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Iodophosphonium salt structures: homonuclear cation–anion interactions leading to supramolecular assemblies

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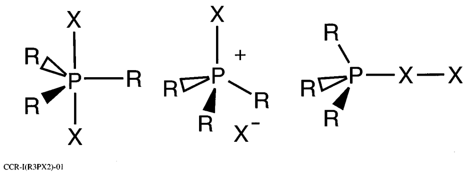
Abstract

The structures of iodophosphonium cations $R_nPI_{4-n}^+$ depend significantly on the nature of their counteranions, which act as nucleophiles towards electrophilic iodine atoms bonded to the formally charged phosphorus atom. This nucleophilic attack leads to P–I bond lengthening, that can be understood as consequence of ($n \rightarrow \sigma^*$) donor–acceptor interactions, i.e. population of the σ^* energy level of the attacked P–I bond. For a given cation, anion ‘iodophilicity’ correlates well with P–I and I–I distances: the phosphane and the anion compete for coordination with the central linearly coordinated iodine atom. When different iodophosphonium cations are compared, however, P–I/I–I correlations are not always that straightforward, since specific effects of the peculiar substituents like size, electronic properties and packing preferences do also play a role. In di- and triiodophosphonium ions, bi- and trifunctionality of the soft Lewis acids $R_2PI_2^+$ and RPI_3^- and the ability of iodide ions to bridge up to five cations allows the formation of rings, chains, columnar, layer and 3D net structures, which are all due to I···I interactions. Comparison of several structures involving the same cation confirms, that I_3^- is a much weaker donor than I^-, and indicates, that in solid compounds bridging I^- anions ‘spread’ their donor ability over several iodophosphonium acceptors; i.e. the individual cation is less affected. This allows to understand, why compounds RPI_4 (R = Me, i-Pr, t-Bu) are stable as solids, but dissociate in inert solvents into RPI_2 and molecular iodine.

Keywords: Phosphorus; Iodine; Iodophosphonium salts; Phosphoranes; Donor–acceptor interactions; Soft–soft interaction; Supramolecular assemblies

1. Introduction

It has since long been recognised, that for phosphorus pentahalides as well as halogenophosphoranes R_nPX_{5-n} (R = organic substituent; X = halogen atom) molecular as well as ionic structures can occur, and that the structures in condensed phases may differ from those in the gas phase. It is also fairly well established, that trigonal–bipyramidal structures of molecules R_nPX_{5-n} prevail, when X = F; and trigonal-bipyramidal as well as ionic structures are known from compounds with X = Cl or Br [1]. There was however, until recently, a surprising lack of information concerning solid state structures even of several ‘classic’ simple compounds like R_3PX_2 (X = Cl, Br, I). The current interest in such compounds [2,3] to elucidate the role of nature and number of R and X bonded to phosphorus as well as the contribution of solvent and packing effects for the solid state structure of a peculiar compound R_nPX_{5-n} was stimulated by the observation, that discussions of the



Scheme 1. Alternative structures of halogenophosphoranes R_3PX_2

tradional antagonism 'phosphorane vs. ionic structure' had neglected the enhanced electrophilicity of the heavier halogen atoms, when they are bonded to phosphonium centers. This enhanced electrophilicity, however, which was recognised by NMR-studies concerning the kinetic lability of iodo- and bromophosphonium ions in presence of tertiary phosphanes [4], and by 'halogenophilic reductions' of iodophosphonium salts [5], has serious structural implications for many halogenophosphonium salts (Scheme 1).

Extremely little was known, until a decade ago, about the structures of 'iodophosphoranes'. Physical measurements on 'phosphine diiodides' R_3PI_2 as well as the lack of configurational stability of compounds $RR'R''_3PI_2$ had led to the suggestion that basically ionic compounds $R_3PI^+I^-$ exist in equilibria with molecular species implying trigonal–bipyramidal environment at phosphorus [6,7]. Related equilibria had been confirmed in the case of certain chloro- and bromophosphoranes [1]; the true structure of 'molecular species' $R_3P{-}I{-}I$, however, has been detected just a decade ago [8]. The finding, that iodine atoms bonded to phosphonium centers are remarkably electrophilic, has led to an improved understanding of the iodination of P^{III} compounds [9] including solution phenomena (NMR) [4,5,8,10]. The donor–acceptor approach also led to a straightforward concept explaining the basic structural chemistry of various iodination products like R_nPI_{5-n}, $R_nPI_{6-n,}$ R_nPI_{7-n}. This includes a new approach to understand the problem of the existence of highly-iodinated phosphorus compounds like RPI_4 and PI_5, in solution and in the solid state.

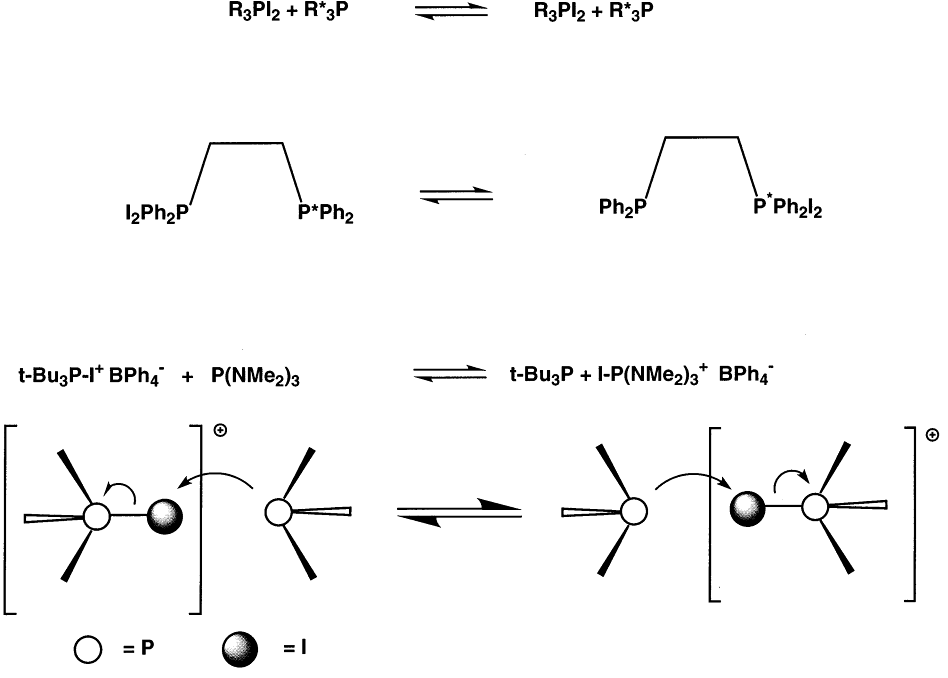
2. The iodination of phosphanes R_nPI_{3-n}

2.1. *The iodination of phosphanes—a survey*

The iodination of phosphanes R_nPI_{3-n} can be easily followed by ^{31}P-NMR in aprotic dipolar solvents [4,5,8,10]. It is important to exclude conditions that would allow hydrolysis of iodophosphonium cations leading to hydroxyphosphonium cations. Many ^{31}P-NMR data previously assigned to iodophosphonium salts (for instance to Ph_3PI^+) in literature are now turning out to be due to products from hydrolysis (for instance Ph_3POH^+ [10]). The t-Bu_3PI^+ cation, however, is quite resistant to hydrolysis, because steric shielding from three t-butyl groups disfavors nucleophilic attack at phosphorus [4,8]. Due to this unusual resistance towards hydrolysis, the compound *t*-Bu_3PI_2 was the first iodophosphonium salt that allowed the determination of reliable ^{31}P-NMR data in various, even protic, solvents. *t*-Bu_3PI_2 can be extracted undecomposed with chloroform or dichloromethane from its (colorless) water solution to give yellow solutions in the corresponding organic solvent. Somewhat less crowded *i*-Pr_3PI_2, however, is very sensitive to moisture. Its hydrolysis leads to salts of the *i*-Pr_3POH^+ cation, which exhibits anion- and concentration-dependent ^{31}P-NMR chemical shifts [11] (as do the parent R_3PI^+ cations).

The extreme steric shielding of phosphorus in *t*-Bu_3PI_2 opened the question, if its reactive properties (detected in 1976 [4]: kinetic lability towards R_3P, but inertness towards H_2O) and its structure (detected in 1987 [8]: a linearly coordinated central iodine atom) were unique among iodophosphoranes or if they were basic for a novel understanding of iodophosphonium ion chemistry. For that reason, it was most important, to solve the solid state structure of Ph_3PI_2 [12] (which has the same 'spoke'-like shape as *t*-Bu_3PI_2) and to reinvestigate thoroughly its NMR-spectra [10] (which reveals kinetic lability, i.e. rapid iodine transfer similar as with *t*-Bu_3PI_2). P^{III}/P^{V}-averaged ^{31}P-NMR signals show, that iodophosphonium ions with non-nucleophilic anions like BPh_4^- or BF_4^- [4,13], and the monoiodinated bidentate compound dppe-I_2, as well, behave kinetically labile (Eqs. 1–3). ^{31}P decoalsecence of dppe-I_2, for instance, is observed below about − 20°C in dichloromethane solution [13,14].

(1,2,3)



CCR-I-transfer

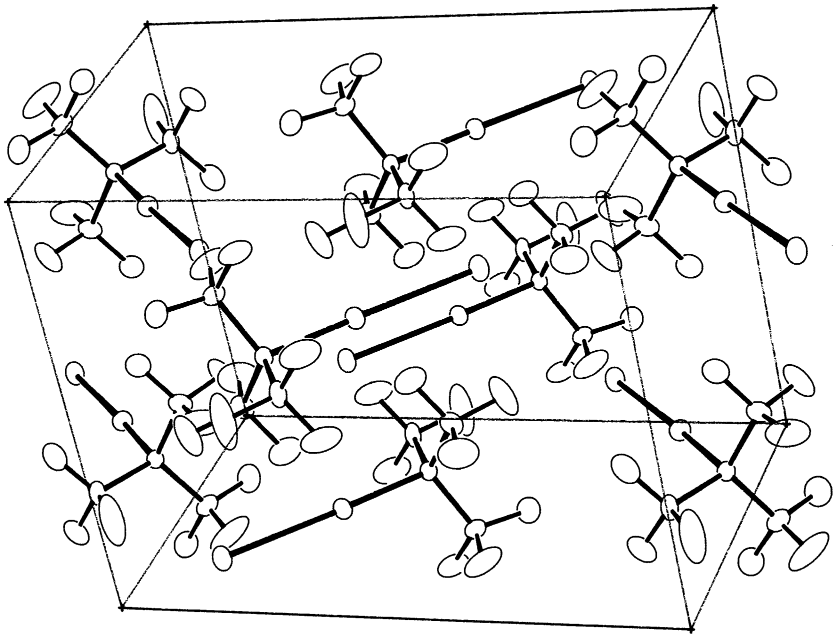
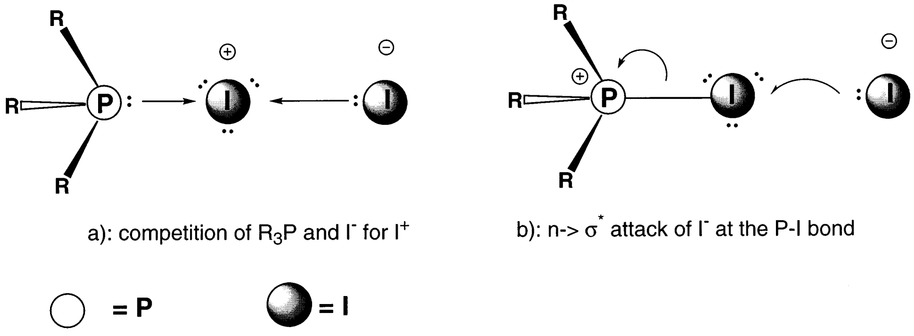


Fig. 1. Packing of t-Bu_3PI_2.



Scheme 2. Ways to describe iodophosphonium iodides.

Comparing the structures of the t-Bu_3PI_2 [8] and Ph_3PI_2 [12] (Figs. 1 and 2) allows the conclusion that, just as in 'classical' donor–acceptor complexes of iodine, the central linearly coordinated iodine atom of R_3PI_2 compounds may be regarded as I^+ cation that is coordinated by two competing nucleophiles, i.e. by a phosphane ligand and by the iodide anion (Scheme 2).

The I–I distance in solid Ph_3PI_2 (316 pm [12]) is longer than the ones in Me_3NI_2 (283 pm [15]), Ph_3AsI_2 (301 pm [16]) or in symmetric I_3^- anions (about 290–293 pm [17]), i.e., Ph_3P is 'a better iodophile' than Me_3N, Ph_3As and I^-. t-Bu_3P, however, is an even better iodophile than Ph_3P, as shown by a I···I separation of 333 pm, which is accompanied by a P–I bond distance (246 pm) that is shorter than that of Ph_3PI_2 (248 pm). When a tertiary phosphane has to compete with an iodometallate like $W(CO)_4I_3^-$ [18] or with I_3^- anions [17,19], which are much poorer iodophiles than the I^- anion, the experimental P–I distances of the resulting solid iodophosphonium salts are in the range of 240 ± 2 pm. These short P–I bonds of rather undisturbed iodophosphonium ions are neighbored by long I···I contacts (about 350–375 pm).

Titration-like iodinations of phosphanes R_3P and R_2PI followed by solution NMR at room temperature allow the following observations [4,10,20,21]:

1. Excess of phosphane: only one averaged ^{31}P-NMR signal appears (broadened depending on temperature) due to fast iodine transfer between phosphane molecules.
2. 1:1 ratio: yellow compounds R_3PI_2 or R_2PI_3 give ^{31}P-NMR shifts that tend to be upfield from those of R_3P or R_2PI.
3. Excess of iodine: still only one averaged ^{31}P-NMR signal appears, which is again shifted in the downfield direction. The downfield shifts of iodine-rich solutions compared with pure compounds R_3PI_2 or R_2PI_3 indicate increased cation-anion separation due to tri- and/or polyiodide formation.

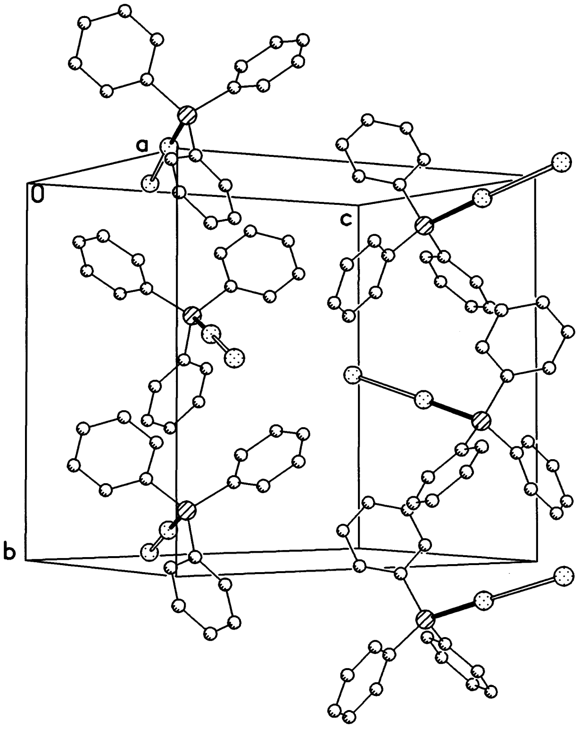


Fig. 2. Packing of Ph_3PI_2.

2.2. A typical experiment: NMR investigation of the stepwise iodination of dialkyliodophosphanes

The titration-like reactions of several dialkyliodophosphanes RR′PI with iodine were followed by ^{31}P- and ^{1}H-NMR spectroscopy [20,21]. Iodine was added stepwise to dichloromethane solutions of the iodophosphanes and to dichloromethane solutions or suspensions of R_2PI_3 compounds. As example, the reactions of iodine with di-*tert*-butyliodophosphane are described in detail: When a very small amount of iodine is added to a solution of t-Bu_2PI, the ^{31}P-NMR signal broadens considerably whereas the ^{1}H-NMR doublet does not; the ^{1}H- and ^{31}P-NMR signals are shifted slightly to lower field, compared with t-Bu_2PI, and the coupling constant $^{3}J(^{31}P, {}^{1}H)$ increases slightly. Separate NMR signals for the reaction product are not observed. Under these conditions rapid iodine transfer between dialkyliodophosphane molecules occurs. Adding about half an equivalent of iodine to the dichloromethane solution of t-Bu_2PI leads to precipitation of yellow t-Bu_2PI_3; the ^{31}P-NMR signal of the remaining t-Bu_2PI in solution again appears broad and slightly shifted to lower field; running the spectrum at -60°C did not lead to decoalescence of the ^{31}P-NMR signal. The 1:1 reaction of t-Bu_2PI with I_2 furnishes t-Bu_2PI_3 as a yellow solid that is sparingly soluble in tetrahydrofuran, trichloromethane and dichloromethane (solubility in CH_2Cl_2: 0.8 g l^{-1}). t-Bu_2PI_3 shows a very broad ^{31}P-NMR signal at $+61$ ppm (75 ppm upfield from t-Bu_2P), the increase of $^{3}J(^{31}P, {}^{1}H)$ is consistent with four-coordination of phosphorus.

The X-ray crystal structure determination of t-Bu_2PI_3 [20] reveals that di-*tert*-butyldiiodophosphonium ions (containing tetrahedrally coordinated phosphorus) are bridged by two-coordinated iodide anions leading to a zig-zag chain polymer. Addition of further amounts of iodine to suspensions containing t-Bu_2PI_3 leads to brown solutions/suspensions, which become darker with increasing amounts of iodine. Such solutions give strong and sharp ^{31}P-NMR singlets that are shifted to lower field, compared with t-Bu_2PI_3. ^{1}H-NMR doublet signals are further shifted downfield and $^{3}J(^{31}P, {}^{1}H)$ increases further, compared with t-Bu_2PI and t-Bu_2PI_3; maximum values ($\delta\,^{31}P = +87.5$ ppm; $^{3}J(^{31}P, {}^{1}H) = 23.8$ Hz) were obtained in presence of a saturated solution of iodine in dichloromethane. Crystallisation from such solutions furnished mixed iodide, triiodides t-Bu_2PI_4 and t-$Bu_2PI_{4.33}$ [20]. Attempts to isolate crystals of the pure triiodide t-Bu_2PI_5 failed even in the presence of excess iodine. Only an intercalation compound of t-Bu_2PI_5 with PI_3 has fortuitously been isolated as single crystal [37] (see Section 4.2). The related diethyl derivate, however, provides pure triiodide Et_2PI_5 [20,22].

The fact that all NMR parameters of R_3PI_2/I_2 and R_2PI_3/I_2 systems are dependent on the iodine content in solution suggests that iodine addition leads to equilibria involving consumption of iodide anions by triiodide formation. Since triiodide is a weaker donor towards iodophosphonium cations, the overall cation-anion soft-soft interactions decrease with increasing addition of iodine [4,5,20,21]. Retrosynthetically, increasing cation-anion soft-soft interaction leads to ^{31}P- and

^{1}H-NMR upfield shifts and decreasing magnitude of $^3J(^{31}P, ^1H)$. Thus the question arose, if the presence of weakly nucleophilic triiodide counterions has already an impact (upfield shift) on the ^{31}P nucleus of the $R_2PI_2^+$ cations. To obtain reference data of a nearly 'free' t-$Bu_2PI_2^+$ cation, the salt t-$Bu_2PI_2^+ AlI_4^-$ was prepared from t-Bu_2PI_3 with aluminum triiodide. As expected, the ^{31}P-NMR singlet signal of t-$Bu_2PI_2^+ AlI_4^-$ appears even further downfield ($\delta^{31}P$ +96.6 ppm) than that of solutions containing t-Bu_2PI_4 with excess of iodine ($\delta^{31}P$ +87.5 ppm).

2.3. Iodination of diiodophosphanes and PI_3

The nucleophilicity of phosphanes decreases in the range $R_3P > R_2I > RPI_2 > PI_3$, i.e. alkyldiiodophosphanes are poorer nucleophiles and should also be poorer iodophiles than dialkyliodophosphanes [5]. Concentration- and solvent-dependent NMR spectra of organyldiiodophosphanes were explained with equilibria of RPI_2 molecules with ionic species $[R(I)_2PP(R)I]^+I^-$ [5,23] which may be in further equilibria with diphosphanes R(I)PP(R)I and oxidised species RPI_4. The reactions of alkyldiiodophosphanes with iodine do not lead to titration-like changes of the ^{31}P-NMR shifts, but dichloromethane, carbon disulfide or benzene solutions exhibit only the resonances of the rather undisturbed diiodophosphanes RPI_2 [5,23,24]. The reactions of RPI_2 with I_2 lead, however, to precipitation of colored solids, that analyse fairly as RPI_4 or as RPI_6 compounds [14,25]. ^{31}P- and ^{13}C-NMR spectra of solid t-$BuPI_4$ indicated, that its structure involves tetracoordinated phosphorus bonded to three iodine atoms [24]. In benzene/carbon disulfide solution t-BuI_4 decomposes into t-$BuPI_2$ and molecular iodine. Structures of products from reactions of RPI_2 molecules with more than one equivalent of iodine have not yet been determined.

Since PI_3 will be an even poorer nucleophile than RPI_2 species, it is no surprise, that solutions containing 'what analyses as PI_5' exhibit the ^{31}P-NMR signal of PI_3 [5,23,24]. The structure of the solid 'that analyses as PI_5' has not yet been elucidated. With help of the less-nucleophilic AlI_4^- anion, the PI_4^+ cation could be generated from $PI_3/I_2/AlI_3$ and characterised by X-ray crystallography [26]. The reaction of PI_3 with AlI_3 (in absence of iodine) gave $P_2I_5^+ AlI_4^-$ [27].

A 'true' molecular iodophosphorane with pentacoordinated phosphorus has been isolated and structurally characterised by Schmutzler et al. (Fig. 1) [28,29]; in this compound, chelating substituents help to stabilise the valence shell- expanded state of phosphorus.

3. Structures of iodophosphonium salts

3.1. Salts of monoiodophosphonium cations R_3PI^+

3.1.1. Iodophosphonium iodides $R_3PI^+I^-$: 'spoke' structures

All yet structurally characterised compounds of the type R_3PI_2 exhibit approximately linear P–I···I cation–anion contacts [8,11,12,30,31]. Within the range of

Table 1
Iodine–iodine distances

	d(I–I) (pm)	Ref.
$I_{2(g)}$	267	[1]
$I_{2(cryst)}$ ($d_{intramol}$)	272	[1]
$Me_3N–I–I$	283	[15]
$Fc_3PI–I_3$ [a] ($I_{3,symm}$)	290	[17]
$Ph_3As–I–I$	301	[33]
$Ph_3P–I–I$	316	[12]
$(Me_4Sb)_3I_8$ ($I_{x,symm}$)	329	[41]
t-$Bu_3P–I–I$	333	[8]
$Me_2(Ph)P–I–I$	341	[30]
t-$Bu_3P–I–I–WI_2(CO)_4$	355	[18]
$Fc_3PI–I_3$ [a] (PI–I)	373	[17]
$I_{2(cryst)}$ ($d_{intermol}$) within I_4	350	[1]
Between I_4 units	397	

[a] Fc = ferrocenyl (Ref. [17]).

$R_3PI–I$ structures, the P–I/I–I distance correlation (Table 1) is not as straightforward as between $R_3PI–I$ and $R_3P–I–I–ML_n$ compounds based on the same phosphane. The role of substituent size effects, packing, and solvent of crystallisation for electrostatic and orbital interactions has yet to be quantified. Ion–dipole interactions between dichloromethane and the anion are suggested by the structures of $(i\text{-}Pr_3P–I–I)_2–CH_2Cl_2$ of the related P–Br compound [3,11] (Figs. 2–5).

3.1.2. Iodophosphonium triiodides

Tri(ferrocenyl)iodophosphonium triiodide was the first structurally characterised iodophosphonium salt [17]. In solid iodophosphonium triiodides the electrophilic iodine atom of the R_3PI^+ cation desires an approximately linear P–I···I contact. In ($Fc_3PI_3^+ I_3^-$) this is achieved by long contacts (373.9) of one the terminal iodine atoms of each triiodide within a zigzag chain with the iodine atom of the neighbored Fc_3PI^+ cation (Fig. 6).

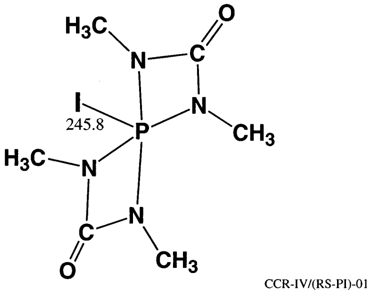


Fig. 3. Constitution of a pentacoordinated iodophosphorane.

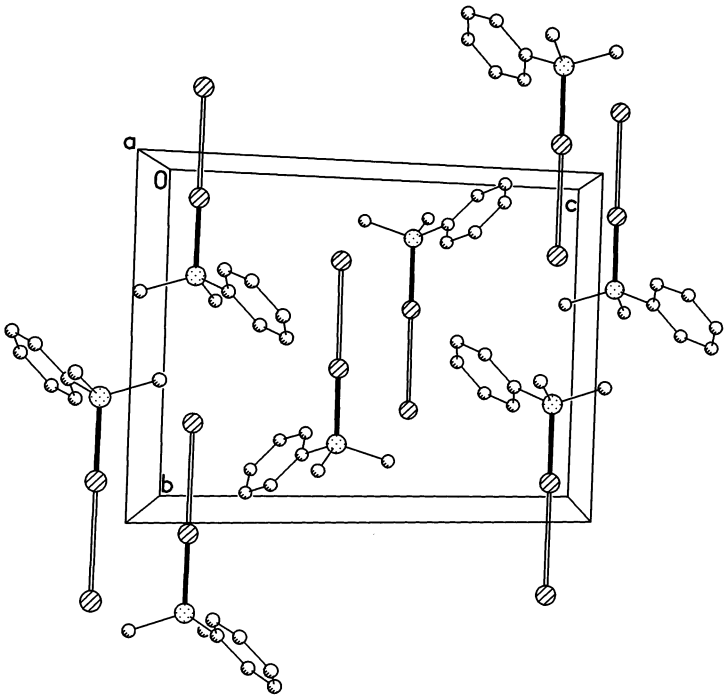


Fig. 4. Packing of $Me_2(Ph)PI_2$.

The distance from the central I atom of each I_3^- to the I atom bonded to P is 399.0 pm. Within the chain of symmetric I_3^- anions, the I atom, that is in contact with the cation, is in a linear position; the non-coordinated iodine atom is in an angular environment. One polymorph of $Ph_3PI^+I_3^-$ adopts a related structure [19]; its triiodide is unsymmetric, however, and the zigzag nature of the triodide chain is less pronounced than in the ferrocenyl derivative [17]. In the other polymorph of $Ph_3PI^+I_3^-$, one triiodide is symmetric and non-coordinating, the other, unsymmetric one, bridges two Ph_3PI^+ cations and one iodine molecule, leading to a salt of the type $[(Ph_3PI)_2I(I_2)]^+[I_3]^-$. The central μ_3-donor–iodine atom of the cation (Fig. 7) is in a trigonal-pyramidal environment.

In the structure of solid i-$Pr_3PI^+I_3^-$, the motif of zigzag triiodides chains are L-shaped moieties from two I_3^- ions [11]. From these two I_3^- ions, one (type 1) is colinear with the terminal atoms of its neighboring triiodides; the other I_3^- (type 2) of each L-shaped moiety is in angled contact with its neighbors (Fig. 8) [11]. Thus, the zigzag chains consist of linear I_5- and I_3-sequences which approximately orthogonal to each other. The acceptor– iodine atom of each i-Pr_3PI^+ cation is in a kind of μ_2-bridging contact with the two outer atoms of a I_5-sequence. The contact with the iodine atom belonging to the 'type 1' triiodide (I1–I5 374 pm) is closer than that with the terminal atom of the I_5-sequence (402 pm), which belongs to the other triiodide. When the latter contact is neglected, one triiodide coordi-

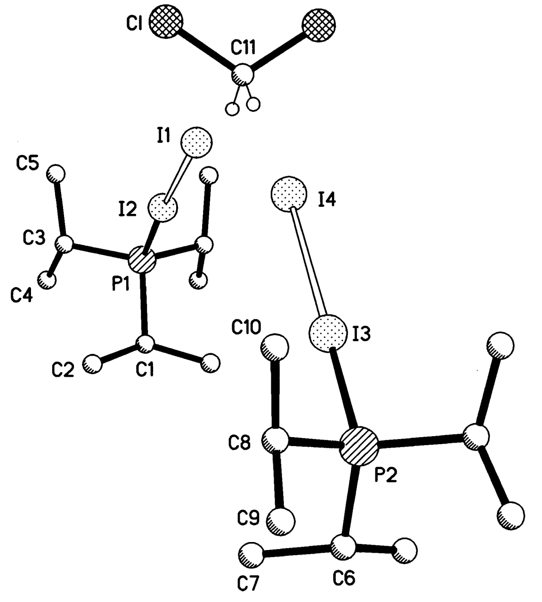


Fig. 5. Interaction of i-Pr_3PI_2 with CH_2Cl_2.

nates two cations very weakly (374 pm), and one ('type 2') is free, suggesting the over-all description [i-Pr_3P–I···I–I–I···I–P-i-Pr_3]$^+I_3^-$ which is an interesting alternative to $[(Ph_3PI)_2I(I_2)]^+[I_3]^-$ (see above).

Shorter P–I and longer I···I distances (compared with R_3PI_2) of all $R_3PI^+I_3^-$ salts reflect, that I_3^- is less nucleophilic that I^-.

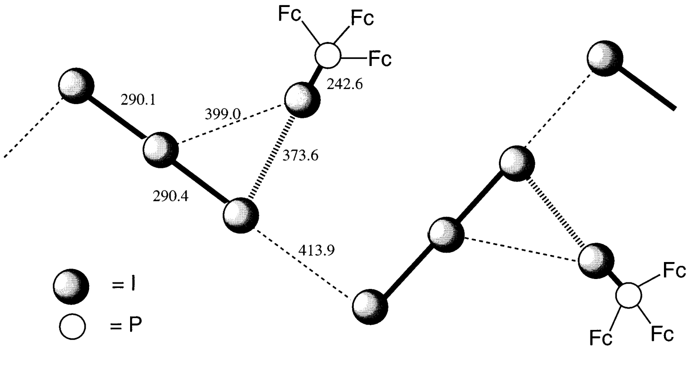


Fig. 6. Soft–soft interactions in $Fc_3PI^+I_3^-$.

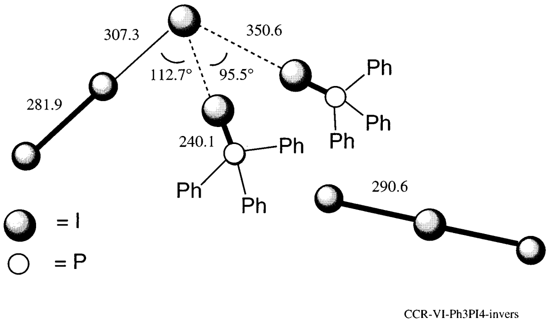


Fig. 7. Geometry of the cation in $(Ph_3PI)_2I{-}I_2^+I_3^-$.

3.1.3. Iodide-bridged iodophosphonium ions $[(R_3PI)_2I]^+$

When one 1/2 equivalent of the iodide anions of a R_3PI_2 compound is exchanged by a less nucleophilic counteranion, the remaining iodide anion has to satisfy the electrophilic needs of two R_3PI^+ cations. This leads to μ_2-donor-iodide bridging of two of these cations. I–I–I moieties of all yet structurally characterised $[(R_3PI)_2I]^+$ cations are non-linear, whereas a linear arrangement has been found in the

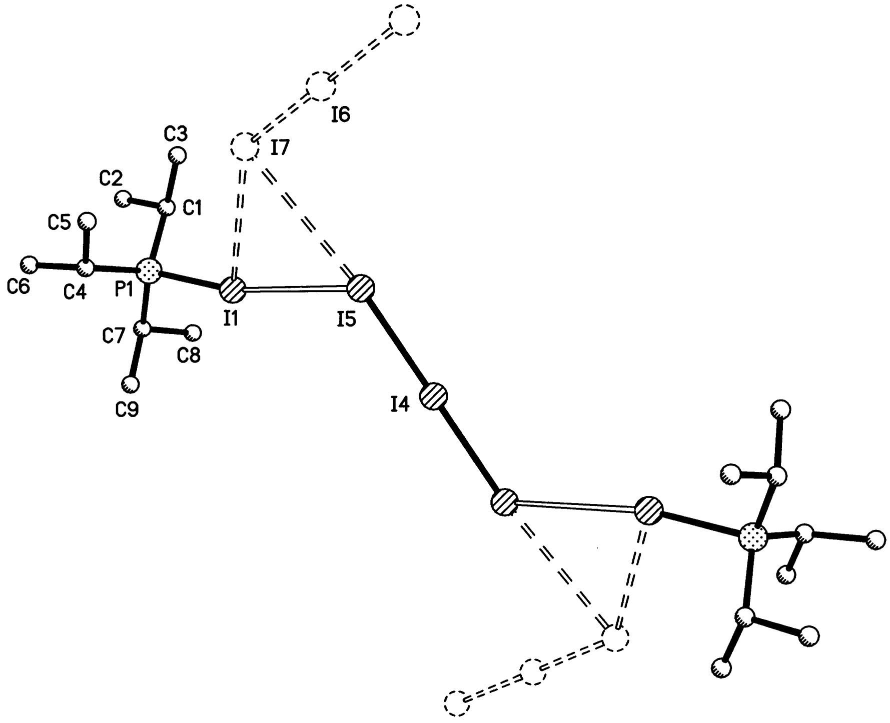


Fig. 8. Soft–soft interactions in $i\text{-}Pr_3PI^+I_3^-$.

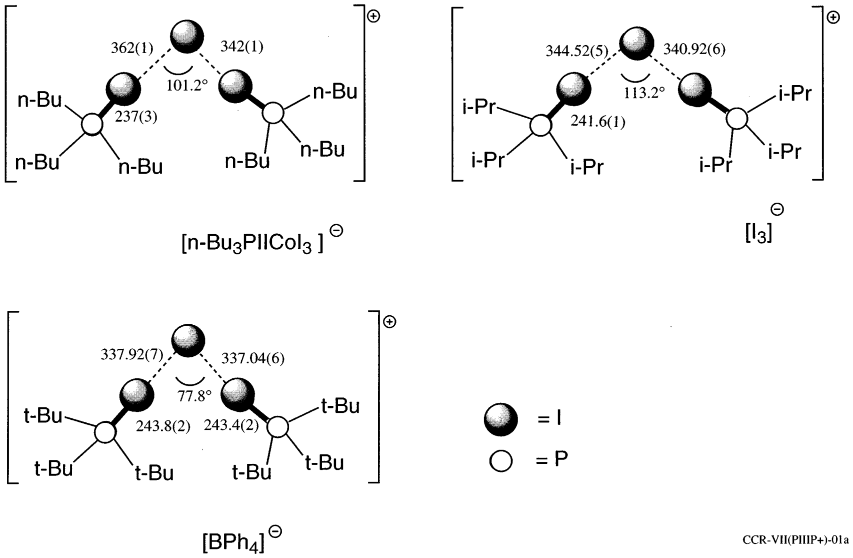


Fig. 9. Iodide-bridged iodophosphonium Ions $[(R_3PI)_2I]^+$ (R = *n*-Bu, *i*-Pr, *t*-Bu).

$[(Ph_3AsI)_2I]^+$ cation [32]. Serving more cations, the μ_2- and μ_3- donor-iodides behave as weaker donors towards each of the iodophosphonium cations than a terminal iodide anion. $[(n\text{-}Bu_3PI)_2I]^+[n\text{-}Bu_3PI{-}ICoI_3]^-$ contains $n\text{-}Bu_3PI^+$ moieties and long I···I contacts in the cation and in the anion [33]. Short P–I distances in both types of $n\text{-}Bu_3PI^+$ groups (237.3 pm) correlate well with rather long I···I contacts (in the cation: 342 and 362 pm; in the anion: 366 pm). Compared with the $[(n\text{-}Bu_3PI)_2I]^+$ cation, α-branching of the alkyl groups at phosphorus in $[(i\text{-}Pr_3PI)_2I]^+$ and $[(t\text{-}Bu_3PI)_2I]^+$ leads to longer P–I distances (with *i*-Pr at P: 241.6 pm, with *t*-Bu at P: 243.4 and 243.8 pm) and shorter average I···I contacts within the $[(R_3PI)_2I]^+$ cations (Fig. 9) [11,33,34]. $[(i\text{-}Pr_3PI)_2I]^+$ cations and I_3^- anions are well separated (I···I > 420 pm) [11].

3.1.4. Other iodophosphonium salts $R_3PI^+X^-$

From the $t\text{-}Bu_3PI^+$ cation, two salts with less-nucleophilic counteranions were X-rayed: When the $W(CO)_4I_3^-$ counterion is present [18], the P–I distance is 6 pm shorter and the I···I contact is 22 pm longer than in solid $t\text{-}Bu_3PI_2$. In solid $t\text{-}Bu_3PI^+BF_4^-$, a well-ordered BF_4^- counteranion is surrounded by four cations, leading to a kind of supramolecular $[(t\text{-}Bu_3PIF)_4B]^{3+}$ cation (Fig. 10) [13,35]. The four P–I···F–B units are linear. The B–F bond distances in this tricationic moiety are 129 pm, i.e. slightly longer those of the three non-coordinated BF_4^- anions (126 pm). This indicates, that towards the electrophilic iodine atoms of R_3PI^+ cations, even the BF_4^- anion is not completely 'innocent' [35].

Attempts to determine the structure of Ph_3PIBr allowed to characterise a solid compound $Ph_3PI_{1.29}Br_{0.71}$ with halogen disorder; the 'spoke' like structure of the

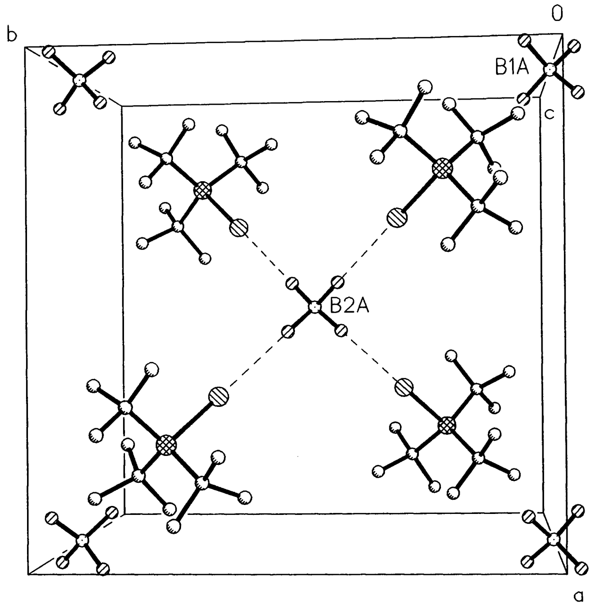


Fig. 10. The supramolecular trication $B[F{-}I{-}P(t\text{-}Bu)_3]_4^{3+}$

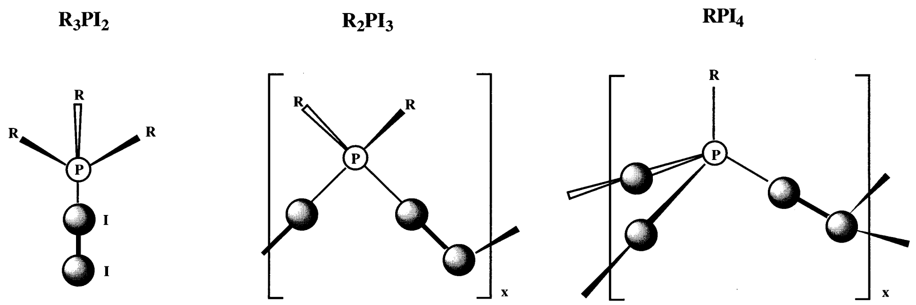
compound, however, being predominantly $Ph_3P{-}I{-}Br$, was unequivocally confirmed [36].

3.2. *Salts of diiodophosphonium cations* $R_2PI_2^+$

3.2.1. *Diiodophosphonium iodides* $RR'PI_2^+I^-$*: ring, chain or helix*

In iodophosphonium cations, each iodine atom attached to four-coordinated phosphorus behaves as a soft electrophile seeking contact with a soft nucleophile. To meet this requirement, triorganyliodophosphonium iodides R_3PI_2 exist as monomeric ion pairs with one linear P–I–I moiety, in diorganyldiiodophosphonium iodides R_2PI_3, iodide anions have to act as μ_2-bridging soft nucleophiles towards two of the diorganyldiiodophosphonium cations and in alkyltriiodophosphonium iodides RPI_4, because each cation contains three acceptor–iodine atoms bonded to phosphorus, iodide counterions have to bridge three RPI_3^+ cations (Scheme 3).

Concerning the bright yellow $R_2PI_2^+I^-$ salts, cation–anion soft–soft interactions between linear two-coordinated acceptor iodine atoms-bonded to tetracoordinated phosphorus-and two-coordinate iodide anions (with angular geometry) lead to ring or chain structures with $[-I-P-I-I-]_x$ backbones ($x = 2$ or ∞). Solid t-Bu_2PI_3 exists as a zigzag chain polymer [20], i-Pr(t–Bu)PI_3 is a helical chain polymer [21], and Ph_2PI_3 was isolated as cyclic dimer [37]. I···I contacts are in the 340 pm range and P–I bonds are longer than in 'undisturbed' cations.



- terminal iodide donor towards the I atom of $R_3PI^{\oplus}$
- μ_2 bridging iodide donor towards two I atoms of two $R_2PI_2^{\oplus}$ cations
- μ_3 bridging $I^{\ominus}$ donor towards three I atoms of three different $RPI_3^{\oplus}$ cations

CCR-VIII(P-I-Schm3)

Scheme 3. Topolgy of iodophosphonium salts R_nPI_{5-n} ($n = 3, 2, 1$).

In each case, the close-range order (coordination geometry of 8-I-2 and 10-I-2 atoms[1] [38] and P according to VSEPR expectations) is governed by overlap effects, whereas the long-range order (manifested as torsion angles, helical versus a zig-zag chain, or cyclic structure) is determined by packing effects of the organic substituents.

Solid (*i*-Pr)(*t*-Bu)PI_3 is a helical chain polymer from (*i*-Pr)(*t*-Bu)PI_2^+ cations bridged by two-coordinated iodide anions [21].

Both iodine atoms adjacent to phosphorus are nearly linearly coordinated (174.7 and 180°), whereas the angles at the bridging iodide anions are 119.2 and 123°. This geometry allows the I···I contacts (335.25(12) and 338.50(13) pm) to be assigned to donor–acceptor interactions involving the bridging two-coordinated iodide ions as [8-I-2] donors and the two-coordinated iodine atoms adjacent to phosphorus as [10-I-2] acceptors. Due to the overlap of iodide (I3 and I4) lone pairs with σ^* orbitals of the P–I1 and P–I2 bonds, these cation-anion I···I interactions are associated with slight elongations of the P–I bonds (242.3(3) and 243.8(3) pm), compared with rather undisturbed iodophosphosphonium ions (240 ± 10 pm). The main difference between helical (*i*-Pr)(*t*-Bu)PI_3, the zigzag chain of *t*-Bu_2PI_3 [20] and the dimeric structure of Ph_2PI_3 [37] are the interplanar angles of adjacent I–P–I units ((*i*-Pr)(*t*-Bu)PI_3: 90°, the others: 0 or 180°) (Figs. 11–13). A dimeric $[-I-P-I-I-]_2$ backbone related to that Ph_2PI_3 exists also in solid $[(Ph_2PI_2^+ AlI_4^-)_2, I_2]$ [37]. One iodine atom of each AlI_4^- anion coordinates weakly with two cations within the ring (374.3 pm), and 50% of one of the other iodine atoms of the AlI_4^- anions coordinate weakly with the iodine molecule (I···I 366 pm,

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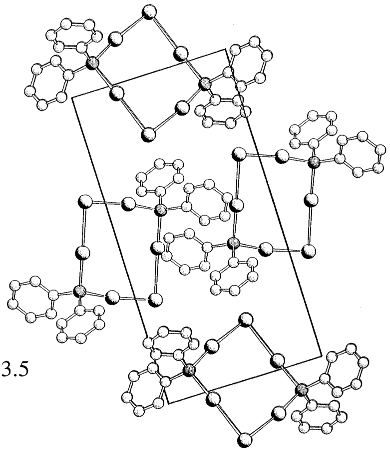
[1] (10-I-2) means: Ten valence electrons and coordination number 2 at the regarded central iodine atom.



d(P-I) 244.8 pm
d(I···I) 329.4 pm,
330.3

<(I-I-I) 77.3
<(I-P-I) 107.3
<(P-I-I) 178.3, 173.5

Fig. 11. Dimeric Ph_2PI_3.

I–I 273 pm) that is intercalated between AlI_4^- anions of two neighbored $(Ph_2PI_2^+AlI_4^-)_2$ dimers [37]. The P–I distances (238–239 pm) are significantly shorter than those in Ph_2PI_3 (where they are 244.8 pm).

3.2.2. Mixed diiodophosphonium mono- and triiodides $RR'PI_n$ $(3 < n < 5)$

Crystallisation of yellow (*i*-Pr)(*t*-Bu)PI_3 from dichloromethane/pentane was accompanied by the formation of red crystals that have a analytical composition close to (*i*-Pr)(*t*-Bu)PI_3, but a completely different crystal structure [21]. Unique among iodophosphonium salts, the 'non-stoichiometric' red compound exists in a tetragonal columnar structure which can be related to unidimensional mixed valence solids built up from staples of partially oxidized chelated d^8 metal cations and of staples containing disordered polyiodide counterions $I(I_2)_x^-$ (x generally between 1 and 2) [39–41]. Elemental analyses of the solid indicated a composition very close to *t*-Bu(*i*-Pr)$PI_{3.2}$, for the refinement of its crystal structure the composition *t*-Bu(*i*-Pr)$PI_{3.25}$ was arbitrarily chosen. The compound can be described as $[t\text{-Bu}(i\text{-Pr})PI_2]_4(\mu_2\text{-I})_2(\mu_4\text{-I})[I(I_2)_x]$ (x close to 0.5): Tetragonal cationic staples of the composition $[t\text{-Bu}(i\text{-Pr})PI_2]_4(\mu_{2-\text{I}})_2(\mu_4\text{-I})^+$ are packed in such a way that *i*-propyl

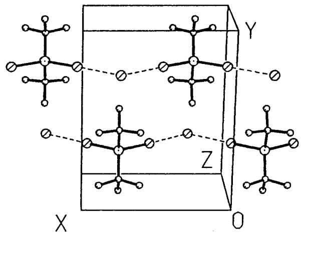


Fig. 12. Zig-zag chains of *t*-Bu_2PI_3.

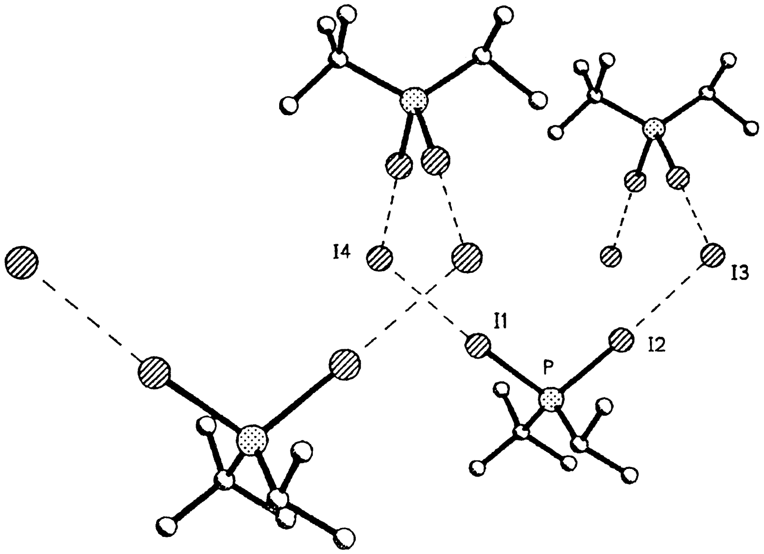


Fig. 13. Helical *i*-Pr(*t*-Bu)PI_3.

groups from *t*-Bu(*i*-Pr)PI_2^+ cations of four different cationic staples surround linear channels filled with iodine anions of the overall composition I_2^- (this corresponds to I^- and I_3^- in an about 1:1 ratio) (Figs. 14 and 15). The oxidation state of iodine within the staples appears to be determined by the necessary negative charge (1 — per asymmetric unit of 7.2 Å), the space available, and by the intrinsic tendency of triiodide formation from I^- and I_2. Like in known columnar structures with linear

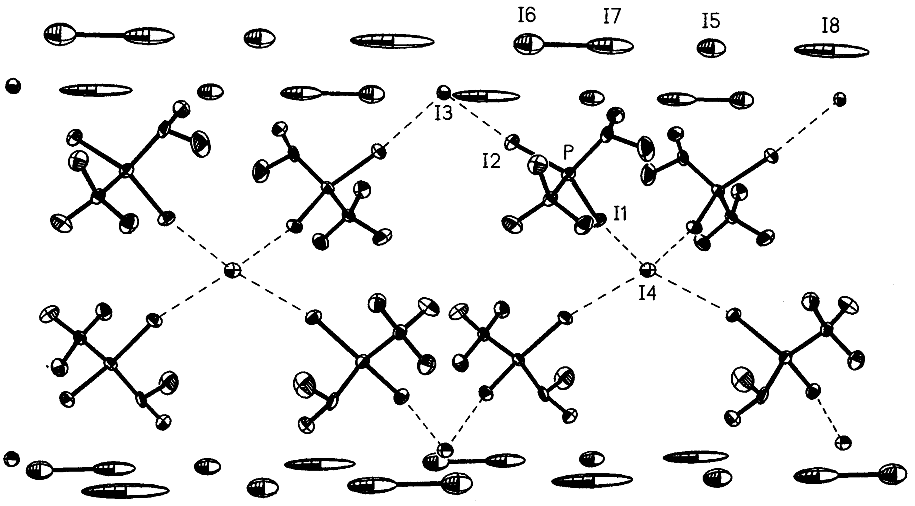


Fig. 14. Columnar structure of *i*-Pr(*t*-Bu)$PI_{3.25}$: view along the *a*-axis.

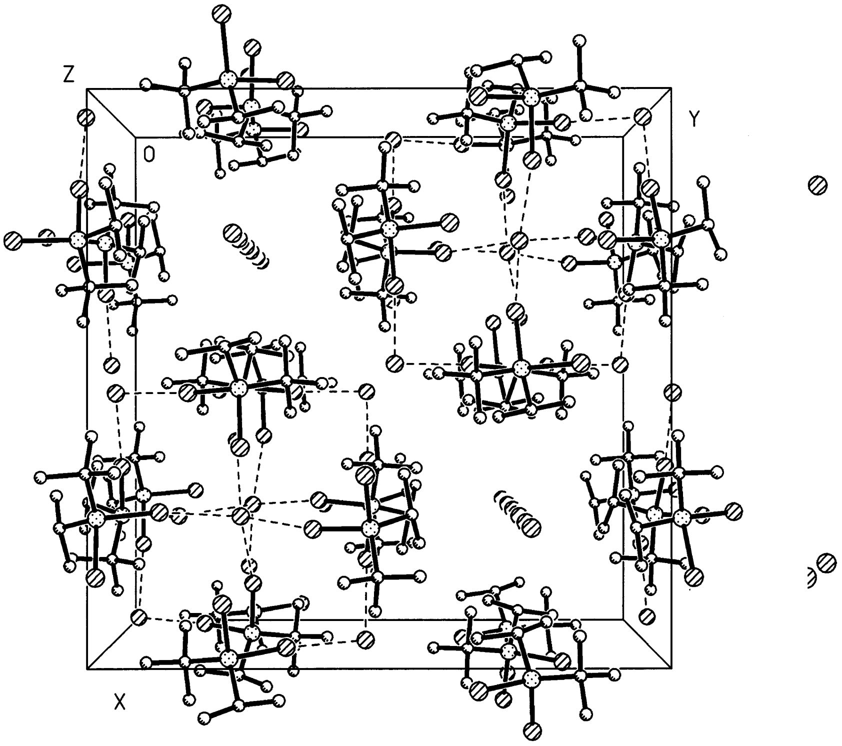


Fig. 15. View of i-Pr(t-Bu)$PI_{3.25}$ along the c-axis.

iodine chains (for instance $Ni(dpg)_2I$ or amylose-polyiodide inclusion compounds containing iodine largely if not exclusively as I_5^-) [39,40], the polyiodide in the staples of t-Bu(i-Pr)$PI_{3.25}$ is highly disordered. The matrix formed from i-propyl groups surrounding the polyiodide channel is less rigid than the one given by tetramethylstibonium ions of $[Me_4Sb]_3[I_8]$, where oxidation state ($I^{-0.375}$) and the unique equidistance of the iodine atoms within the chains are enforced by packing preferences (Me_4Sb···I interactions with exactly 50% of the iodine atoms) of solid $[Me_4Sb]_3[I_8]$ [41].

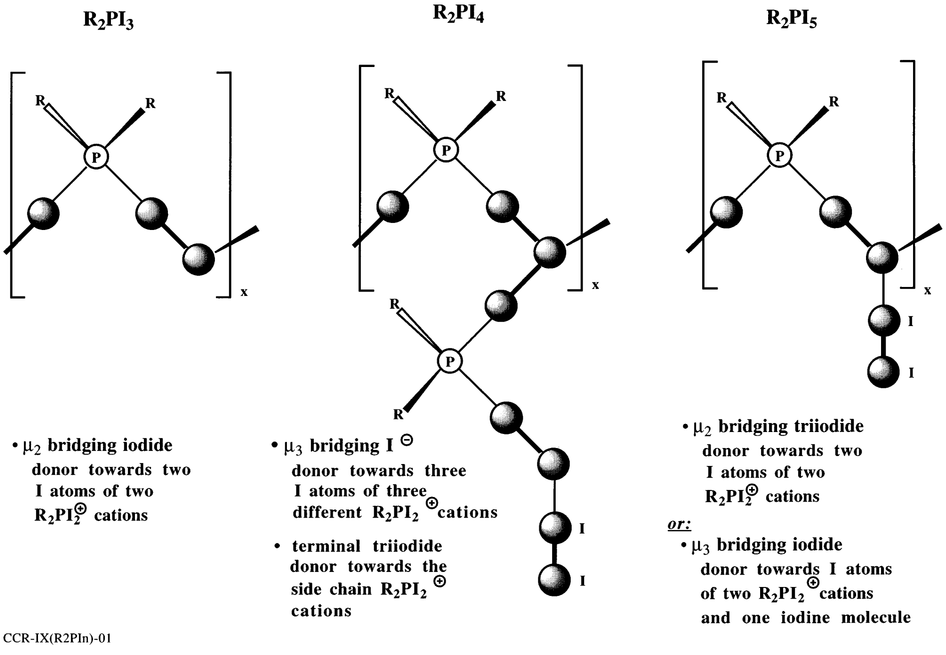
The cationic staples of t-Bu(i-Pr)$PI_{3.25}$ are built up from 16-membered rings that consist from four t-Bu(i-Pr)PI_2–I-moieties with I3 as bidentate bridging donor and I1 and I2 as linear acceptors. This moiety appears like a kind of hypothetic tetrameric (i-Pr)(t-Bu)PI_3. These 16-membered rings $[t\text{-Bu}(i\text{-Pr})PI_2]_4I_4$ are connected in a *spiro*-way by sharing μ_4-iodide anions (I4); this sharing of μ_4-iodide anions leaves at the staple one positive charge per $[t\text{-Bu}(i\text{-Pr})PI_2]_4I_3$ moiety. I2···I3 contacts involving the μ_2-iodide anion within the 16-membered ring (331.5 pm) are significantly shorter than I1···I4 contacts of the μ_4-bridging iodide anion (357.1 pm). The shorter I2···I3 contact coincide with the longer P–I2 bonds (243.3 pm) adjacent to μ_2-I; the quadruply bridging iodide anion has to distribute its donor ability to four P–I bonds which are 'less disturbed' (P–I1 241.5 pm).

When addition of a half equivalent of iodine to diorganyldiiodophosphonium iodides R_2PI_3 leads to consumption of half of the iodide ions by triiodide formation, the remaining iodide ions have to bridge more than two $R_2PI_2^+$ cations. Thus in i-Pr_2PI_4, which is $[(i\text{-}Pr_2PI_2^+)_2(I^-)(I_3^-)]_x$, donor–iodide anions become μ_3-bridging whereas the triiodide anions act as terminal donors towards sidechain $R_2PI_2^+$ cations (Scheme 4). Due to attachment of these side chains, all iodide anions of the helical chains become μ_3-bridging between three i-$Pr_2PI_2^+$ cations. The coordination geometry of these μ_3-bridging iodide ions is rather distorted, i.e. between pyramidal and a T-type structure (angles I–I–I are 76.5° [within the helical chain], 109 and 171.6°).

Crystalline i-Pr_2PI_4, containing helices with $[–I–P–I–I–]_x$ backbones, is *not* chiral.

Attempting to attach a chiral marker in the side chain of the chiral $[–I–P–I–I–]_x$ backbone, a iodophosphane with R = i-Pr, R′ = t-Bu was used as precursor for the formation of a $RR'PI_4$ chain polymer. The backbone of the chain structure of crystalline t-Bu(i-Pr)PI_4 consists of –P–I–I–I– units from $[t\text{-Bu}(i\text{-Pr})PI_2]^+$ ions and μ_3-donor iodide each of which is connected with one iodine atom of a further *side chain* $[t\text{-Bu}(i\text{-Pr})PI_2]^+$ ion. The other iodine atom of this side chain cation is coordinated by a terminal triiodide ion. Although the compound crystallizes in a chiral space group ($P2_12_12_1$), no chiral helices are formed.

Another example of the class of compounds $RR'PI_4$ is bis[1-adamantyl-(methyl)diiodophosphonium] iodide, triiodide [42]. This salt, made from 1-$AdaPI_2$



Scheme 4. Topolgy of iodophosphonium salts R_2PI_n ($n = 3, 4, 5$).

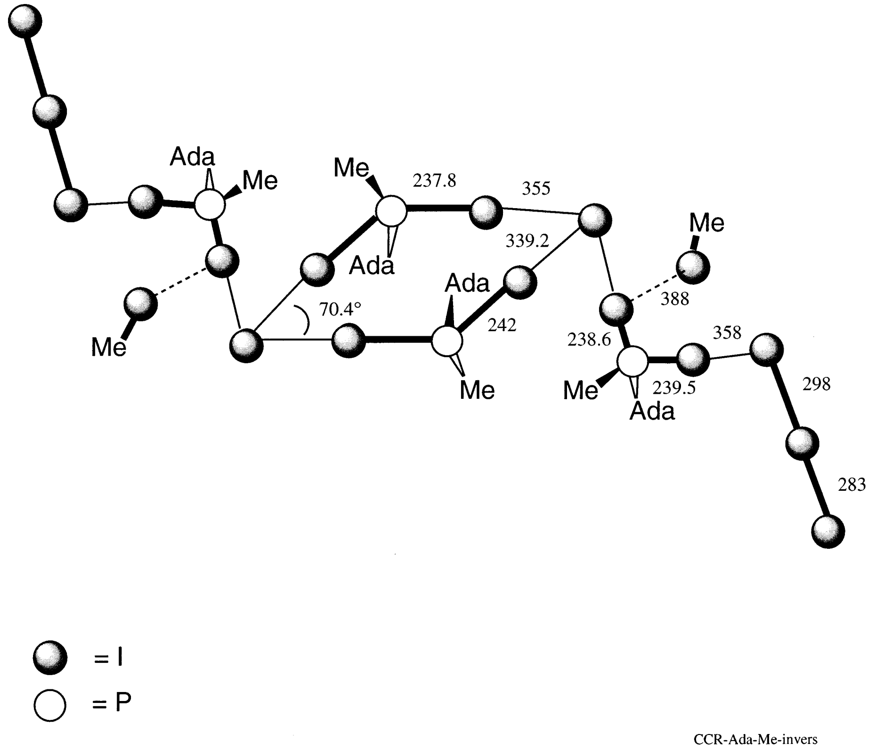


Fig. 16. Schematic drawing of $[(1\text{-Ada(Me)PI}_2^+)_2(I^-)(I_3^-)(CH_3I)]_2$.

with CH_3I, crystallised with one equivalent of CH_3I. The backbone of this compound consists of cyclic dimers (Fig. 16) which are closely related to those of solid Ph_2PI_3. They are built from two $[1\text{-Ada(Me)PI}_2]^+$ ions and two μ_3-donor iodide ions each of which is connected with one iodine atom of a further *side chain* $[1\text{-Ada(Me)PI}_2]^+$ ion. This iodine atom is also in very weak contact (388 pm) with the I atom of the intercalated CH_3I molecule. The other iodine atom of each of these side chain cations is coordinated by a terminal triiodide ion (I···I 358 pm). The P–I distances range from 237.7 to 242.6 pm [42].

Precipitation of t-Bu(i-Pr)PI_4 was accompanied by crystallisation of t-Bu(i-Pr)$PI_{4.33}$ that is a mixed iodide, bis(triiodide) $[(t\text{-Bu}(i\text{-Pr})PI_2^+)_3(I^-)(I_3^-)_2]$ [21].This compound contains three cations with altogether six acceptor iodine atoms per formula unit, but only one iodide anion. Surprisingly, in the solid, this iodide anion satisfies the acceptor needs of five of the six acceptor iodine atoms; only one of the six acceptor iodine atoms has an acceptor–donor contact to a donating triiodide anion! The structure consists of a double-chain backbone of μ_2-acceptor phosphonium ions (at P1, P2) and μ_5-bridging donor iodide ions. Four I···I contacts of these μ_5-bridging donor iodide ions are within the double chain, the fifth is to a *side chain* t-Bu(i-Pr)PI_2^+ ion which is also connected to a terminal triiodide anion by I···I

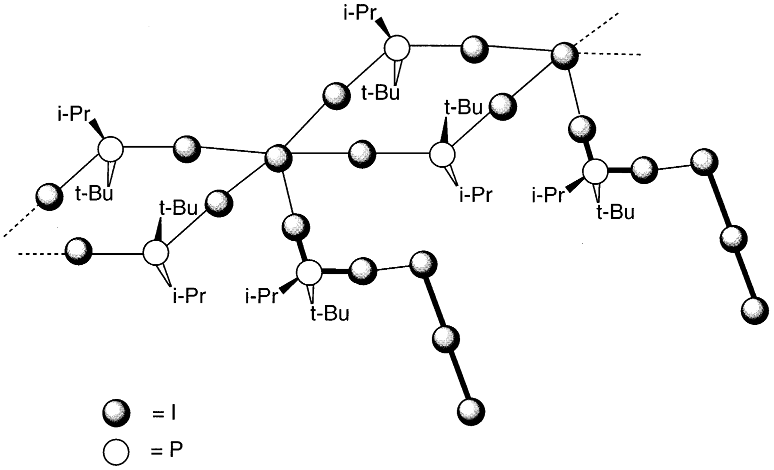


Fig. 17. Schematic drawing of one unit of the cationic double chain $[(t\text{-Bu})(i\text{-Pr})PI_2^+]_3(I^-)(I_3^-)]^+$ of $(t\text{-Bu})(i\text{-Pr})PI_{4,33}$.

interaction (344.1(2) pm) (Fig. 17). A further triiodide anion has no soft–soft interaction with the cationic network. This triiodide ion may be identified as the source of the strong Raman emission at 113 cm^{-1} [21].

3.2.3. Diiodophosphonium triiodides $RR'PI_2^+I_3^-$

The X-ray crystal structure determination of Et_2PI_5 (Fig. 3) reveals that the compound consists of chains of $Et_2PI_2^+$ ions bridged by I···I contacts with triiodide ions, leading to a pleated ribbon structure (Fig. 18) when weak I···I contacts (4.2 Å) between chains are considered [20].

The average I···I distance in Et_2PI_5 is about 10 pm longer than in mixed iodide triiodides R_2PI_4 and nearly 20 pm longer than in the iodides R_2PI_3. The longer (weaker) I···I interaction is reflected by comparatively strong ('undisturbed‘) P–I bonds in the $Et_2PI_2^+$ cations. Obviously, the nucleophilicity of the triiodide anion is not sufficient to lead to a *significant* destabilisation of the P–I bonds by population of σ^*(P–I) orbitals of two $Et_2PI_2^+$ cations. The bridging iodine atom (I3) may, like the central iodide anion in the cation $[(Ph_3PI)_2I–I_2]^+$ [19], be regarded as a trigonal-pyramidal iodide anion with strong coordination to an iodine molecule (I4, I5) and with weaker interaction with two acceptor iodine atoms of two different $Et_2PI_2^+$ cations. Concerning its close-range order (chains of $Ph_2PI_2^+$ ions bridged by I···I contacts with triiodide ions) the donor–acceptor relations within Ph_2PI_5 are analogous to those of Et_2PI_5. Ph_2PI, however, is a weaker donor than Et_2PI, and the requirements of aryl group packing lead to a quite different kind of assembly of the pairs of the indefinite $–[I–P–I–I(I_2)–]_x$ chains (Fig. 19) [37]. The P–I distances in $Ph_2PI_2^+I_3^-$ (243.5; 243.7 pm) are 3 pm longer and the I···I contacts are about 10–15 pm shorter (334.5; 339.5) than in $Et_2PI_2^+I_3^-$ [20]. These comparatively strong

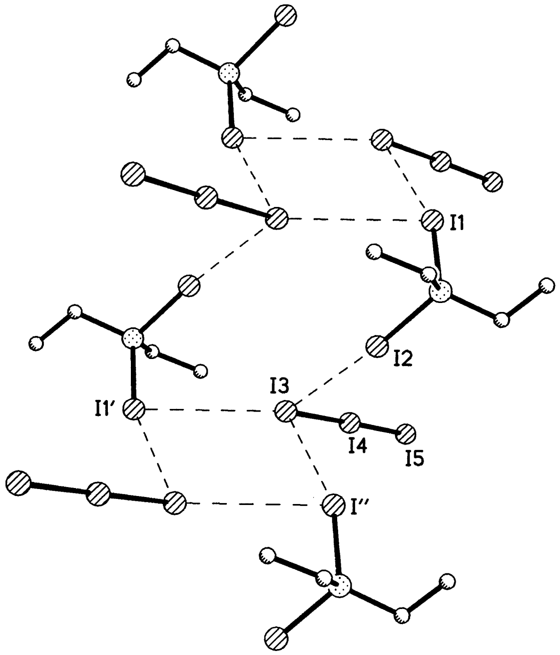


Fig. 18. Chains of Et_2PI_5.

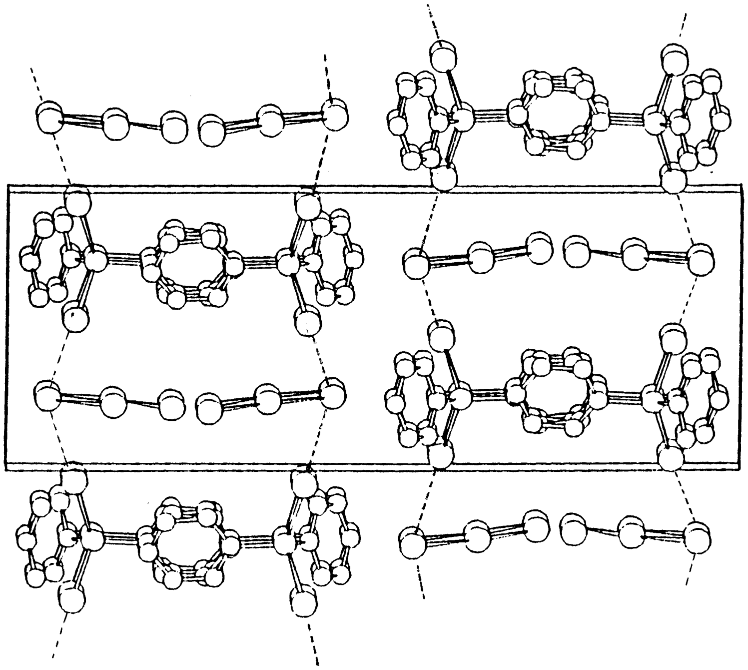


Fig. 19. Chains of Ph_2PI_5.

I···I cation–anion contacts within the extended chains of Ph_2PI_5 correlate well with the extreme distortion of the triiodide moieties (276. 1 and 315.0 pm [37]). For the structure of [t-$Bu_2PI_2^+$, I_3^-, PI_3], see Section 4.2.

3.3. *Salts of triiodophosphonium cations RPI_3^+*

3.3.1. *Interpenetrating layers*

In diiodophosphonium salts, the formation of chains allows both optimised donor–acceptor and polar cation–anion interactions and fair packing. In triiodophosphonium iodides RPI_4, cations and anions act as trifunctional donors and acceptors, i.e. large condensed rings have to be formed to meet the requirements of number and direction of cation–anion contacts. The smallest ring-size yet found in compounds RPI_4 is 12, i.e. 'trimeric' units involving six P-bonded linear 10-I-2 iodine atoms held together by three bridging iodide anions can be formed. Improved packing of these large condensed rings can obviously be achieved, when independent donor–acceptor networks interpenetrate each other (Figs. 20–22).

The structures of $MePI_4$, i-$PrPI_4$, and $PhPI_4$ are closely related. They are made up from interpenetrating layers built up from 12-membered rings (Figs. 20 and 21) [24,37]. The 12-membered rings $(MeP)_3I_9$ (of which every second member is an approximately linearly coordinated iodine atom) form a layer that is related to the

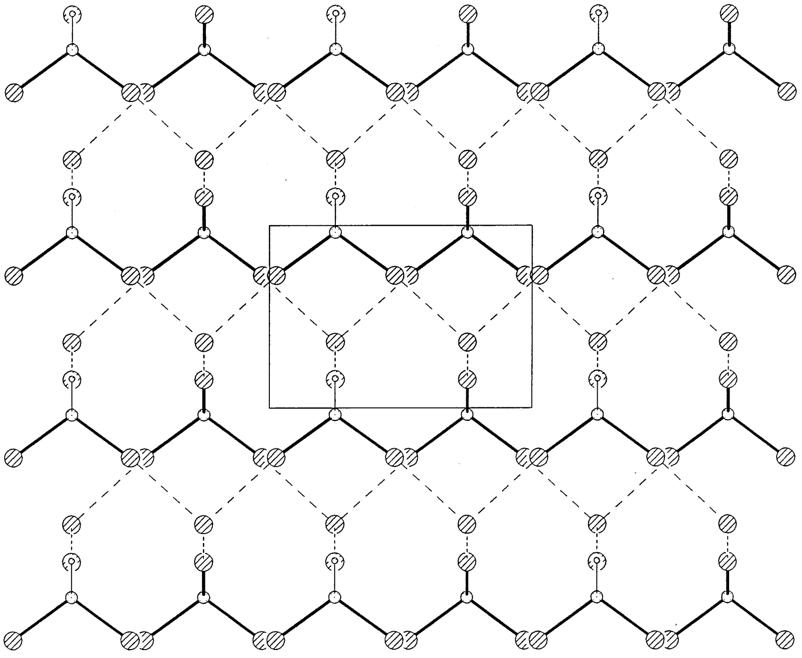


Fig. 20. Two interpenetrating layers of $MePI_4$.

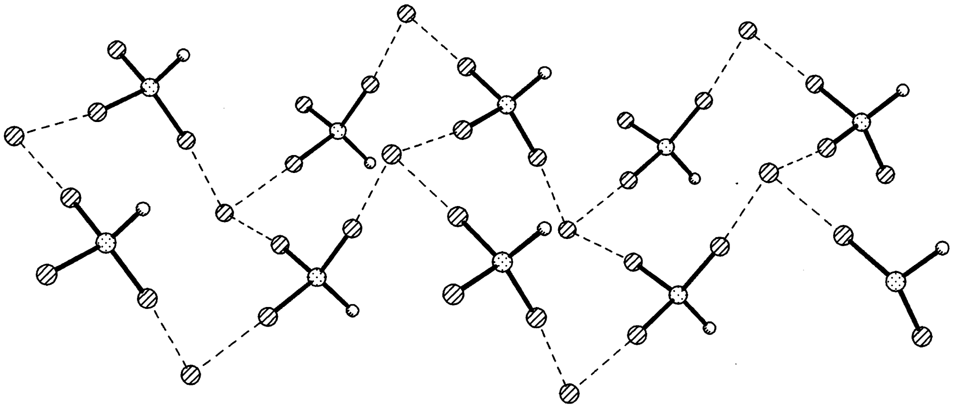


Fig. 21. Excerpt from one layer of $MePI_4$.

connectivity of chairlike P_6 rings within the layer structure of black phosphorus (Fig. 21). The center of each 12-membered ring is the position of a linearly coordinated acceptor iodine atom of the interpenetrating 'antipode' layer. There are no donor–acceptor contacts of any significance between the acceptor iodine atoms of the one and donor iodine atoms of the other (neighbored) interpenetrating layer. All methyl, *i*-propyl or phenyl groups attached to one layer are orientated in the same direction.

All P–I distances (242–244 pm) are slightly longer than in undisturbed iodophosphonium ions; I···I contacts (332–335) are similar to those of *t*-Bu_3PI_2 [8]. Exchange of the μ_3-bridging iodide ion of $PhPI_4$ by the less nucleophilic AlI_4^- ion leads to decreasing P–I distances ($PhPI_4$: 243.6–244.8 pm; $PhPI_3AlI_4$: 238.3–241.3 pm) and increasing I···I distances ($PhPI_4$: 327.6–332.7 pm; $PhPI_3AlI_4$: 356.1–364 pm) [37]. From each AlI_4^- anion, one iodine atom is bridging two cations within a dimeric $[-I-P-I-I-]_2$ moiety, and another one is in contact with another cation within a 12-membered $[I-P-I-I-Al-I-I-]_2$ ring (Fig. 23).

3.3.2. The 3D net of *t*-$BuPI_4$

Hypothetic opening of a P–I···I contact that was shared by two condensed 12-membered rings of RPI_4 (R = Me, *i*-Pr) by exchanging the shared P–I···I contact with a (nonbonded) {P–R I} moiety leads to a new 20-membered ring $(RP)_5I_{15}$ (of which every second member is an approximately linearly coordinated iodine atom) made out of five phosphonium centers, ten linear acceptor iodine atoms, and five bridging donor–iodide ions. The 3D net of *t*-$BuPI_4$ contains such 20-membered rings, which are condensed to give 29-membered moieties (P_7I_{22} cages) that are based on 15 iodine–iodine donor–acceptor contacts. Such a C_3-symmetric bicyclic system is schematically drawn in Fig. 24. The carbon atom of a *t*-butyl group and the opposite μ_3-donor iodide of each of the triptycene-resembling cages lie on a

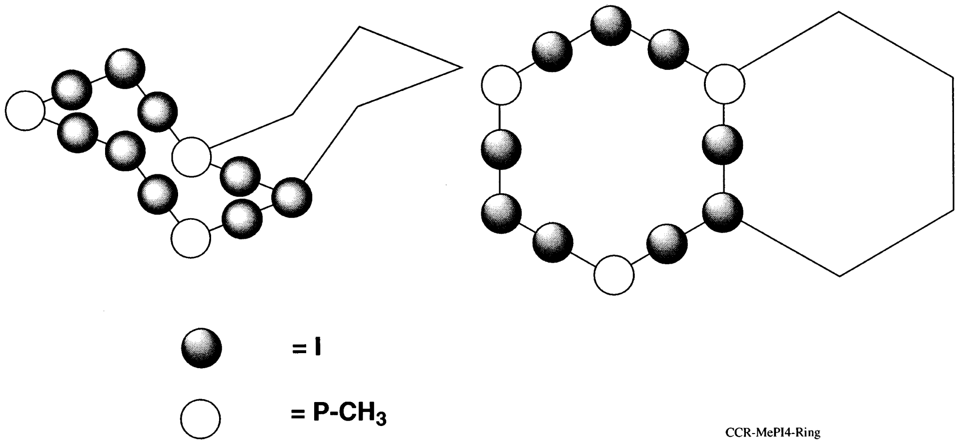


Fig. 22. Twelve membered ring within a layer of MePI$_4$ (schematic).

shared C_3 axis (Figs. 24–26). The structure of solid *t*-BuP$_4$ is completed by interpenatration of two independent 3D nets from the mentioned triptycene-resembling (*t*-BuP)$_7$I$_{22}$ cages.

An alternative description of *t*-BuPI$_4$ can be derived from the CsCl structure: a *t*-BuPI$_3^+$ cation is in the center of a cubic environment from eight I$^-$ ions. Four of

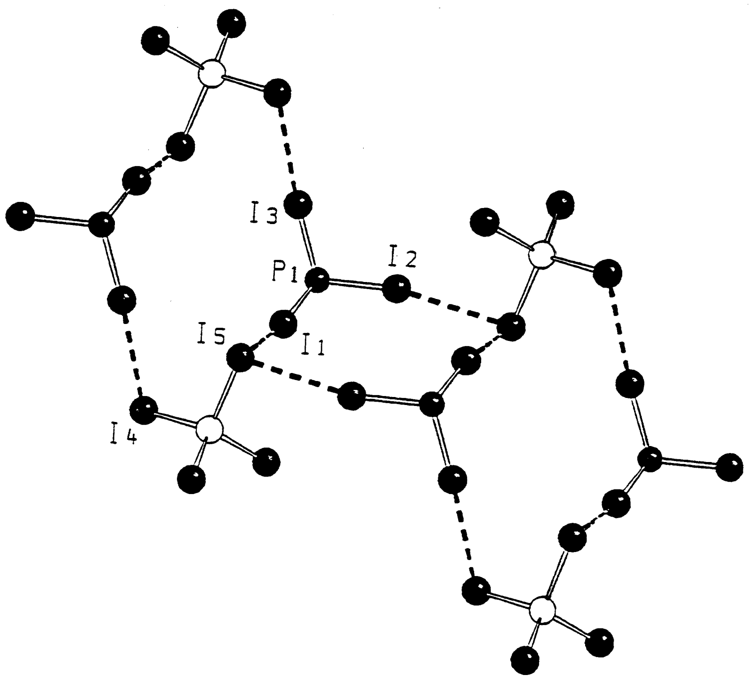


Fig. 23. Iodine-iodine contacts in PhPI$_3^+$AlI$_4^-$ (phenyl groups omitted).

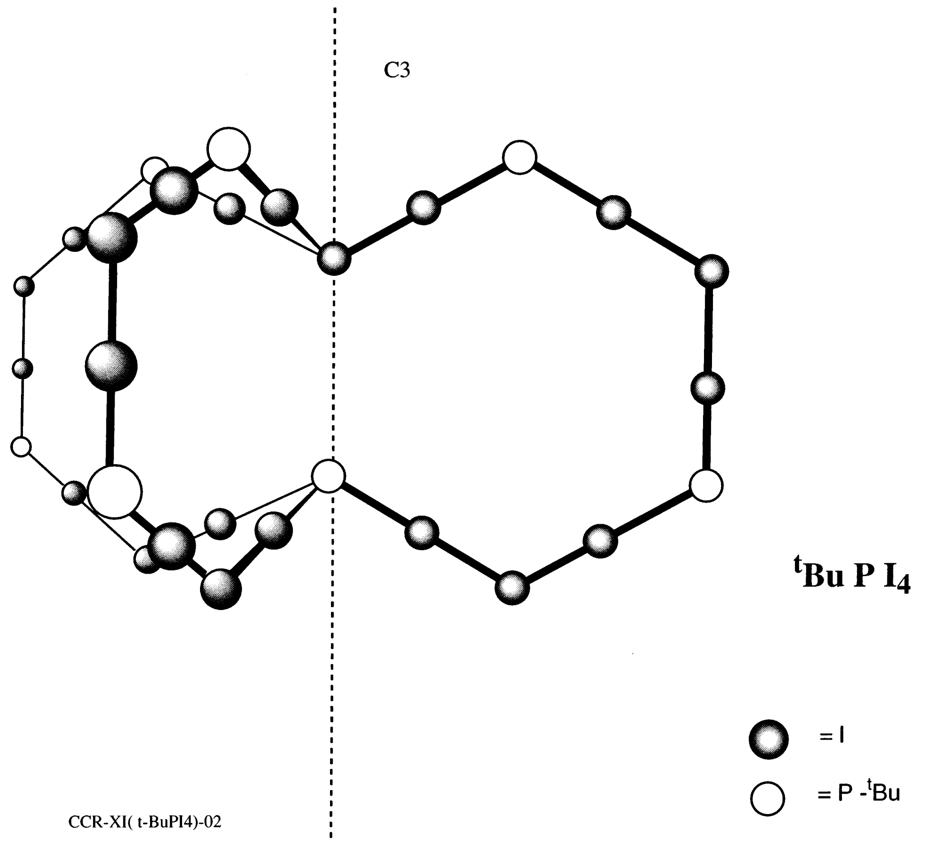


Fig. 24. The P_7I_{22} bicycle in solid t-$BuPI_4$ (schematic).

these I^- ions belong to the 'other' interpenetrating network, which is not in donor–acceptor contact with the network of the regarded t-$BuPI_3^+$ cation. The other four I^- ions create a tetrahedral environment around the regarded cation. Three of these I^- anions are involved in contacts with the cation (334 pm), the remaining one is the aforementioned μ_3-donor iodide ion opposite to the t-butyl group of the regarded phosphorus atom (with which it a shares a C_3 axis) (Fig. 27). The slight expansion of the P–I bond distance in t-$BuPI_4$ (244 pm) in the typical range for $P^+–I\cdots I^-$ donor–acceptor networks.

3.4. *Iodophosphonium derivatives of PI_3 and PI_5*

3.4.1. $PI_4^+AlI_4^-$

Phosphorus triiodide is such a weak iodophile (nucleophile), that it cannot successfully compete with iodide anions for coordination with the I^+ cation. Allowing an iodide anion to react with the PI_4^+ cation leads to 'iodophilic attack', i.e. to nucleophilic substitution at an electrophilic iodine atom that leads to iodine formation accompanied by removal of PI_3 as leaving group. By coordination of I^- with AlI_3, however, the thermally stable solid iodophosphonium salt $PI_4^+AlI_4^-$ can be obtained. Since the I atoms bonded to phosphorus behave as electrophiles and iodide atoms of the AlI_4^- possess still some residual nucleophilicity, a complex network from a number of weak donor–acceptor contacts between cation and anion iodine atoms is expressed in the solid state structure of $PI_4^+AlI_4^-$ [26]. These interactions, that lead to P–I···I angles between 169 and 174° and Al–I···I angles between 87 and 103°, are structure-determining. The tetrahedra of cations and anions are significantly distorted exhibiting angles between 107.3 and 112.1° (PI_4^+) and between 106.1 and 112.2° (AlI_4^-); P–I distances vary from 237 to 241.8 pm, Al–I distances from 246.8 to 257.1 pm [26]. Cation-anion I···I distances between 339 and 345 pm and the rather short average of P–I distances (239.6 pm) are accordance with the structures of other predominantly ionic iodophosphonium iodometallates.

3.4.2. $P_2I_5^+AlI_4^-$

When AlI_3 abstracts an I^- ion from PI_3, the hypothetical 6-electron species PI_2^+ coordinates with another molecule of PI_3, which behaves as a P-nucleophile in this reaction. The resulting cation $[I_3P–PI_2]^+$ can also be regarded as iodophosphonium ion based on the oxidation (iodination) of one of the phosphorus atoms of P_2I_4. It is known, that iodophilic reduction of PI_3 can lead to P_2I_4 [5].

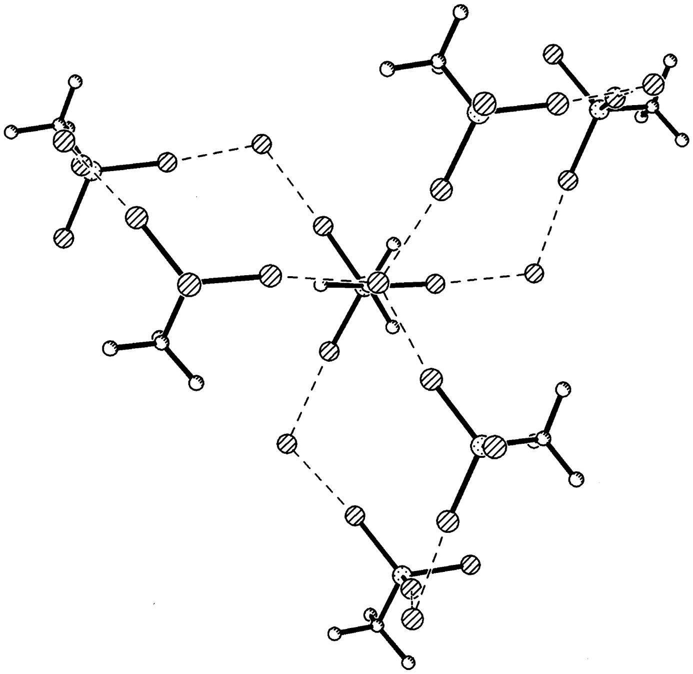


Fig. 25. The P_7I_{22} bicycle in solid t-$BuPI_4$ (excerpt from the structure, view along the C_3 axis).

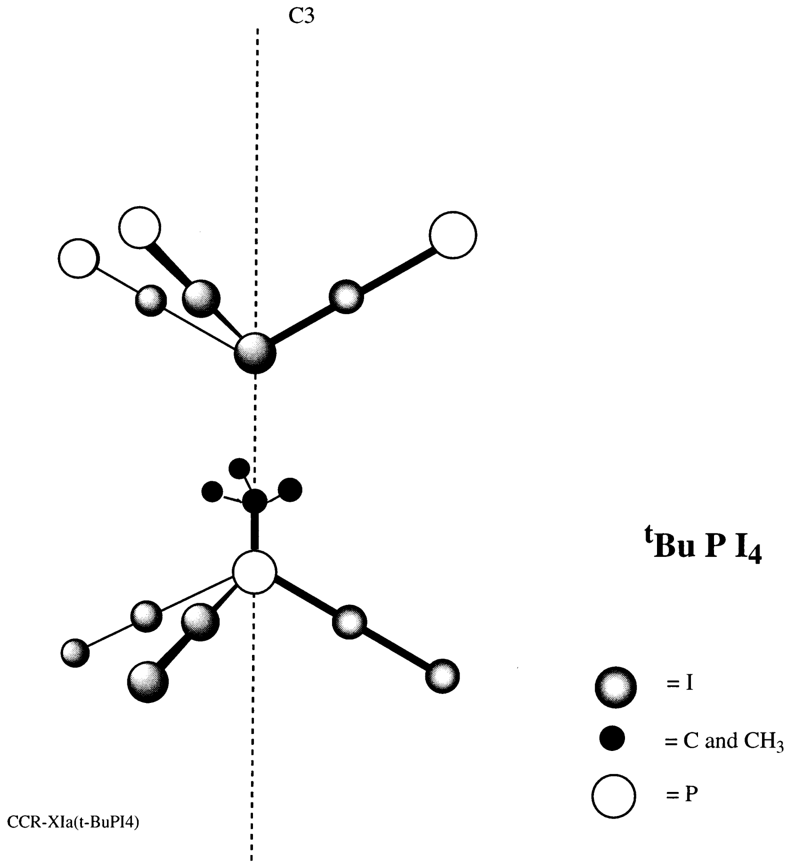


Fig. 26. $I^-\cdots t$-Bu contact in the C_3 axis.

$P_2I_5^+AlI_4^-$ is the only known structurally characterised example of compounds with a iodophosphonium center bonded to tricoordinated phosphorus atom [27]. The P–P distance of the $[I_3P{-}PI_2]^+$ cation is close to that of P_2I_4. The P–I bonds of four-coordinated (formally plus-charged) phosphorus are slightly shorter (240–241 pm) than the P–I bonds of P^{III} (242 pm). Only the iodine atoms attached to the onium center exhibit significant I···I cation–anion contacts (between 343 and 345 pm) [27].

4. Summary: destructive versus cooperative I···I interactions in solution and in the solid state

4.1. I···I interactions

In donor–acceptor complexes of iodine, I–I distances can be tuned in a wide range by appropriate choice of a donor (Table 1). In all yet structurally analysed iodophosphonium ions, I–I distances are significantly longer than those of symmetrical triodides (which may be used as reference for 'bond order 0.5'). The shortest I–I contacts were observed in Ph_3PI_2: the 316 pm distance corresponds to an extremely distorted (widened) triiodide, like the anion in $Ph_2PI_2^+I_3^-$ [37].

The iodophosphanes Ph_2PI and RPI_2 are even weaker donors than Ph_3P, however, their solid iodophosphonium iodides are stable compounds with I···I contacts that are longer than the one of Ph_3PI_2. It may appear surprising, that compounds like RPI_4, and PI_5 exist apparently in the solid state, but decompose completely in solution. Iodine–iodine interactions are 'destructive' at the molecular level (leading to P–I bond weakening, finally to iodine elimination), however, they can be cooperative in solids. In the solid state the effect of 'destructive' iodophilic nucleophilicity of iodide ions seems to be overcome by cooperative effects that result from favorable electrostatic interactions and favorable extended donor–acceptor networks. μ_3- and μ_4-bridging iodide anions are weaker nucleophiles towards each of the three or four neighbored iodophosphinium ions, i.e. the effective donor ability of the iodide (observable as P–I bond lengthening due to σ^* population) is 'spread' over several iodophosphonium acceptors. A similar observation can be made, when the iodophosphonium iodide *t*-Bu(*i*-Pr)PI_3 is compared with the 'iodide-deficient' structures of *t*-Bu(*i*-Pr)PI_4 and *t*-Bu(*i*-Pr)$PI_{4.33}$ (see P–I and I–I distances in Table 2).

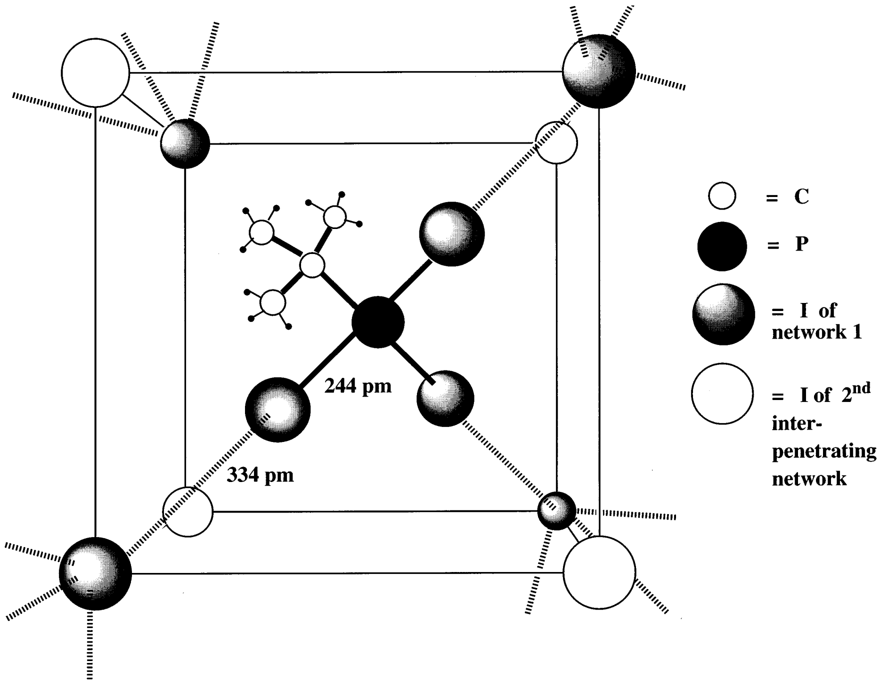


Fig. 27. The CsCl-related structure of *t*-$BuPI_4$.

Table 2
Correlation of *d*(P–I) and *d*(I–I) of iodophosphonium ions regarding different coordination numbers of donating iodide ions

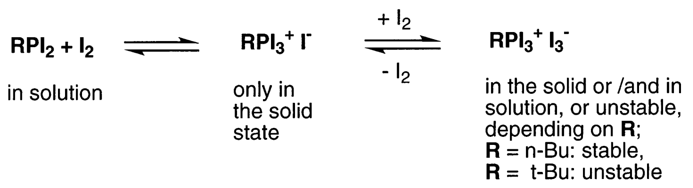
	d(P–I) (pm)	C.N. of I^-	*d*(I–I) (pm)
Ph_3PI_2 [12]	248.1	1	316.1
$[(2,4,6\text{-}MeO)_3C_6H_2]_3PI_2$, CH_2Cl_2 [31]	248.2	(1)	333.9
$i\text{-}Pr_3PI_2$, $0.5CH_2Cl_2$ [11]	240.9	(1)	338.3
	242.0		337.2
Ph_2PI_3 [37]	244.8	2	329.4
			330.3
$t\text{-}Bu(i\text{-}Pr)PI_3$ [21]	243.8	2	335.3
	242.3	2	338.5
$t\text{-}Bu(i\text{-}Pr)PI_{3.2}$ [21]	241.5	4	357.5
	243.3	2	331.5
$t\text{-}Bu(i\text{-}Pr)PI_4$ [21]	241.6	3	342.7
	242.4	3	337.6
	242.5	3	337.1
	241.2	($I^-_{3\ \mathrm{terminal}}$)	345.2
$t\text{-}Bu(i\text{-}Pr)PI_{4.33}$ [21]	240.9	5	$349.0_{(\mathrm{basal})}$
	241.1	5	$346.6_{(\mathrm{basal})}$
	240.8	5	$346.7_{(\mathrm{basal})}$
	240.6	5	$347.5_{(\mathrm{basal})}$
	241.7	5	$358.0_{(\mathrm{apical})}$
	242.0	($I^-_{3\ \mathrm{terminal}}$)	344.1

4.2. The coexistence of t-$Bu_2PI_2^+$*,* PI_3 *and* I_3^- *in a solid compound: two isomers of '*RPI_4*' modelling solid* PI_5

One way for the suppression of undesired iodophilic reduction is the use of Lewis acids that lower the nucleophilicity of I^-. Towards I^-, the I_2 molecule is a Lewis acid, that leads to significantly diminished cation–anion interactions of iodophosphonium triiodides compared with the monoiodides.

Compounds RPI_4 decompose into RPI_2 and I_2 in non-basic solvents; solutions of n-$BuPI_6$ [25] and of $(Me_3Si)_2CHPI_6$ [14], however, give ^{31}P-NMR-resonances that indicate the presence of RPI_3^+ cations like those in solid *t*-$BuPI_4$ [24] or in *t*-$BuPI_3^+AlI_4^-$ [14].

(4)



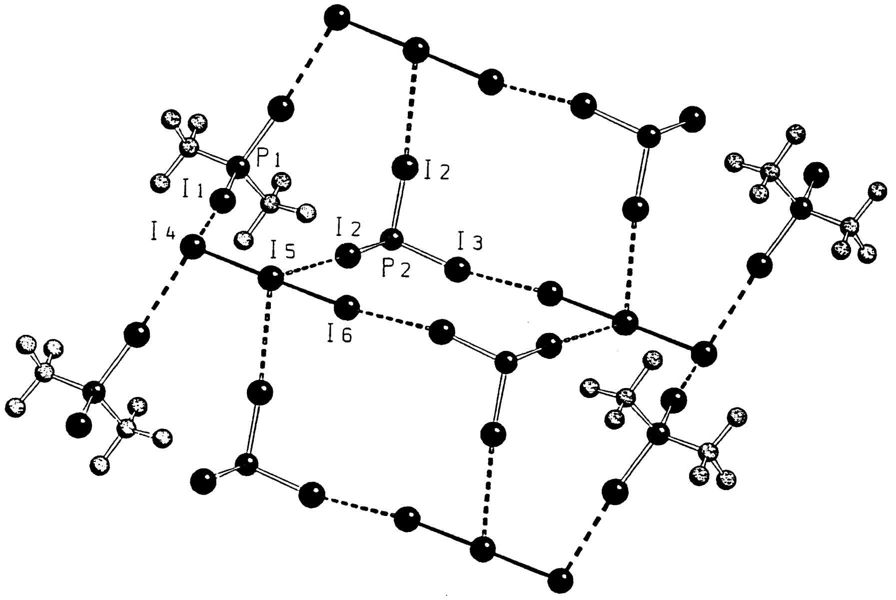


Fig. 28. Structure of solid [t-$Bu_2PI_2^+$, I_3^-, PI_3].

This is due to the fact, that triiodide formation helps to shift the equilibria somewhat toward the oxidised phosphorus species. For solid PI_5, one should imagine a cubic structure related to t-$BuPI_4$, made out of PI_4^+ cations connected by μ_4-bridging I^- anions. This structure would have to rely on the above described cooperative effects like compounds RPI_4. An alternative possibility for 'PI_5' could be a structure that would imply triiode formation, like [PI_4^+, I_3^-, PI_3]. Fortuitously, a stable solid closely related to the latter second hypothetic polymorph of PI_5 has been isolated and characterised by Binnewies and Kopitzky [37]. The lattice of the double chain-structured compound [t-Bu_2PI_5,PI_3] is built from t-$Bu_2PI_2^+$ cations bridged by I_3^- anions, and PI_3 molecules (Figs. 28 and 29). Analytically, it is an isomer of cubic t-$BuPI_4$.

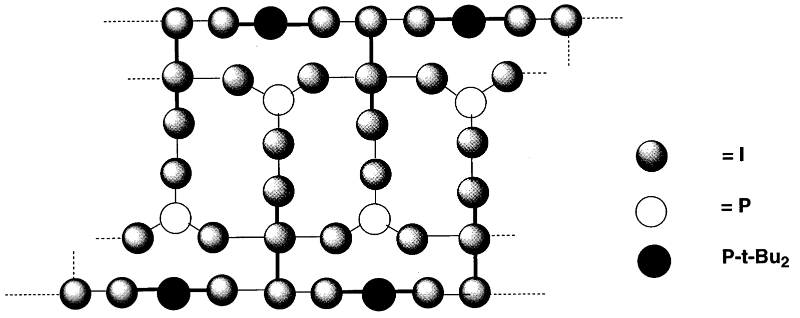


Fig. 29. Topology of solid [t-$Bu_2PI_2^+$, I_3^-, PI_3] (schematic).

The compound can be regarded as an intercalation compound of the unknown salt t-$Bu_2PI_2^+ I_3^-$ with molecular PI_3. Two t-$Bu_2PI_2^+ I_3^-$ chains are held together by a network of weak interaction of I_3^- ions (I–I 287.8 and 295.9 pm) with PI_3 molecules [d(P–I) 244.9 pm]. Two iodine atoms of each PI_3 molecule are in contact (384.7 pm) with central iodine atoms of two triiodide anions from the same t-$Bu_2PI_2^+ I_3^-$ chain; the third iodine atom of the PI_3 molecule is directed towards the terminal iodine atom (I6 in Fig. 24) of a triiodide anion of the opposite t-$Bu_2PI_2^+ I_3^-$ chain.

The presence of weak soft–soft-contacts of I_3^- ions with intercalated PI_3 molecules helps apparently to avoid the decomposition of one half of the triiodide anions of t-$Bu_2PI_2^+ I_3^-$ that would lead to the known stable compound t-Bu_2PI_4 (vide supra [21]). This example shows, how subtle and still unpredictable minor contributions from polar and soft–soft interactions may influence equilibria when iodophosphonium ions are involved.

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