The Isolation from Diethyl Ether of Ionic $[(Me_2N)_3PI]I$ and $[(CH_2{=}CHCH_2)_2PhPI]I$, and the Crystallographically Characterised Molecular 'Spoke' Structure $PhMe_2PI_2$†

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Ten new compounds of stoichiometry R_3PI_2 [R_3 = (o-MeO$C_6H_4)_3$, (o-MeO$C_6H_4)_2$Ph, (o-MeOC_6H_4)Ph_2, (p-F$C_6H_4)_2$Ph, (p-FC_6H_4)Ph_2, (p-$CH_2{=}CHC_6H_4$)Ph_2, $(CH_2{=}CHCH_2)_2Ph$, $(C_6H_{11})Ph_2$, $(PhCH_2CH_2)_3$ or $(Me_2N)_3$] have been prepared by the direct reaction of PR_3 and I_2 in diethyl ether solution. The compounds have been characterised by Raman and solid-state ^{31}P-{H} magic angle spinning (MAS) and solution NMR spectroscopy. Solid-state ^{31}P-{H} MAS NMR studies indicate that the predominant solid-state species is the molecular 'spoke' structure R_3P–I–I; however, in some cases a minor peak was also assignable to the ionic species, $[R_3PI]I$. Additionally, solid-state ^{31}P-{H} MAS NMR studies of $(Me_2N)_3PI_2$ and $(CH_2{=}CHCH_2)_2PhPI_2$ indicate that, in contrast to all other compounds of stoichiometry R_3PI_2 prepared in diethyl ether, they are exclusively ionic, $[R_3PI]I$. The crystal structure of $PhMe_2PI_2$ shows it to have the molecular 'spoke' geometry, $PhMe_2$P–I–I, d(I–I) = 3.408 Å, previously observed for Ph_3PI_2, in agreement with solid-state ^{31}P-{H} MAS NMR results.

Although the adducts formed between tertiary phosphines and dihalogens have received significant study over the past 100 years,[1,2] it is only very recently that the precise structural nature of compounds of stoichiometry R_3PI_2 has been established, especially in the solid state.[3–5]

What has emerged from recent studies[3–5] is that the structure of the solid compounds is crucially dependent on the solvent in which they were prepared. For Ph_3PI_2[6] and Me_3PI_2,[7,8] prepared in nitrobenzene, vibrational spectra pointed to a solid-state ionic $[R_3PI]I$ structure. These results are in agreement with all solution studies on these compounds, principally the conductimetric titration studies reported by Harris and co-workers,[9] in which it was found that all the compounds of stoichiometry R_3PI_2 (R = Ph, n-octyl, n-hexyl or n-butyl) completely ionise in acetonitrile solution to form $[R_3PI]I$.

Other work has also established the delicate balance between ionic and molecular forms for compounds of stoichiometry R_3PX_2. For example, Gates and co-workers[10] have prepared both an ionic $[Ph_3PCl]Cl$, and a molecular trigonal-bipyramidal form of Ph_3PCl_2, the latter being synthesised by the passage of chlorine gas over the surface of a toluene solution of PPh_3. Dillon and Waddington[11] prepared a sample of Ph_3PI_2 from nitrobenzene solution and characterised it using ^{31}P-{H} solid-state NMR spectroscopy. From the solid-state ^{31}P-{H} NMR shift of δ 42.8 it was concluded that the compound is ionic, $[Ph_3PI]I$, in the solid state.

However, we have recently reported[3,4] the synthesis of Ph_3PI_2 from diethyl ether solution, *i.e.* a much less polar solvent, and have shown that this sample has a four-co-ordinate molecular 'spoke' structure, Ph_3P–I–I, from crystallographic and solid-state ^{31}P-{H} magic angle spinning (MAS) NMR studies. Extensive studies on compounds of stoichiometry R_3PI_2 isolated from diethyl ether indicate that all the compounds R_3PI_2 (R_3 = Ph_3, $PhMe_2$ or Me_3) adopt this molecular four-co-ordinate structure in the solid state and that this structure may be common for compounds of this stoichiometry.[3,4] In $CDCl_3$ solution all the compounds ionise completely to form $[R_3PI]I$, in agreement with previous studies.[9]

We now report the synthesis and characterisation of a further series of compounds of stoichiometry R_3PI_2 [R_3 = (o-MeO$C_6H_4)_3$, (o-MeO$C_6H_4)_2$Ph, (o-MeOC_6H_4)Ph_2, (p-F$C_6H_4)_2$Ph, (p-FC_6H_4)Ph_2, (p-$CH_2{=}CHC_6H_4$)Ph_2, $(CH_2{=}CHCH_2)_2Ph$, $(C_6H_{11})Ph_2$, $(PhCH_2CH_2)_3$ or $(Me_2N)_3$] prepared in diethyl ether, none of which has been previously reported. In agreement with previous studies, all the compounds ionise in $CDCl_3$ solution. However, the solid-state ^{31}P-{H} MAS NMR spectra of $(Me_2N)_3PI_2$ and $(CH_2{=}CHCH_2)_2PhPI_2$ clearly show them to be ionic $[R_3PI]I$, in the solid state, in contrast to the four-co-ordinate molecular compounds R_3PI_2 (R_3 = Ph_3, $PhMe_2$ or Me_3).

Results and Discussion

Table 1 lists the diiodotriorganophosphorus compounds synthesised in this study. The compounds are readily prepared by the reaction of equimolar amounts of molecular iodine with the tertiary phosphine in dry diethyl ether under argon for three days according to the published method.[1]

^{31}P-{H} *NMR Spectra.*—(*a*) $CDCl_3$ *solution spectra.* The solution ^{31}P-{H} NMR spectra of the compounds recorded in $CDCl_3$ indicate complete ionisation of R_3PI_2 to $[R_3PI]I$ in this solvent, Table 1. Addition of a further equivalent of diiodine to these diiodotriorganophosphorus compounds to produce the tetraiodotriorganophosphorus compounds, $[R_3PI]I_3$, resulted in a pronounced darkening of the solution (due to I_3^- formation) but did not result in any change in the position of the ^{31}P-{H} resonance. The formation of the I_3^- ion was confirmed by the presence of bands at 366 and 294 nm in the UV/VIS spectra of all the compounds.[12] The tetraiodotriorganophosphorus compounds $[R_3PI]I_3$ are known to be ionic in

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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 the compounds R_3PI_2

Compound	Colour	Analysis[a] (%) C	H	I	$\delta(^{31}P-\{H\})$[b]	$\tilde{\nu}$(P–I)/cm^{-1}
$(o\text{-}MeOC_6H_4)_3PI_2$	Brown	39.3 (41.6)	3.6 (3.5)	41.9 (41.9)	50.3	152
$(o\text{-}MeOC_6H_4)_2PhPI_2$	Yellow	42.0 (41.7)	3.3 (3.3)	43.7 (44.1)	47.5	144
$(o\text{-}MeOC_6H_4)Ph_2PI_2$	Yellow	42.1 (41.8)	2.8 (3.1)	46.1 (46.5)	46.8	150
$(p\text{-}FC_6H_4)_2PhPI_2$	Yellow	39.1 (39.1)	3.4 (2.4)	44.3 (46.0)	44.3	168
$(p\text{-}FC_6H_4)Ph_2PI_2$	Yellow	39.2 (40.4)	2.7 (2.6)	46.7 (47.6)	41.8	175
$(p\text{-}CH_2{=}CHC_6H_4)Ph_2PI_2$	Yellow	43.7 (44.3)	3.3 (3.1)	43.7 (44.1)	40.4	175
$(CH_2{=}CHCH_2)_2PhPI_2$	Yellow	33.2 (32.1)	3.7 (4.5)	55.7 (56.5)	8.8	205
$(C_6H_{11})Ph_2PI_2$	Yellow	41.2 (41.4)	4.0 (4.0)	48.6 (48.7)	52.7	179
$(PhCH_2CH_2)_3PI_2$	Yellow	48.3 (48.0)	4.8 (4.5)	41.8 (42.3)	82.0	163
$(Me_2N)_3PI_2$[c]	Peach	17.4 (17.3)	4.6 (4.3)	60.9 (60.9)	25.4	222
$PhMe_2PI_2$[d]		24.6 (24.5)	3.1 (2.8)	64.6 (64.8)	61.9	204

[a] Required values given in parentheses. [b] Recorded in $CDCl_3$ solution, shifts relative to 85% phosphoric acid standard. [c] N 9.8 (10.2)%. [d] Ref. 3.

Table 2 Solid-state $^{31}P-\{H\}$ MAS NMR data for selected R_3PI_2 compounds[a]

Compound	$\delta(^{31}P-\{H\})$ Solid state Molecular $R_3P–I–I$	Ionic $[R_3PI]I$	$CDCl_3$ solution
$(p\text{-}FC_6H_4)_2PhPI_2$	−22.2	42.8	44.3
$(o\text{-}MeOC_6H_4)_2PhPI_2$	−41.7	—	47.5
$(o\text{-}MeOC_6H_4)_3PI_2$	−33.1	—	50.3
$(C_6H_{11})Ph_2PI_2$	10.3	52.1	52.7
$(PhCH_2CH_2)_3PI_2$	19.9	89.7	82.0
$(o\text{-}MeOC_6H_4)Ph_2PI_2$	−28.1	42.2	46.8
$(p\text{-}CH_2CHC_6H_4)Ph_2PI_2$	−27.7	42.2	40.4[b]
$(CH_2{=}CHCH_2)_2PhPI_2$	—	6.9	8.8
$(Me_2N)_3PI_2$	—	25.7, 26.6, 27.3	25.4

[a] All shifts recorded relative to 85% phosphoric acid standard. [b] Also contains a peak at δ 25.6.

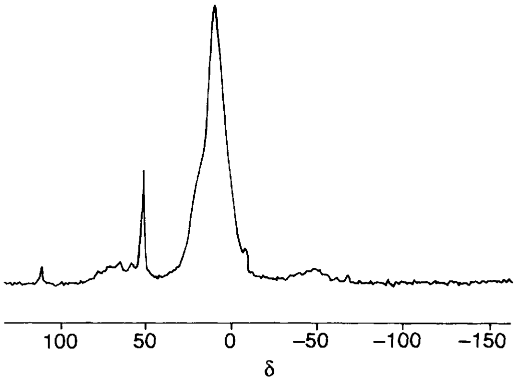

Fig. 1 The solid-state $^{31}P-\{H\}$ MAS NMR spectrum of $(C_6H_{11})Ph_2PI_2$

solution[3,9] and, since they display identical shifts in the $^{31}P-\{H\}$ NMR spectra to that of the corresponding diiodotriorganophosphorus compounds, then the latter must completely ionise to form $[R_3PI]I$ in $CDCl_3$ solution. The $^{31}P-\{H\}$ NMR values for $(CH_2{=}CHCH_2)_2PhPI_2$ and $(Me_2N)_3PI_2$ appear to be rather low, δ 8.8 and 25.4, respectively, when compared to the other diiodotriorganophosphorus compounds described herein and previously reported.[3] However, in keeping with the other compounds described, addition of a further equivalent of diiodine to produce $[R_3PI]I_3$ did not result in a change in position of the $^{31}P-\{H\}$ NMR spectrum indicating that, as expected, both of these compounds ionise to form $[R_3PI]I$ in $CDCl_3$ solution.

(*b*) *Solid-state spectra.* With the exception of $(Me_2N)_3PI_2$ and $(CH_2{=}CHCH_2)_2PhPI_2$ the solid-state NMR data indicate that the predominant solid-state species is molecular $R_3P–I–I$. However, in five of the samples, $(C_6H_{11})Ph_2PI_2$ (Fig. 1), $(p\text{-}FC_6H_4)_2PhPI_2$, $(PhCH_2CH_2)_3PI_2$ (Fig. 2), $(o\text{-}MeOC_6H_4)Ph_2PI_2$ and $(p\text{-}CH_2{=}CHC_6H_4)Ph_2PI_2$, we also observed significant peaks assignable to the ionic $[R_3PI]I$ species, Table 2. The reason for the simultaneous formation of molecular $R_3P–I–I$ and ionic $[R_3PI]I$ remains unknown. The solid-state $^{31}P-\{H\}$ NMR spectrum of $(PhCH_2CH_2)_3PI_2$ is illustrated in Fig. 2. The proportion of the two species (covalent : ionic) is approximately 95 : 5. Clearly, although this compound is predominantly molecular, $R_3P–I–I$, a small but significant amount of the ionic species, $[R_3PI]I$ is also present as shown by comparison with solution values. Nevertheless, this illustrates the interesting structures adopted by compounds of stoichiometry R_3PI_2 and their close proximity to the ionic/covalent structural borderline. Despite the simultaneous existence of an ionic and a molecular form, the predominant solid-state structures for all the compounds, except for $[(Me_2N)_3PI]I$ and $(CH_2{=}CHCH_2)PhPI_2$, is the molecular structure $R_3P–I–I$.

The solid-state $^{31}P-\{H\}$ NMR spectrum of $(Me_2N)_3PI_2$ is illustrated in Fig. 3. In contrast to the compounds R_3PI_2 (R_3 = Ph_3, $PhMe_2$ or Me_3),[1,4] and the R_3PI_2 [R_3 = $(p\text{-}FC_6H_4)_2Ph$, $(o\text{-}MeC_6H_4)Ph$, $(o\text{-}MeC_6H_4)_3$ or $(C_6H_{11})Ph_2$] compounds described herein, $(Me_2N)_3PI_2$ has a solid-state $^{31}P-\{H\}$ NMR spectrum exhibiting three peaks of close proximity at δ 25.7, 26.6 and 27.3, *i.e.* values in excellent agreement with the solution value recorded in $CDCl_3$, δ 25.4, for the ionic species $[(Me_2N)_3PI]I$ and $[(Me_2N)_3PI]I_3$. Clearly this diiodotriorganophosphorus compound and $(CH_2{=}CHCH_2)PhPI_2$ represent unique examples of exclusively ionic compounds in the solid state, $[R_3PI]I$, prepared from diethyl ether. The ionic nature of these compounds is in direct contrast to other compounds of this stoichiometry, prepared from diethyl ether solution, which have been shown by solid-state MAS $^{31}P-\{H\}$ NMR spectroscopy [R_3 = $(o\text{-}MeOC_6H_4)_3$, $(o\text{-}MeOC_6H_4)_2Ph$, Ph_3, $PhMe_2$ or Me_3] and crystallographic methods (R_3 = Ph_3 or $PhMe_2$) to exclusively adopt the molecular four co-ordinate geometry $R_3P–I–I$,[3,4] and the compounds $(o\text{-}MeOC_6H_4)Ph_2$ and $(C_6H_{11})Ph_2$ described herein which exist predominantly as the molecular species, $R_3P–I–I$, with evidence for the existence of some of the ionic $[R_3PI]I$ form.

Moreover, the ionic nature of $[(Me_2N)_3PI]I$ and $[(CH_2{=}CHCH_2)PhPI]I$ cannot simply be explained by the existence of trace quantities of moisture in the solvent since, firstly, rigorously anhydrous and anaerobic conditions were applied (see Experimental section) and, secondly, the addition of trace quantities of moisture to R_3PI_2 solutions in acetonitrile has

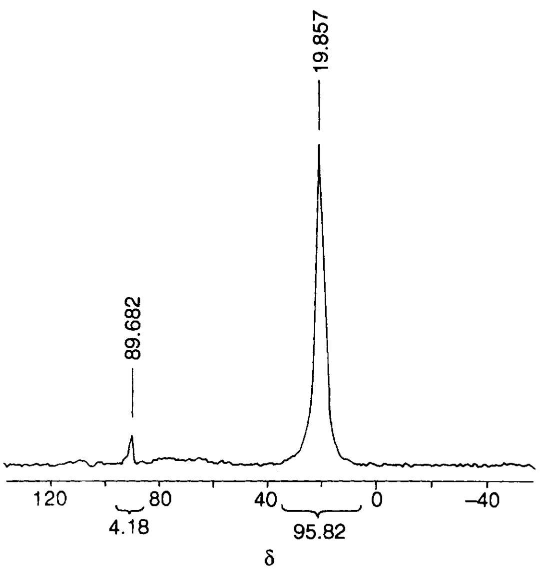

Fig. 2 The solid-state ^{31}P-{H} MAS NMR spectrum of $(PhCH_2CH_2)_3PI_2$

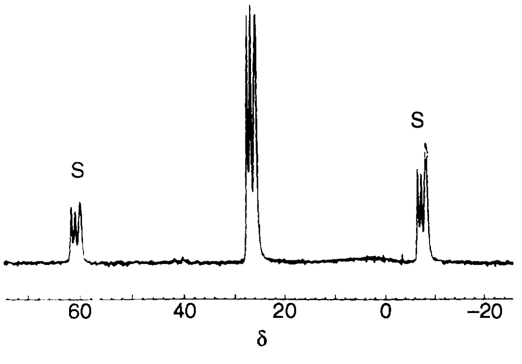

Fig. 3 The solid-state ^{31}P-{H} MAS NMR spectrum of $[(Me_2N)_3PI]I$ (S = spinning sideband)

been shown by Emeleus and Harris[13] to result in the isolation of the hydrolysis product, $[R_3PH]I$. Therefore, $[(Me_2N)_3PI]I$ and $[(CH_2{=}CHCH_2)_2PhPI]I$ are the only known examples of ionic diiodotriorganophosphorus compounds isolated from diethyl ether and further underlines the close ionic/molecular borderline for compounds of stoichiometry R_3PX_2. The existence of three peaks in the solid-state ^{31}P-{H} MAS NMR spectrum of $[(Me_2N)_3PI]I$, all of very similar shift, are difficult to explain.

Raman Spectra.—The frequency of the Raman band assigned to ν(P–I) is also given for each compound, Table 1. None of the compounds described have previously been the subject of a Raman spectroscopic study, but assignment of the band to ν(P–I) can be made with confidence by comparison with the Raman spectra of other compounds of this stoichiometry recorded by us.[3,4] Moreover, no other band occurs in this region of the spectrum.

As expected, the diiodotriorganophosphorus compounds containing electron-withdrawing groups exhibit lower frequency bands and those containing more basic tertiary phosphine groups have the highest ν(P–I) wave numbers. In particular the ν(P–I) value for $(Me_2N)_3PI_2$, 222 cm^{-1}, is appreciably higher than those recorded for the other diiodotriorganophosphorus compounds, indicating a strong P–I bond in this compound, as would be predicted.

Crystal Structure of $PhMe_2PI_2$.—Single-crystal X-ray crystallographic studies have been performed on the molecular compounds Ph_3PI_2[4] and $Bu^t{}_3PI_2$.[5] The I–I bond lengths were found to be 3.162(1) and 3.332(2) Å, respectively. We have previously reported[4] the solid-state ^{31}P-{H} MAS NMR spectrum of $PhMe_2PI_2$, which indicates that this compound also adopts the four-co-ordinate molecular structure R_3P–I–I. Since the I–I interaction in $PhMe_2P$–I–I must constitute a covalent bond (from solid-state ^{31}P-{H} NMR studies) we were intrigued to know its exact length and thus how weak a bond it represents, since previous studies have shown that the I–I bond considerably weakens upon increasing basicity of the tertiary phosphine. We thus grew crystals of $PhMe_2PI_2$ from diethyl ether solution at *ca.* 0 °C. The pale yellow crystals were isostructural with Ph_3PI_2 and exhibit the molecular structure $PhMe_2P$–I–I, Fig. 4, in agreement with solid-state ^{31}P-{H} NMR data. However, as expected, considerable lengthening of the I–I bond has occurred, the *d*(I–I) in $PhMe_2PI_2$ being 3.409(1) Å (*cf.* van der Waals radius of diiodine, 4.3 Å; *d*(I–I) in molecular iodine, 2.67 Å). Selected bond lengths and angles for $PhMe_2PI_2$ are given in Table 3 and fractional atomic coordinates for the non-hydrogen atoms are listed in Table 4. This is an interesting result, since it clearly shows that although the I–I bond is lengthened by almost 0.8 Å relative to diiodine, it still constitutes a covalent I–I bond and illustrates the lengthening of an X–X (X = halogen) bond which can occur in charge-transfer adducts. The lengthening of I–I bonds has also been reported in two compounds of stoichiometry Ph_3PI_4 by Cotton and Kibala,[14] I–I linkages of between 2.82 and 3.74 Å being observed.

Conclusion

The studies reported here and our previous studies[3,4] show that in diethyl ether solution the vast majority of R_3P compounds form molecular charge-transfer complexes with I_2, which in the solid state have a four-co-ordinate molecular 'spoke' structure, R_3P–I–I. In all of these complexes the I–I bond considerably lengthens [*d*(I–I): Ph_3PI_2, 3.16 Å[4]; $Bu^t{}_3PI_2$, 3.33 Å[5]; $PhMe_2PI_2$, 3.41 Å] upon adduct formation [*d*(I–I) in I_2 = 2.67 Å], as expected, since electron density is put into the σ-antibonding orbitals of the diiodine by the electron donor, R_3P. Not only is this phenomenon apparent from crystallographic data, but it is also reflected in the ν(P–I) values from the Raman spectra. Interestingly, for the solid compounds $(C_6H_{11})Ph_2PI_2$ and $(p\text{-}FC_6H_4)_2PhPI_2$, there is evidence for the simultaneous existence of both the ionic and the molecular forms, but for $[(Me_2N)_3PI]I$ and $[(CH_2{=}CHCH_2)_2PhPI]I$ only the ionic structure prevails, although all the compounds were prepared from diethyl ether. The structures adopted by R_3PI_2 compounds (ionic or covalent) are clearly critically dependent on R.

Experimental

The moisture sensitivity of compounds of formula R_3PI_2 has previously been stressed and all the compounds described herein were prepared according to the previously published method, *viz.* the direct reaction of tertiary phosphine with diiodine in rigorously dry diethyl ether.[1] Elemental analyses were performed by the UMIST Microanalytical Service and the results are presented in Table 1. Raman spectra and ^{31}P-{H} solid-state MAS NMR and solution NMR spectra were recorded as previously described.[3]

X-Ray Crystallography.—A trapezoid crystal (0.3 × 0.2 × 0.2 mm) was mounted in a Lindeman tube under dry-box conditions (argon). All measurements were performed on a Rigaku AFC6S diffractometer using graphite-monochromated Mo-Kα radiation. Crystal data and details of refinement are given in Table 5.

Lorentz, polarisation and adsorption (azimuthal scans; minimum, maximum transmission 0.85, 1.00) corrections were applied.

Table 3 Selected bond lengths (Å) and angles (°) in $PhMe_2PI_2$

I(1)–I(2)	3.408(2)	P–C(2)	1.773(9)
I(1)–P	2.410(2)	P–C(3)	1.783(6)
P–C(1)	1.784(8)		
I(1)–P–C(1)	109.6(3)	C(1)–P–C(3)	110.4(4)
I(1)–P–C(2)	108.6(3)	C(2)–P–C(3)	110.7(4)
I(1)–P–C(3)	108.6(2)	P–C(1)–C(4)	120.4(5)
C(1)–P–C(2)	108.9(5)	P–C(3)–C(8)	120.5(6)

Table 4 Fractional atomic coordinates for the non-hydrogen atoms in $PhMe_2PI_2$

Atom	*x*	*y*	*z*
I(1)	0.265 71(6)	0.093 27(4)	0.084 69(4)
I(2)	0.251 34(6)	−0.235 66(4)	0.086 15(4)
P	0.290 8(2)	0.325 1(2)	0.084 3(1)
C(1)	0.128(1)	0.396 8(8)	0.121 8(7)
C(2)	0.279(1)	0.376(1)	−0.039 6(7)
C(3)	0.481 8(7)	0.369 2(6)	0.168 9(5)
C(4)	0.490(1)	0.465 0(7)	0.240 7(6)
C(5)	0.637(1)	0.498 9(9)	0.305 4(7)
C(6)	0.777(1)	0.434 6(9)	0.301 0(7)
C(7)	0.771(1)	0.339(1)	0.231 4(7)
C(8)	0.622(1)	0.307 9(8)	0.165 2(6)

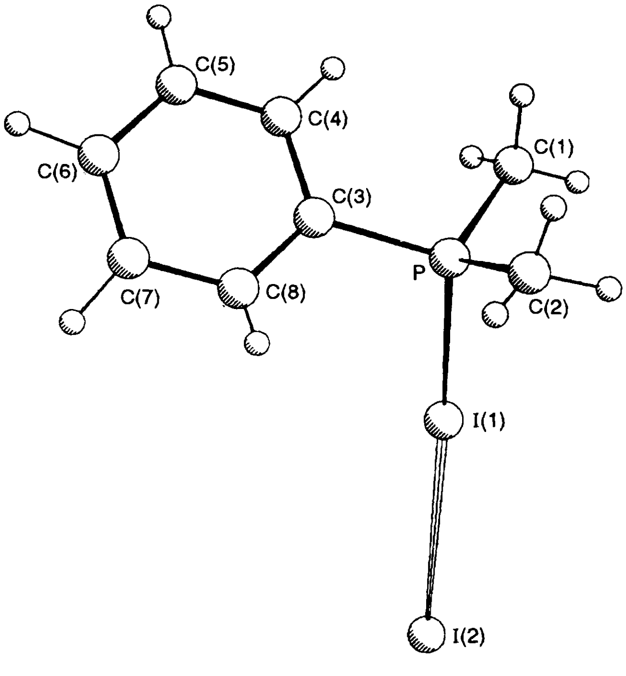

Fig. 4 The crystal structure of molecular $PhMe_2PI_2$

The structure was solved by direct methods.[15] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. Neutral atom scattering factors were taken from ref. 16*a*. Anomalous dispersion effects were included in F_{calc}; the values for $\Delta f'$ and $\Delta f''$ were taken from ref. 16*b*. All calculations were performed using the TEXSAN crystallographic software package.[17]

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

Table 5 Crystal data and details of refinement for $PhMe_2PI_2$

M	391.96
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
a/Å	8.560(6)
b/Å	10.353(7)
c/Å	13.874(5)
β/°	106.36(3)
U/Å^3	1180(2)
Z	4
D_c/g cm^{-3}	2.207
$F(000)$	720
μ/cm^{-1}	53.59
Total data measured	2370
Maximum 2θ/°	50.1
No. unique reflections	2216
No. observed reflections [$I > 2.00\,\sigma(I)$]	1597
No. of parameters	145
$\rho_{min,\,max}$/e Å^{-3}	−1.27, 1.07
Maximum least-squares shift-to-error ratio	0.14
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0.03
Final R^a	0.034
Final R'^b	0.039

[a] $R = \Sigma|F_o| - |F_c|/|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

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