Crystal Structure, Nuclear Magnetic Resonance Spectroscopy and Individual Gauge for Localised Orbitals (IGLO) Calculations of $C_6H_4P_2S_6$, a New Tetrathiadiphosphorinane, and Comparison with Related P–S Compounds†

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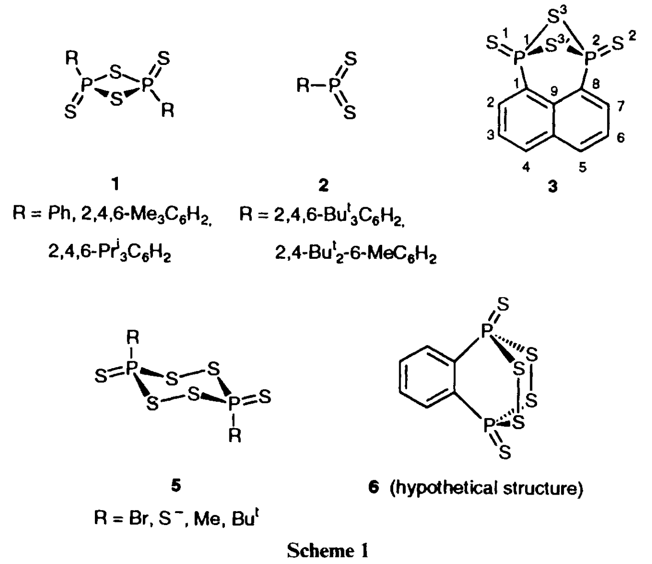
The reaction of 1,2-diphosphinobenzene with sulfur yielded a new constitution of a tetrathiadiphosphorinane ring: 4,6-(1,2-phenylene)-4,6-dithioxo-1,2,3,5,4λ^5,6λ^5-tetrathiadiphosphorinane the crystal structure of which has been determined, orthorhombic, space group *Pbca* (no. 61), a = 12.846(4), b = 16.929(7), c = 11.178(6) Å and Z = 8. The tetrathiadiphosphorinane ring has a chair structure with axial positions of the 1,2-phenylene carbons and equatorial positions of the terminal sulfur atoms. One molecule per unique volume is an independent structural unit. This is consistent with the fact that the solid-state ^{31}P cross-polarisation magic angle spinning (CP MAS) NMR spectra give two sets of slightly different principal values of the nuclear magnetic shielding tensor. A comparison with the crystal structure and the solid-state NMR data of *trans*-2,4-diphenyl-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane and *cis*-2,4-(1,8-naphthalenediyl)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane shows that the nuclear shielding does not only depend on the molecular structure. Short intermolecular S···S distances lead to deshielding effects on the ^{31}P nucleus. Results of individual gauge for localised orbitals (IGLO) calculations of the ^{31}P nuclear shielding of isolated molecules agree, nevertheless, satisfactorily with the experimental principal values and additionally allow the determination of the orientation of the principal axes in the molecular framework. The IGLO calculations indicate that the principal 3 axis for the most shielded principal value lies nearly parallel with the P=S bond.

The reaction of arylphosphanes PH_2R with sulfur usually yields 2,4-diaryl-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes[1,2] **1** or dithioxophosphoranes **2**.[2–4] This is also true if sulfur is used in excess.[1]

Slavin *et al.*[5] have synthesised a *cis*-dithiadiphosphetane **3** by reaction of α-bromonaphthalene with P_4S_{10}. It is not clear whether an analogous *cis*-dithiadiphosphetane, $C_6H_4P_2S_4$, can be formed by reaction of 1,2-diphosphinobenzene with sulfur because the steric hindrance is high. It was found from preliminary studies that $C_6H_4P_2S_6$ **4** is obtained containing a higher proportion of sulfur. In this paper we will present an unexpected tetrathiadiphosphorinane structure for this product determined by X-ray diffraction.

Continuing our investigations of ^{31}P shielding tensors in ring compounds[2,6,7] containing phosphorus and sulfur we measured cross-polarisation magic angle spinning (CP MAS) NMR spectra from which the tensor principal values can be detected. Comparing the isotropic ^{31}P chemical shifts in the solid state and in solution it becomes obvious that in many cases they are similar, but in some cases the solid-state isotropic chemical shifts show a deshielding effect. Moreover, in some compounds, containing two phosphorus atoms the isotropic shifts are significantly different, although, the crystal structure shows nearly symmetric relations. To understand these observations the crystal structure data and nuclear shielding parameters are compared with those of compounds containing the same moiety $RP(S)(S_{ring})_2$.



Scheme 1

In order to obtain information about the orientation of the principal axes in the molecular framework, which is not available from crystal-powder MAS NMR measurements, quantum mechanical calculations of the nuclear magnetic shielding tensors of isolated molecules were performed using the individual gauge for localised orbitals (IGLO) method.[8]

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

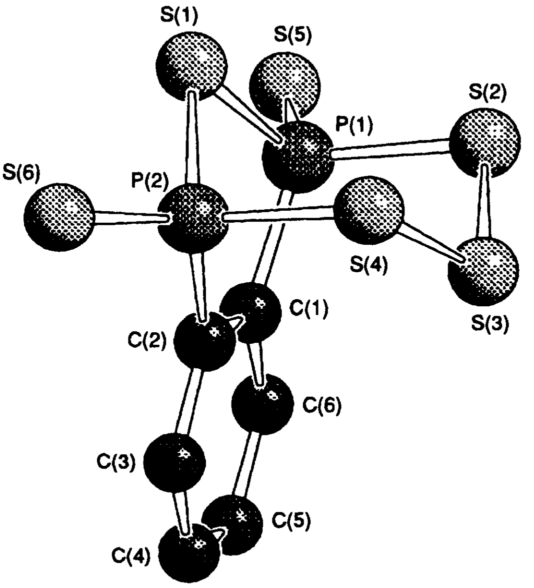


Fig. 1 The molecular structure of the tetrathiadiphosphorinane $C_6H_4P_2S_6$, **4**

Table 1 Bond lengths (Å) and angles (°) for $C_6H_4P_2S_6$ **4**

P(1)–S(1)	2.1036(7)	P(2)–S(1)	2.1007(11)
P(1)–S(2)	2.1241(9)	P(2)–S(4)	2.1114(8)
P(1)–S(5)	1.9140(8)	P(2)–S(6)	1.9185(8)
S(2)–S(3)	2.0602(8)	S(3)–S(4)	2.0594(11)
P(1)–C(1)	1.802(2)	P(2)–C(2)	1.8023(14)
C(1)–C(2)	1.394(2)	C(4)–C(5)	1.375(3)
C(5)–C(6)	1.394(2)	C(3)–C(4)	1.384(2)
C(6)–C(1)	1.388(2)	C(2)–C(3)	1.391(2)
S(1)–P(1)–S(2)	103.89(3)	S(1)–P(2)–S(4)	105.13(3)
S(1)–P(1)–S(5)	114.78(4)	S(1)–P(2)–S(6)	114.06(2)
S(1)–P(1)–C(1)	99.23(5)	S(1)–P(2)–C(2)	99.61(5)
S(2)–P(1)–C(1)	105.83(6)	S(4)–P(2)–C(2)	105.64(5)
S(2)–P(1)–S(5)	110.72(3)	S(4)–P(2)–S(6)	110.68(4)
S(5)–P(1)–C(1)	120.59(5)	S(6)–P(2)–C(2)	120.20(5)
P(1)–S(1)–P(2)	93.99(3)	S(2)–S(4)–S(4)	108.75(3)
P(1)–S(2)–S(3)	101.36(3)	P(2)–S(4)–S(3)	100.49(3)
P(1)–C(1)–C(2)	117.75(10)	P(2)–C(2)–C(1)	117.80(10)
P(1)–C(1)–C(6)	121.75(11)	P(2)–C(2)–C(3)	121.93(11)
C(2)–C(1)–C(6)	120.43(13)	C(1)–C(2)–C(3)	120.22(13)
C(1)–C(6)–C(5)	118.69(15)	C(2)–C(3)–C(4)	119.03(15)
C(4)–C(5)–C(6)	120.76(15)	C(3)–C(4)–C(5)	120.84(14)

Results and Discussion

Unlike all reactions of arylphosphanes with sulfur[1,2] known so far, the reaction of 1,2-diphosphinobenzene with sulfur does not yield any dithiadiphosphetane. The ^{31}P chemical shift in the reaction product **4** is at δ 93.2 and hence, does not lie in the region of dithiadiphosphetanes with aromatic substituents (δ 15–20). Discussing the mass spectrum the sum formula of the compound can be determined as $C_6H_4P_2S_6$. This sum formula indicates that the compound contains a phosphorus-sulfur six-membered ring (by analogy with the constitution of the tetrathiadiphosphorinane ring **5** with alternating P and S_2 units[9–11]) instead of a dithiadiphosphetane ring.

However, because of the *ortho* position of the phosphorus atoms on the phenyl ring, a bicyclooctane analogue compound **6** should be able to be formed.

Molecular Structure and Packing.—The assumption of a symmetric structure of type **6** was not confirmed by single-crystal X-ray diffraction. The unexpected molecular structure of the new tetrathiadiphosphorinane **4** is shown in Fig. 1.

The chair conformation of the phosphorus-sulfur six-membered ring with axial positions of the 1,2-phenylene carbons and equatorial positions of the terminal sulfur atoms is obviously energetically more favourable than a boat conformation **5**. Bond lengths and angles are given in Table 1.

The S–S bond lengths in the S_3-bridge are very similar to the corresponding values of the known cyclohexasulfur[12] (S–S 2.068 Å) also crystallising in chair conformation. The bond angle S–S–S (108.8°) in the S_3-bridge of **4** differs significantly from that in S_6 (102.6°). The dihedral angles between the least-squares plane P(1)P(2)S(2)S(4) and the planes P(1)S(1)P(2) and S(2)S(3)S(4) are 72.7 and 65.4°, respectively. The first value is very close to that of the corresponding dihedral angles in S_6 (73.8°).[12]

As can be seen from the crystal structure of **4**, the molecule does not possess a mirror plane and therefore, one molecule is an independent structural unit and both phosphorus atoms represent crystallographically non-equivalent sites. Hence, the molecule shows only slight deviations from a C_s symmetry caused by crystal-packing effects. The values on the left-hand side of Table 1 characterise the surroundings of P(1), the values on the right-hand side correspond to those of P(2). Only a few rows show significantly different values. The biggest differences in relation to the asymmetry of the phosphorus atoms are 0.013 Å, and 1.2°, for the bond lengths P(1)–S(2) and P(2)–S(4), and for the bond angles S(1)–P(1)–S(2) and S(1)–P(2)–S(4), respectively. Looking at the dihedral angles the biggest difference is 4.7° for S(2)–P(1)–C(1)–C(2) and S(4)–P(2)–C(2)–C(1).

The molecular packing of **4** is shown in Fig. 2. All distances between sulfur atoms of two different molecules are almost similar to or greater than twice the van der Waals radius of sulfur (3.60 Å).[13] The shortest distance is 3.58 Å for S(1) ··· S(3). This observation is important to the interpretation of the ^{31}P NMR data in the solid state.

Solution and Solid-state NMR.—In addition to the NMR data of the tetrathiadiphosphorinane **4** those of *trans*-2,4-diphenyl-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane **1** (R = Ph) and 2,4-(1,8-naphthalenediyl)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane **3** are given for comparison. All these compounds contain the same $RP(S)(S_{ring})_2$ moiety but have, as known from crystal structure investigations,[5,14] different bond angles and torsion angles including the phosphorus atoms.

Fig. 3 shows the ^{31}P CP MAS spectra of the investigated compounds. Since in **4** only slight differences in the atomic environments of P(1) and P(2) occur, the NMR non-equivalence is only small ($\Delta\delta_{iso}$ = 1.4 ppm). Consequently, the principal values of the nuclear magnetic shielding σ_{ii} of both phosphorus atoms differ only slightly (Table 2).

The symmetry distortions appear also in the ^{13}C CP MAS spectrum. In addition to one signal for the two *ortho* carbons at δ 128.6 a group of four poorly resolved signals in the range δ 135.5–138.5 is found. In solution the molecule of **4** shows the expected C_s symmetry which leads to one signal in the ^{31}P spectrum and only three signals in the ^{13}C spectrum (Table 3). The latter signals can be analysed to a good approximation as X-parts of AA′X spectra giving the P–C coupling constants.

For compound **3** the solid-state ^{31}P NMR spectrum shows two isotropic chemical shifts with an unexpectedly large difference of 7.5 ppm, although the crystallographic non-equivalence of the two phosphorus atoms is small[5] and comparable with that of **4**. The biggest differences in the vicinity of the phosphorus atoms of **3** are 0.03 Å, and 1.2°, for the bond lengths C(1)–C(9) and C(8)–C(9), and for the bond angles C(1)–C(9)–C(10) and C(8)–C(9)–C(10), respectively (for labelling see structure of **3** in Scheme 1). Looking at the dihedral angles the biggest difference is 0.9° for S(1)–P(1)–S(3)–P(2) and

Table 2 Experimental ^{31}P NMR data of *trans*-dithiadiphosphetane **1**, *cis*-dithiadiphosphetane **3** and tetrathiadiphosphorinane **4**

		Solution		Solid state			
Compound		δ	$J(PP)$/Hz[a]	δ_{iso}	σ_{11}	σ_{22}	σ_{33}
1 (R = Ph)[b]	P(1), P(2)	18.5	1.0	30.7	131	192	568
3	P(1)	18.0	6.5	22.4	201	201	515
	P(2)			29.9	187	207	500
4	P(1)	93.2	17.2	96.3	140	186	369
	P(2)			97.7	140	187	363

[a] Determined from the ^{13}C satellites in the ^{31}P NMR spectrum. [b] See refs. 7 and 15.

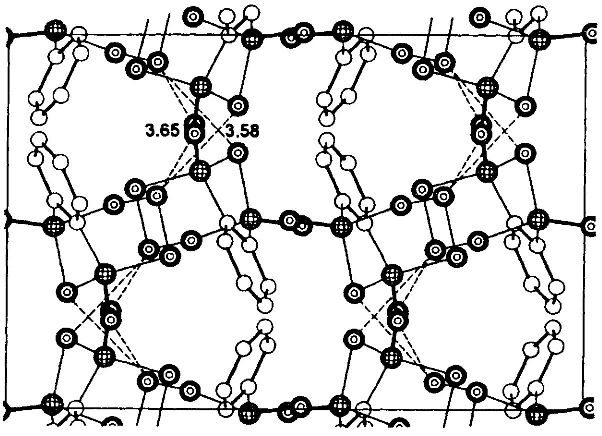


Fig. 2 View of the unit cell of **4** along the *a* axis

S(2)–P(2)–S(3)–P(1). Hence, the geometry of a single molecule cannot be the reason for the different isotropic shifts obtained. It is obvious that in this case the crystal packing influences the chemical shift of the phosphorus atoms. A detailed examination of the intermolecular distances shows the presence of some short S • • • S distances (3.38 and 3.48 Å) in comparison to their van der Waals radii. As can be seen in Fig. 4(*b*), the shortest intermolecular distances between S(2) and S(3) are asymmetrically situated with respect to both phosphorus atoms of **3**. The electronic surroundings of P(1) and P(2) are differently affected *via* the distortion of the sulfur lone pairs and hence their chemical shifts differ considerably.

The symmetry distortions are also visible in the ^{13}C CP MAS NMR spectrum. In the range δ 122–138 ten poorly resolved signals are observed. In solution the molecule of **3** shows the expected C_{2v} symmetry which leads to one signal in the ^{31}P NMR spectrum and only six signals in the ^{13}C NMR spectrum (Table 3). Comparing the ^{31}P NMR chemical shifts of **3** in solution (δ 18.0) and in the solid-state we can conclude that intermolecular S • • • S interactions lead to some deshielding of the ^{31}P nuclei and that this effect is stronger for P(2) (29.9 ppm) than for P(1) (22.4 ppm).

A single ^{31}P isotropic line (Fig. 3) in the solid-state NMR spectrum of **1** (R = Ph) is consistent with the crystallographic equivalence[14] of the two phosphorus atoms being related by a centre of symmetry. The ^{13}C CP MAS NMR spectrum shows six signals at δ 138.9 for C(1) and at δ 136.1, 135.2, 132.3, 130.7 and 128.9 for the other carbon atoms. This is in accord with the molecular structure which shows a dihedral angle of 23° between the least-squares plane of the phenyl ring and the S=P–C plane. Only for a dihedral angle of 90° three lines are expected. On the other hand, a fast conformational rotation around the P–C bond accounts for the three lines in the solution ^{13}C NMR spectrum (Table 3). Owing to *trans–cis* isomerization[15] line broadening was observed in this spectrum.

The large difference between the ^{31}P chemical shifts of **1** in solution (δ 18.5) and in solid state (δ 30.7) can be understood by analysing the molecular packing. As shown in Fig. 4(*a*), the shortest S • • • S distances (3.46 Å) are 0.14 Å smaller than the sum of the sulfur van der Waals radii. These short intermolecular distances lead to an additional deshielding of the ^{31}P nuclei in the solid state. Since the short S • • • S interactions are symmetrical to both phosphorus atoms of **1** only one isotropic line is observed for both phosphorus atoms (Table 2). In this connection, the quite similar values of the isotropic shifts in the solid state and in solution of the tetrathiadiphosphorinane **4** can be understood, because the shortest S • • • S intermolecular distances are of the order of twice the van der Waals radius (Fig. 2).

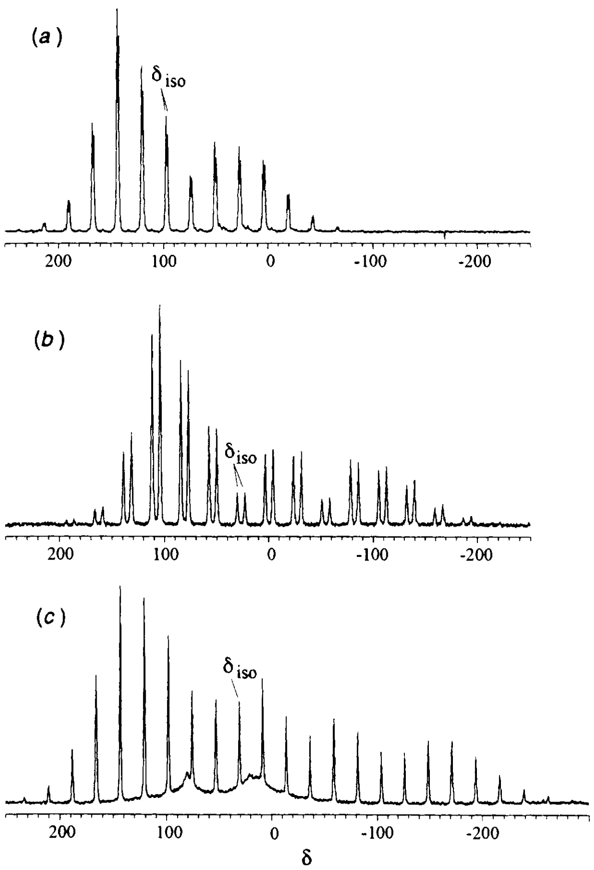


Fig. 3 Phosphorus-31 CP MAS NMR spectra at 121.5 MHz: (*a*) tetrathiadiphosphorinane **4**, (*b*) *cis*-dithiadiphosphetane **3** and (*c*) *trans*-dithiadiphosphetane **1** (R = Ph)

The orientation of the principal axes in a local molecular framework can be determined by analysing MAS NMR spectra of crystalline powders if a heteronuclear *J* coupling leads to a

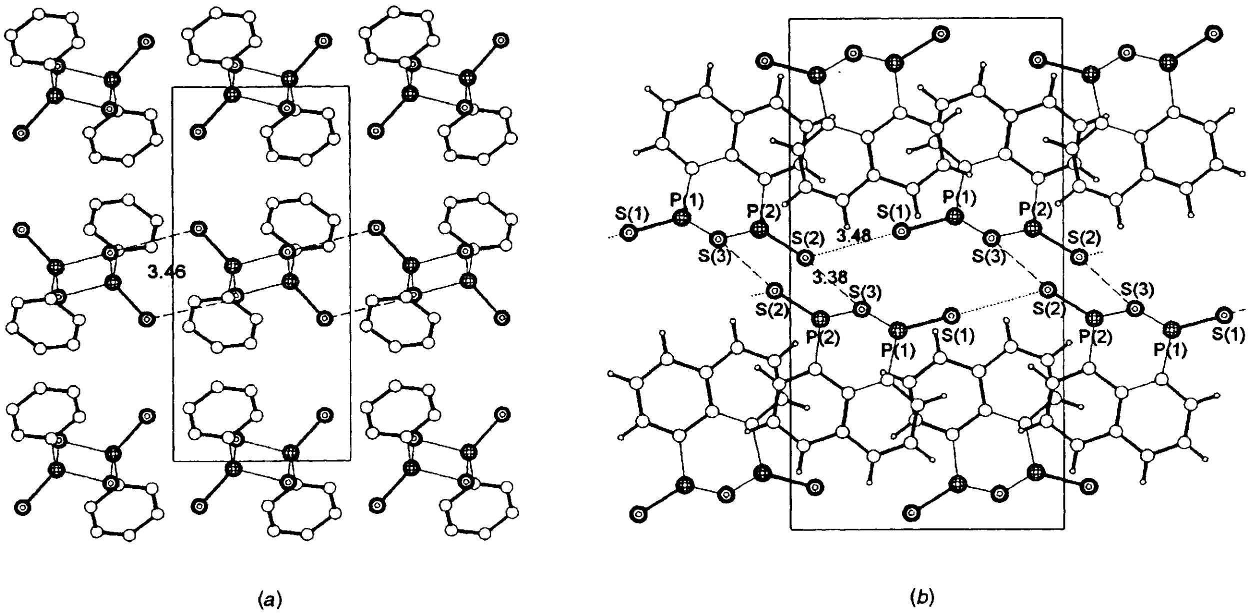
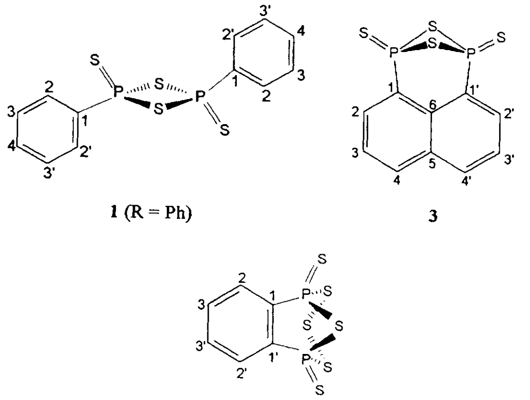


Fig. 4 The molecular packing (*a*) of *trans*-dithiadiphosphetane **1** (R = Ph, view along the *c* axis)[14] and (*b*) *cis*-dithiadiphosphetane **3**[5] (view along the *a*-axis)

Table 3 Carbon-13 NMR data of *trans*-dithiadiphosphetane **1**, *cis*-dithiadiphosphetane **3** and tetrathiadiphosphorinane **4** in $CDCl_3$ (see Scheme 2 for atom numbering)

	1 (R = Ph)[a]		**3**[b]			**4**		
Compound	δ	$^nJ_{PC}$/Hz(*n*)	δ	$^nJ_{PC}$/Hz(*n*)	$^mJ_{PC}$/Hz(*m*)	δ	$^nJ_{PC}$/Hz(*n*)	$^mJ_{PC}$/Hz(*m*)
$C^{1,1'}$	139.4	90 (1)	132.7	+85.0 (1)	+1.7(3)	138.8	+87.0 (1)	+15.3 (2)
$C^{2,2'}$	132.4	14 (2)	133.0	+14.1 (2)	−1.3 (4)	127.1	+29.3 (2 + 3)[c]	
$C^{3,3'}$	128.9	16 (3)	125.5	+17.8 (3)	+0.6 (5)	134.1	+14.7 (3)	−3.7 (4)
$C^{4,4'}$	133.4	—	135.5	+4.3 (4)	−2.3 (4)	—	—	—

[a] The ^{13}C NMR spectrum of this compound shows broadened lines so that the small coupling constants are not resolved; the line broadening is caused by slow exchange between the major *trans* and minor *cis* configuration, see ref. 15. [b] δ (C^5) 134.0, $^3J_{PC}$ = +11.8 Hz; δ (C^6) 128.1, $^2J_{PC}$ = +10.0 Hz. [c] Absence of the outer combination lines prevents separation of the contributions of the two coupling constants.



Scheme 2

visible line splitting.[16] For crystalline powders containing one dominant dipolar interaction this information can be obtained from solid-state spectra without rotation even if two chemically and magnetically equivalent nuclei interact.[17] Such investigations were performed for the Lawesson reagent, a *trans*-dithiadiphosphetane **1** with R = 4-methoxyphenyl by Wasylishen *et al.*[18] and recently by Nakai and McDowell.[19] The described methods are applicable for compound **1** (R = Ph) while for **3** and **4** a precise analysis of the orientation of the principal axes is more difficult due to the non-equivalence of the interacting nuclei. Therefore, we have carried out IGLO calculations for all three compounds.

IGLO Calculations.—The calculated principal values of the ^{31}P shielding tensors summarised in Table 4 agree in a satisfactory manner with the experimental data in Table 2. This allows the utilisation of another result of these calculations, namely the orientation of the principal axes in a local molecular framework.

The orientation of the principal axes results from the local structure of the environment of the considered nucleus and therewith by its microsymmetry.[20] We define a local molecular framework for any phosphorus as follows: the origin is at the ^{31}P nucleus under consideration, the *z* axis coincides with the P=S direction, the *x* axis lies in the S=P–C plane and is directed towards C whereas the *y* axis is established by the right-hand rule. The relation between the principal axes 1, 2, 3 and the local molecular framework *x*, *y*, *z* will be characterised by the angles α, β, γ (see Table 4). In Fig. 5 this relation is shown for both phosphorus nuclei of **4**.

The orientation of the principal axes is unambiguous for molecules **1** and **4**, whereas no clear result can be obtained for **3**. Although the phosphorus nuclei in this compound have no axial microsymmetry the principal values σ_{11} and σ_{22} are

Table 4 Characterisation of the ^{31}P nuclear shielding tensors from IGLO calculations of *trans*-dithiadiphosphetane **1**, *cis*-dithiadiphosphetane **3** and tetrathiadiphosphorinane **4**

		Principal values/ppm			Angles[a]/°		
Compound		σ_{11}	σ_{22}	σ_{33}	α	β	γ
1 (R = Ph)	P(1), P(2)[b]	156	195	579	19.0	0.0	19.0
	P(1), P(2)[c]	157	205	567	31.6	24.6	19.5
3[d]	P(1)	211	212	506	(17.9)[e]	(8.4)[e]	15.9
	P(2)	211	214	505	(88.4)[e]	(88.4)[e]	15.8
4	P(1)	175	205	404	41.0	40.8	2.6
	P(2)	176	206	398	44.5	44.3	3.4

[a] For definition of the local molecular framework see text. [b] Values obtained *via* geometry optimisation with TURBOMOLE in C_{2h} symmetry, see ref. 7. [c] Values obtained *via* crystal structure data from ref. 14. [d] Values obtained *via* crystal structure data from ref. 5. [e] This formally calculated angle is not significant since the tensor is nearly quasi-axial.

Table 5 LMO contributions to the principal values σ_{ii} (ppm) of *trans*-dithiadiphosphetane **1**, *cis*-dithiadiphosphetane **3** and tetrathiadiphosphorinane **4**

	1 (R = Ph)			**3**[a]			**4**[a]		
LMO	σ_{11}	σ_{22}	σ_{33}	σ_{11}	σ_{22}	σ_{33}	σ_{11}	σ_{22}	σ_{33}
Core P[b]	769	775	815	772	772	809	766	769	795
P=S	−314	−283	−24	−329	−288	−13	−329	−319	12
lp S=(1)[c]	−8	−2	27	−8	0	28	−7	−2	41
lp S=(2)[c]	−2	4	50	0	2	46	6	−2	43
lp S=(3)[c]	6	−4	45	4	−1	46	−3	5	41
P–S	−112	−18	−120	−70	−40	−140	−102	−30	−148
P–S′	−14	−98	−111	−39	−68	−140	−35	−90	−169
4 lp S–[d]	−11	−18	13	−3	−16	−8	−12	−9	−35
P–C	−144	−141	−112	−113	−135	−113	−95	−113	−164

[a] LMO contributions are given only for P(1). The values for P(2) are very similar. [b] Core P are the contributions of the K and L shells of the considered phosphorus. [c] lp S=(*n*) denotes the contributions of each of the three lone-pair LMOs of the terminal sulfur atom. [d] 4 lp S– denotes the sum of the contributions of the lone-pair LMOs of the neighbouring ring sulfur atoms.

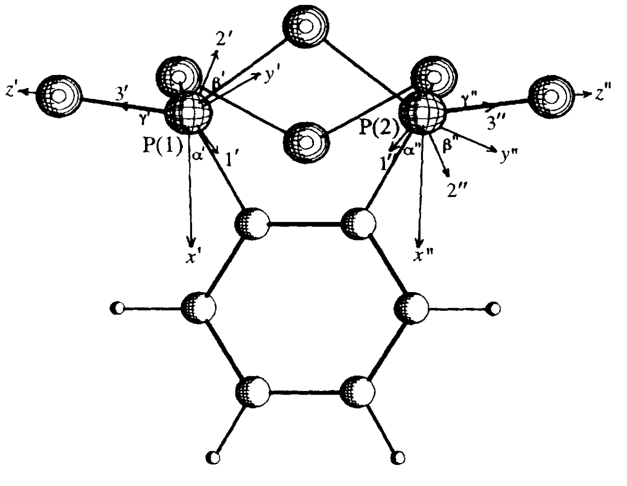


Fig. 5 The calculated principal axes 1′, 2′, 3′ and 1″, 2″, 3″, the chosen local molecular coordinate systems x', y', z' and x'', y'', z'' and the angles α', β', γ' and α'', β'', γ'' between these coordinate systems for the atoms P(1) and P(2) in the tetrathiadiphosphorinane **4**

nearly equal. This quasi-axial tensor is characterised by an uncertain orientation of the axes 1 and 2 in the plane which is perpendicular to axis 3. Considering the small values of the angle γ of the compounds investigated the conclusion may be drawn that in all four-co-ordinate phosphorus compounds containing a P=S bond the 3 axis of the most shielded principal value lies nearly parallel to this bond.

The application of local molecular orbitals (LMOs) within the IGLO scheme[8] allows an analysis of the individual bond contributions to σ_{ii}. A detailed discussion of LMO contributions for **1** is given in ref. 7. As can be seen from Table 5 the contributions of the core electrons are strongly shielding and almost the same for all three compounds. The largest deshielding contributions are caused by the P=S, P–S and P–C bonds. If one considers that the LMO contributions to a given σ_{ii} depend on the electronic structure in a plane perpendicular to the principal axis *i* (ref. 21) bonds almost perpendicular to a certain principal axis should mainly affect the magnitude of σ_{ii}. The deshielding contribution of the P=S bond is reflected by σ_{11} and σ_{22} values and this is in good agreement with angles 1–P=S and 2–P=S close to 90° for **1**, **3** and **4**. The deshielding contributions of both P–S bonds are reflected either by σ_{11} and σ_{33} or by σ_{22} and σ_{33} corresponding to angles 1–P–S and 3–P–S or 2–P–S′ and 3–P–S′, respectively, nearest to 90°. It is observed that the deshielding contribution of the P–C bond to the σ_{ii} values differs for the three compounds which is in agreement with the fact that different axes of these compounds are almost perpendicular to the P–C bond. However, such a qualitative discussion of LMO contributions to σ_{ii} is restricted because deshielding contributions to σ_{ii} values, furthermore, depend on the effective interaction between occupied and low-lying virtual orbitals of appropriate symmetry.[7]

The larger deshielding of the phosphorus in compound **4** ($\delta_{iso} \approx 93$) in comparison to **1** and **3** ($\delta_{iso} \approx 18$) is mainly caused by the magnitude of σ_{33} (see Table 2). From Table 5 it follows that the P–C bond significantly enhances the deshielding in compound **4**. The angles 3–P–C are 61 and 63° for this compound and 45 to 47° for the compounds **1** and **3**. Thus, the large shielding differences of **4** compared to **1** and **3** are mainly due to the differences in the surroundings of the P atoms in these compounds (the three C–P–S angles are *ca.* 99, 106, 120° for **4** on the one hand and 107, 107, 116° for **1** and 104, 104, 117° for **3** on the other).

Table 6 Fractional atomic coordinates for $C_6H_4P_2S_6$ **4**

Atom	*x*	*y*	*z*
P(1)	0.070 80(3)	0.668 50(2)	0.139 20(3)
P(2)	0.246 78(3)	0.579 33(2)	0.010 66(3)
S(1)	0.203 10(3)	0.602 82(2)	0.188 23(3)
S(2)	0.131 87(4)	0.780 77(2)	0.091 52(4)
S(3)	0.197 35(3)	0.756 65(2)	−0.072 71(4)
S(4)	0.322 94(3)	0.682 80(3)	−0.048 16(4)
S(5)	−0.032 12(4)	0.678 77(3)	0.262 04(4)
S(6)	0.335 67(4)	0.489 02(3)	−0.007 12(4)
C(1)	0.040 08(10)	0.619 94(8)	0.000 18(12)
C(2)	0.120 42(10)	0.580 94(8)	−0.059 37(11)
C(3)	0.103 01(13)	0.547 40(10)	−0.171 19(13)
C(4)	0.004 83(14)	0.552 68(11)	−0.221 50(14)
C(5)	−0.074 92(13)	0.590 06(10)	−0.162 1(2)
C(6)	−0.058 66(12)	0.623 83(10)	−0.049 9(2)

Experimental

Preparation.—For the preparation of the new compound **4** tetraethyl phenylene-1,2-diphosphonate (3.6 g, 10.3 mmol) dissolved in diethyl ether (30 cm^3) was added slowly dropwise to a suspension of lithium aluminium hydride (2 g, 53 mmol) in diethyl ether (50 cm^3) under gentle refluxing. After stirring for 45 min the solution was refluxed for 1 h and then hydrolysed with 6 mol dm^{-3} HCl (30 cm^3) in an ice-bath and with vigorous stirring. After 10 min the ethereal phase was separated taking care to exclude oxygen. The aqueous phase was washed twice with ether. After filtration the ethereal phases were combined and dried with sodium sulfate.

The ether was removed *in vacuo* and the residue dissolved in toluene (50 cm^3). This solution was added dropwise to a suspension of sulfur (2.6 g, 10.2 mmol) in toluene (20 cm^3) and the mixture was refluxed for 2 h. After cooling a yellow crystalline precipitate was obtained. The product was separated from the excess of sulfur by repeated washing with toluene (0.5 g, 12%), m.p. 178 °C. Mass spectrum: (field desorption) *m/z* 330 (relative intensity 50%, M^+), 298 (8, M − S), 266 (100, M − 2 S), 234 (18, M − 3 S), 202 (84, M − 4 S), 171 (57, M − 4 S − P), 170 (38, M − 5 *S*), 139 (47, M − 5 S − P) and 107 (37, M − 6 S − P).

Compounds **1** (R = Ph) and **3** were prepared as described in the literature by reaction of phenylthiophosphonic dichloride with H_2S[22] and by reaction of P_4S_3 with S_8 in α-bromonaphthalene,[5] respectively. According to a powder X-ray diffractogram the crystal modification of **3** was identical with that of the investigated single crystal.[5]

Crystallography.—Crystal data. $C_6H_4P_2S_6$ **4**, M = 330.39, orthorhombic, space group *Pbca* (no. 61) a = 12.846(4), b = 16.929(7), c = 11.178(6) Å, U = 2431 $Å^3$ [by least-squares refinement on diffractometer angles for 20 automatically centred reflections, $\lambda = 0.710\ 73$ Å], $Z = 8$, $D_c = 1.81$ g cm^{-3}, $F(000) = 1328$. Yellow prisms (from toluene). Crystal dimensions: 0.50 × 0.32 × 0.32 mm, μ(Mo-Kα) = 1.34 cm^{-1}.

Data collection and processing. Enraf-Nonius CAD4 diffractometer, ω–2θ mode with ω scan width = 0.66 + 0.74 tan θ, ω scan speed 1.3–8.2° min^{-1}, graphite-monochromated Mo-Kα radiation; 11 424 reflections measured ($2.4 \leqslant \theta \leqslant 40.0°$), 5814 unique (merging $R = 0.0247$), giving 3756 with $I > 2\sigma(I)$.

Structure analysis and refinement. Direct methods (P, S and C atoms) followed by normal procedures by means of the SHELXS 86 program.[23] Full-matrix least-squares refinement using the SHELXL 93 program [24] with all non-hydrogen atoms anisotropic and hydrogens in calculated positions with one, overall, refined U_{iso} [=0.08(2) $Å^2$]. The weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 0.2356P]$, where $P = (F_o^2 + 2F_c^2)/3$ gave satisfactory agreement analysis. Final R_1 = 0.0324 for 3756 reflections with $F_o > 4\sigma(F_o)$ and 0.0663 for all 5814 data. R_1 = 0.0661 for 5814 unique reflections after merging; wR_2 (based on F^2) = 0.0894. Fractional atomic coordinates are given in Table 6.

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

NMR Spectroscopy.—The NMR spectra were recorded using a Bruker MSL 300 spectrometer (121.5 MHz for ^{31}P and 75.5 MHz for ^{13}C). The ^{31}P chemical shifts are relative to 85% H_3PO_4 and ^{13}C are relative to $SiMe_4$. For the determination of the anisotropy parameters ^{31}P CP MAS NMR spectra were measured at spinning frequencies of 2.5–2.8 kHz using cross polarisation with a pulse sequence containing two contact pulses.[25] The spinning sideband systems have been computed by means of the program WIN-MAS of Jeschke.[26] The standard deviations of the principal values of the chemical shift tensors caused by phase and basis line correction are 2 ppm while the systematic deviations are estimated to 5 ppm. The principal values of the shielding tensors were calculated from the chemical shift tensors[27] with $\sigma_{ii} = (328 - \delta_{ii})$ ppm and have been labelled according to the convention $\sigma_{33} \geqslant \sigma_{22} \geqslant \sigma_{11}$.

IGLO Calculations.—The calculations were performed with coordinates from the X-ray diffraction studies for the molecule **1** (R = Ph)[14] in C_i symmetry and for **3**[5] and **4** in C_1 symmetry. In a first step the electronic ground state was calculated with the TURBOMOLE package.[28]

The ^{31}P shielding tensors were calculated with the direct IGLO program (DIGLO)[29] using the following Huzinaga basis sets[30] named II′ according to Kutzelnigg, Fleischer and Schindler:[8b] (3s) contracted to [2 1] for H, (7s 3p) contracted to [4 1 1 1, 2 1] for C and (11s 7p 2d) contracted to [7 1 1 1 1, 6 1, 2] for P and S (the d exponents for P and S were 1.40, 0.35 and 1.60, 0.40 respectively).

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