBPY	This work, 3
Me_3AsBr_2	c.t.	This work
R_3AsI_2 (R = Ph or Me)	c.t.	This work, 14,15
Ph_3AsIBr	c.t.	27
R_3SbX_2 (R = Ph or Me; X = Cl, Br or I)	TBPY	23,31,32

[a] TBPY = Trigonal bipyramidal; c.t. = charge-transfer molecular 'spoke' structure. [b] No single-crystal X-ray data available. [c] Several crystallographic modifications of this structure are known.

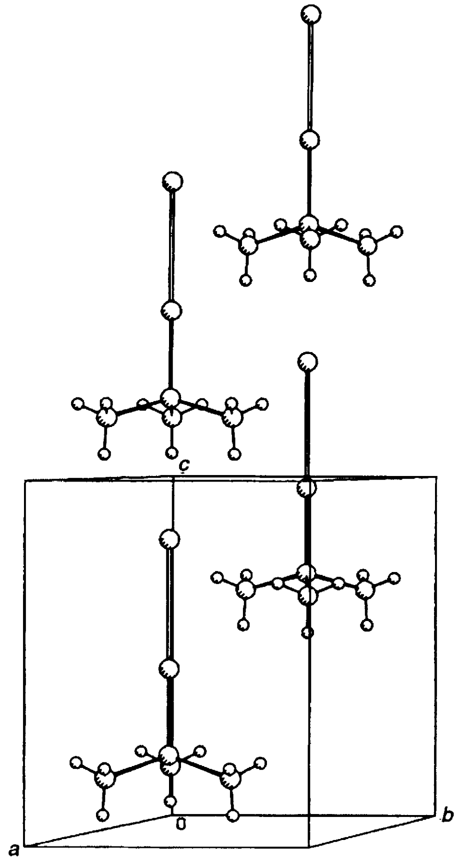
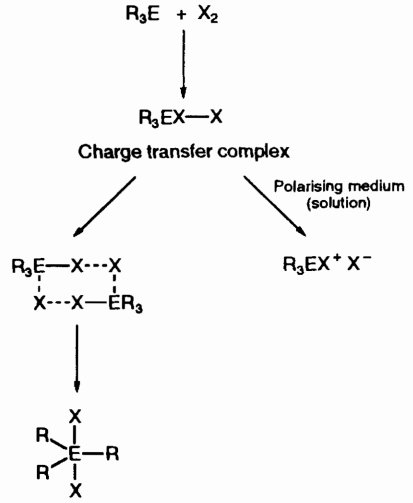


Fig. 5 Packing of Me_3AsBr_2 molecules in the unit cell illustrating the interaction between the independent molecules

In intermediate cases, such as R_3AsBr_2, a polarising environment is able to discourage the formation of a trigonal-bipyramidal product. In the case of Ph_3AsBr_2, the bulky phenyl groups inhibit coulombic interactions between the centres of positive and negative charge; however, if we examine the crystal packing of Me_3AsBr_2, Fig. 5, it can be seen that the small methyl groups of the Me_3As ligand allow several As–Br··· $BrMe_3As$ interactions in the solid state, whereas this is not possible with the bulky phenyl groups of Ph_3As. In all compounds of general formula R_3EX_2 a competing reaction takes place depending on the acidity of the E atom or the nature of the X atom in R_3EX. If the E atom has the greater acidity a



Scheme 2

trigonal-bipyramidal species is formed, if the X atom has greater acidity a charge-transfer molecular species R_3E–X–X is formed, Scheme 2. This hypothesis also explains why the structures of R_3EX_2 compounds are acutely solvent dependent, since the polarising power of the solvent will clearly affect the product formed.

Solution Stabilities of (p-$MeOC_6H_4)_3AsI_2$, Ph_3AsI_2 *and* (p-$FC_6H_4)_3AsI_2$. *The Preparation of* R_3AsI_2 (R = p-$MeOC_6H_4$ *or* Ph) *and Attempted Preparation of* (p-$FC_6H_4)_3PI_2$.—Klaboe and co-workers[16] studied the stability of Ph_3AsI_2 in CCl_4, and calculated the formation constant of Ph_3AsI_2 at 20 °C as K = 1400 dm^3 mol^{-1}. During our studies into the synthesis of R_3AsI_2 compounds we, in agreement with previous workers,[16–18] found that Ph_3AsI_2 could not be prepared from diethyl ether solution and instead employed the method described by Beveridge and Harris[12] which uses light petroleum (b.p. 100–120 °C) as solvent. Both Me_3AsI_2 and (p-$MeOC_6H_4)_3AsI_2$ can easily be prepared from diethyl ether solution, but (p-$FC_6H_4)_3AsI_2$ could not be prepared at all by us, regardless of the solvent used. This prompted us to investigate the stability of (p-$MeOC_6H_4$)AsI_2 in CCl_4 solution, so that a direct comparison with the stability of Ph_3AsI_2 in the same solvent,[16] could be made. Clearly, the substituted groups on the phenyl rings of R_3AsI_2 (R = aryl) compounds has an important bearing on the stability of the charge-transfer complex.

When a solution of (p-$MeOC_6H_4)_3As$ in CCl_4 was added to a solution of diiodine in CCl_4 a single UV absorption band with a maximum at 333 nm was observed, resulting from the formation of the (p-$MeOC_6H_4)_3AsI$–I charge-transfer complex. Solutions with the same diiodine concentrations and varying (p-$MeOC_6H_4)_3As$ concentrations exhibited UV spectra which passed through an isosbestic point at 469 nm, Fig. 6, indicating the formation of only one complex. The stability constant, K, of the complex was calculated using the method of Rose and Drago.[34] In this method various values of the absorption coefficient ε_c were selected at random and the corresponding values of K^{-1} were calculated using equation (2) for each set of

$$K^{-1} = \frac{A}{\varepsilon_c} - c_I - c_D + \frac{c_D c_I}{A}\varepsilon_c \qquad (2)$$

experimental data used in Fig. 6, A = absorbance at 333 nm, c_I = concentration of the diiodine solution in CCl_4 and c_D = concentration of (p-$MeOC_6H_4)_3As$ solution in CCl_4.

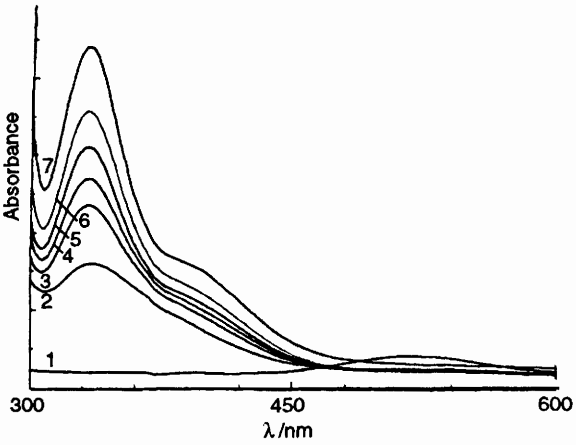


Fig. 6 The UV absorption spectra of diiodine (8.69 × 10^{-5} mol dm^{-3}) and (p-$MeOC_6H_4)_3As$ in CCl_4 at 20 °C. Concentrations of (p-$MeOC_6H_4)_3As$ (10^{-4} mmol dm^{-3}): 0 (1), 1.313 (2), 2.626 (3), 3.939 (4), 5.525 (5), 7.878 (6) and 13.13 (7)

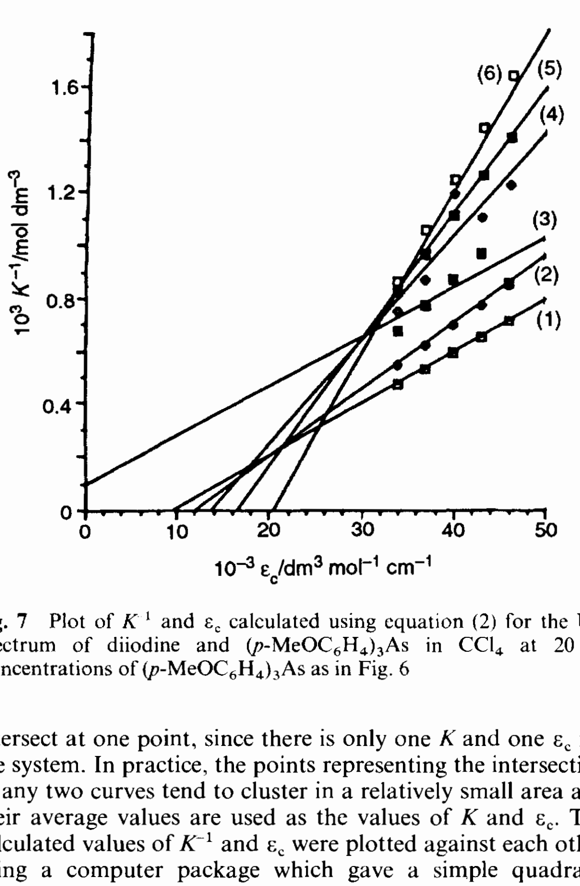


Fig. 7 Plot of K^{-1} and ε_c calculated using equation (2) for the UV spectrum of diiodine and (p-$MeOC_6H_4)_3As$ in CCl_4 at 20 °C. Concentrations of (p-$MeOC_6H_4)_3As$ as in Fig. 6

The values of K^{-1} for each set of experimental data are plotted against ε_c, in Fig. 7. Ideally all the curves should intersect at one point, since there is only one K and one ε_c for the system. In practice, the points representing the intersection of any two curves tend to cluster in a relatively small area and their average values are used as the values of K and ε_c. The calculated values of K^{-1} and ε_c were plotted against each other using a computer package which gave a simple quadratic equation for each curve. These were solved to find the value of ε_c at every intersection. The mean of these values was taken to represent ε_c which was found to be approximately 23 600 dm^3 mol^{-1} cm^{-1}. From this the value of K^{-1} (and thus K) was calculated. At 20 °C, K was found to be 3500 dm^3 mol^{-1} (ε_c = 23 600 dm^3 mol^{-1} cm^{-1}).

Comparing these results to those for Ph_3AsI_2,[16] (p-$MeOC_6H_4)_3AsI_2$ is 2.5 times more stable than Ph_3AsI_2. This result helps explain why (p-$MeOC_6H_4)_3AsI_2$ can be prepared in diethyl ether, a solvent in which it is impossible to prepare Ph_3AsI_2. Additionally, since (p-$FC_6H_4)_3AsI_2$ cannot be prepared in any solvent we employed these results clearly illustrate the surprising dependence of the stability of R_3AsI_2 compounds on the nature of R. The stability of these compounds is also clearly dependent on the nature of the solvent, since, when $(p\text{-MeOC}_6\text{H}_4)_3\text{As}$ is added to a solution of I_2 in MeCN, a pronounced darkening of the solution occurs and the UV spectrum developed two strong bands at 360 and 294 nm, assignable to the I_3^- ion, suggesting that reaction (3)

$$2(p\text{-MeOC}_6\text{H}_4)_3\text{As–I–I} \longrightarrow [(p\text{-MeOC}_6\text{H}_4)_3\text{AsI}]\text{I}_3 + (p\text{-MeOC}_6\text{H}_4)_3\text{As} \quad (3)$$

had occurred. Thus, $(p\text{-MeOC}_6\text{H}_4)_3\text{AsI}_2$ can be prepared in diethyl ether, in contrast to Ph_3AsI_2 which cannot; Ph_3AsI_2 can only be prepared in CCl_4 or light petroleum (b.p. 100–120 °C), and $(p\text{-FC}_6\text{H}_4)_3\text{AsI}_2$ cannot be prepared in any solvent used by us.

Conclusion

Unlike R_3PX_2 compounds, which are molecular four-co-ordinate[19–22] and R_3SbX_2 compounds which are all trigonal bipyramidal,[23,31,32,35] R_3AsX_2 may adopt either structure. Which structure is adopted is dependent both on R and X. Thus Ph_3AsI_2 is molecular four-co-ordinate, as is Me_3AsBr_2, but Ph_3AsBr_2 described herein and $(Me_3CCH_2)_3AsBr_2$ described previously by Pazic and George[3] are both trigonal bipyramidal. Both Ph_3AsI_2 and Me_3AsI_2 are molecular four-co-ordinate. The compound Ph_3AsIBr is also molecular four-co-ordinate but, unlike Ph_3PIBr, has halogen sites which show no evidence of mixing, *i.e.* no dual occupancy. As can be seen from Table 8, there are no X-ray crystallographically characterised R_3ECl_2 compounds; this is most surprising.

Solution studies on the compounds R_3AsI_2 ($R = p\text{-FC}_6\text{H}_4$, Ph or $p\text{-MeOC}_6\text{H}_4$) again illustrate the sensitivity of R_3AsX_2 compounds to the nature of R. The compound $(p\text{-FC}_6\text{H}_4)_3\text{AsI}_2$ cannot be prepared in any solvent, only $(p\text{-FC}_6\text{H}_4)_3\text{AsI}_4$ can be isolated, Ph_3AsI_2 cannot be prepared in Et_2O but may be formed under special conditions (see Experimental section) in light petroleum,[12] $(p\text{-MeOC}_6\text{H}_4)_3\text{AsI}_2$ is the quantitative product from the direct combination of the tertiary arsine and diiodine in Et_2O with no evidence for the formation of $(p\text{-MeOC}_6\text{H}_4)_3\text{AsI}_4$, and Me_3AsI_2 is the quantitative product from the reaction of Me_3As and I_2. Clearly the solution stability of the R_3As–I–I charge-transfer complex is increased with increased basicity of the parent tertiary arsine. Thus, in accord with previous studies both by us and other workers,[12,16–18] the results presented here clearly illustrate the critical structural dependence compounds of the type R_3EX_2 have on the nature of the solvent in which they are prepared.

Experimental

All of the compounds described are moisture sensitive, some intensely so; therefore strictly anaerobic and anhydrous conditions were employed for their synthesis. Any subsequent manipulations were carried out inside a Vacuum Atmosphere HE-493 glove-box (argon atmosphere, < 100 ppm dioxygen). Diethyl ether (BDH) was dried by standing over sodium wire for *ca.* 1 d and subsequently refluxed over CaH_2 in an inert atmosphere and distilled directly into the reaction vessel. Tertiary arsines were either synthesised by standard Grignard techniques or obtained from Aldrich ($AsPh_3$). The purity of all the tertiary arsines was confirmed by elemental analysis prior to use. Diiodine, dibromine and iodine monobromide were obtained commercially (Aldrich) and used as received. All glassware was heated to 200 °C for ≈1 d before being transferred, hot, to the glove-box.

All the R_3AsX_2 compounds were synthesised in a similar way except Ph_3AsI_2, which is described later. The synthesis of Ph_3AsBr_2 is typical. Triphenylarsine (3.00 g, 9.80 mmol) was dissolved in diethyl ether (*ca.* 100 cm^3) and subsequently dibromine (1.57 g, 0.50 cm^3, 9.80 mmol) was added. After *ca.* 3 d the resultant white solid was isolated using standard Schlenk techniques and dried *in vacuo*. It was then transferred to pre-dried argon-filled ampoules which were flame-sealed. The yields for all the R_3AsX_2 compounds were quantitative. The R_3AsI_4 compounds were synthesised by direct reaction of R_3As with 2 molar equivalents of diiodine; R_3AsI_4 ($R = Ph$ or $p\text{-FC}_6\text{H}_4$) is the only product obtainable from the direct reaction in diethyl ether regardless of the stoichiometry of the reactants. The compound Ph_3AsI_2 was synthesised by dropwise addition of a saturated solution of diiodine in light petroleum (b.p. 100–120 °C) to a saturated solution of triphenylarsine in the same solvent, total reaction time *ca.* 5 h. The yield is again quantitative. It is essential to maintain a large excess of triphenylarsine during reaction to prevent the formation of any

Table 9 Crystal structures and details for refinement

Formula	Ph_3AsBr_2	Me_3AsBr_2	Me_3AsI_2
M	466.05	279.83	373.83
Crystal system	Orthorhombic	Hexagonal	Hexagonal
Space group	$P2_12_12_1$ (no. 19)	$P6_3mc$ (no. 186)	$P6_3mc$ (no. 186)
a/Å	12.261(6)	7.076(3)	7.132(1)
b/Å	13.254(4)		
c/Å	10.678(5)	9.307(7)	9.359(2)
U/Å^3	1735(2)	403.6(6)	412.2(1)
Z	4	2	2
D_c/g cm^{-3}	1.784	2.303	3.011
$F(000)$	904	260	332
μ/cm^{-1}	65.06	139.06	114.27
Crystal size/mm	0.2 × 0.2 × 0.1	0.3 × 0.05 × 0.05	0.3 × 0.1 × 0.1
Total data measured (θ_{max})	1777	2081	189
No. of unique reflections		465	189
No. of observed reflections [$F_o > 5\sigma(F)$]	537	299	109
No. of parameters	100	16	12
Transmission factors	0.89–1.06	0.94–1.02	0.088–1.11
Minimum, maximum electron density/e Å^{-3}	0.47, −0.43	1.51, −1.17	
Maximum least-squares shift/error ratio	0.05	0.04	< 0.01
Weighting scheme parameter g in $w = 1[\sigma^2(F) + gF^2]$	0.03	0.02	0.01
Final R	0.042	0.042	0.044
Final R'	0.041	0.040	0.038

Ph_3AsI_4. Attempts to prepare $(p\text{-}FC_6H_4)_3AsI_2$ by this method failed, equimolar quantities of $(p\text{-}FC_6H_4)_3As$ and $(p\text{-}FC_6H_4)_3AsI_4$ being formed.

Elemental analyses were performed by the analytical laboratory of this department and the results are presented in Table 1. Raman spectra were recorded by the University of Manchester Raman service using a Coherent Innova 90 5 W argon-ion laser and a SPEX 1403 double monochromator (focal length 0.85 m) fitted with a BGCS microscope sampling attachment. The radiation was detected using a Hamamatsu R928 photomultiplier tube which was cooled to −30 °C in a Products for Research Inc. TE 177 RF-005 cooler housing. The data were processed on a SPEX DM1B data station. Solution UV spectra were recorded on a Shimadzu UV-2101PC UV/VIS scanning spectrophotometer. X-Ray powder diffraction patterns were recorded on a Scintag 2000 XRD powder diffractometer ($\lambda = 1.5418$ Å).

X-Ray Crystallography.—All X-ray measurements were performed using graphite-monochromated Mo-Kα radiation; the structures were solved using direct methods.[36]

A Siemens R3/v diffractometer was used for Me_3AsBr_2 and a Rigaku AFC6S for the other two compounds. Unit-cell dimensions were derived from the setting angles of 25 accurately centred reflections and the data collections performed by means of ω–2θ scans. An absorption correction was applied in each case using the azimuthal scan technique. Details of the X-ray measurements and subsequent structure determinations are presented in Table 9. Hydrogen atoms were confined to chemically reasonable positions. Neutral atom scattering factors were taken from ref. 37(*a*). Anomalous dispersion effects were taken from ref. 37(*b*). All calculations were performed using the TEXSAN crystallographic software package.[38]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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References

1 A. Augustine, G. Ferguson and F. C. March, *Can. J. Chem.*, 1975, **53**, 1647.
2 M. B. Hursthouse and I. A. Steer, *J. Organomet. Chem.*, 1971, **27**, C11.
3 J. C. Pazic and G. George, *Organometallics*, 1989, **8**, 482.
4 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1990, ch. 17, p. 934.
5 E. Maslowsky, *J. Organomet. Chem.*, 1974, **70**, 153.
6 M. H. O'Brien, G. O. Doak and G. G. Long, *Inorg. Chim. Acta*, 1967, **1**, 34.
7 K. M. Mackay, D. B. Sowerby and W. C. Young, *Spectrochim. Acta, Part A*, 1970, **26**, 1581.
8 S. Elbel, H. Esgaard and L. Carlsen, *J. Chem. Soc., Dalton Trans.*, 1987, 481.
9 T. B. Brill and G. G. Long, *Inorg. Chem.*, 1970, **9**, 1980.
10 K. B. Dillon, R. J. Lynch and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 1976, 1478.
11 K. A. Jensen, *Z. Anorg. Allg. Chem.*, 1954, **277**, 258.
12 A. D. Beveridge and G. S. Harris, *J. Chem. Soc.*, 1964, 6076.
13 L. Verdonck and G. P. Van der Kelen, *Spectrochim. Acta, Part A*, 1977, **33**, 601.
14 C. A. McAuliffe, B. Beagley, G. A. Gott, A. G. Mackie, P. P. MacRory and R. G. Pritchard, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 264.
15 B. Beagley, C. B. Colburn, O. El-Sayrafi, G. A. Gott, D. G. Kelly, A. G. Mackie, C. A. McAuliffe and R. G. Pritchard, *Acta Crystallogr., Sect. C*, 1988, **44**, 38.
16 E. Augdahl, J. Grundness and P. Klaboe, *Inorg. Chem.*, 1965, **4**, 1475.
17 K. R. Bhaskar, S. N. Bhat, S. S. Singh and C. N. R. Rao, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1915.
18 S. N. Bhat and C. N. R. Rao, *J. Am. Chem. Soc.*, 1966, **88**, 3216.
19 S. M. Godfrey, D. G. Kelly, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and S. M. Watson, *J. Chem. Soc., Chem. Commun.*, 1991, 1163.
20 N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1992, 355.
21 N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and P. J. Kobryn, *J. Chem. Soc., Dalton Trans.*, 1993, 101.
22 N. Bricklebank, S. M. Godfrey, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1993, 2261.
23 N. Bricklebank, S. M. Godfrey, H. P. Lane, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1994, 1759.
24 F. W. Parrett, *Spectrochim. Acta, Part A*, 1969, **25**, 1271.
25 A. Finch, P. N. Gates and A. S. Muir, *J. Raman Spectrosc.*, 1988, **19**, 91.
26 N. Bricklebank, S. M. Godfrey, H. P. Lane, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1995, 2421.
27 B. Beagley, S. M. Godfrey, N. Jaibon, C. A. McAuliffe and R. G. Pritchard, *Acta Crystallogr.*, in the press.
28 F. Weller, D. Nuszhar, K. Dehnicke, F. Gingl and J. Strahle, *Z. Anorg. Allg. Chem.*, 1991, **602**, 7; K. M. Doxsee, E. M. Hanawalt and T. J. R. Weakley, *Acta Crystallogr., Sect. C*, 1992, **48**, 1288.
29 N. Bricklebank, S. M. Godfrey, H. P. Lane, C. A. McAuliffe, R. G. Pritchard and J.-M. Moreno, unpublished work.
30 W. W. duMont, M. Batcher, S. Pohland and W. Saak, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 912.
31 M. J. Begley and D. B. Sowerby, *Acta Crystallogr., Sect. C*, 1993, **49**, 1044.
32 A. F. Wells, *Z. Kristallogr.*, 1938, **99**, 367.
33 K. O. Stromme, *Acta Chem. Scand.*, 1959, **13**, 268.
34 N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, 1959, **81**, 6138.
35 M. J. Begley and D. B. Sowerby, *Acta Crystallogr., Sect. C*, 1993, **49**, 1044.
36 G. M. Sheldrick, SHELXS 86, University of Göttingen, 1986.
37 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, (*a*) Table 2.2A; (*b*) Table 2.31.
38 TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985.

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