Phosphorus-31 Solid-state Nuclear Magnetic Resonance Spectroscopy, Individual Gauge for Localized Orbitals Calculations and Crystal Structures of Dithiadiphosphetanes $[RSP(S)S]_2$ (R = alkyl or aryl)†

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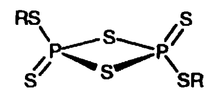
For a number of dithiadiphosphetanes $[RSP(S)S]_2$ **1** the ^{31}P nuclear magnetic shielding tensor has been investigated. Phosphorus chemical shift δ_{iso} and principal values of the shielding tensor σ_{ii} have been calculated from CP MAS (cross polarization magic angle spinning) spectra. The orientation of the principal axes of the shielding tensor with respect to the dipolar coupling vector has been determined from the static powder spectra of $[MeSP(S)S]_2$ **1a**. *Ab initio* calculations of the ^{31}P shielding tensor have been performed using the individual gauge for localized orbitals method. The calculated data correspond well with the experimental. The most shielded component (the corresponding axis is 3) is approximately perpendicular to the PS_2P ring plane {angle P···P–3 ≈107° for $[MeSP(S)S]_2$}. Axis 2 is perpendicular to the S=P–S(3) plane. Since axis 1 is perpendicular to axes 2 and 3 it intersects the S–P–S angle of both the terminal S atoms. The crystal structures of compounds $[C_6H_{11}SP(S)S]_2$ **1c** and $[PhCH_2SP(S)S]_2$ **1d** have been determined. Both compounds crystallize in the monoclinic space group no. 14 (**1c** $P2_1/a$, **1d** $P2_1/n$). The unit cell of **1c** contains two crystallographically independent molecules.

Solid-state NMR spectroscopy has become a powerful tool in investigations of polycrystalline samples. In particular, the ^{31}P nucleus is an excellent probe (high sensitivity, large chemical shift anisotropy). Slight differences in the local geometry of the observed nucleus are reflected much more strongly by the chemical shift anisotropy than by the isotropic chemical shift in solution. For instance, the ^{31}P chemical shift (δ_{soln}) of different 2,4-bis(organosulfanyl)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes **1** [esters of the hexathiometadiphosphoric acid $(HPS_3)_2$] ranges from δ 21 to 26 (see also ref. 1). The influences of solvent and substituent on δ_{soln} are of the same order of magnitude. Since these compounds are not very stable in solution their characterization as well as a test of their purity are preferably done in the solid state. The same is true for the salts of hexathiometadiphosphoric acid since their low solubility prevents an investigation in solution.

So far chemical shift anisotropy values have been published for only one salt of hexathiometadiphosphoric acid, $Ag_2P_2S_6$.[2] The large anisotropy is discussed in connection with the local phosphorus co-ordination characterized by an extremely large distortion of the ideal tetrahedral geometry (S–P–S bond angles between 93.7 and 118°).

The first results of systematic solid-state NMR investigations into dithiadiphosphetanes $[RP(S)S]_2$ were presented by Großmann *et al.*[3] in 1990. Recently, Wasylishen *et al.*[4] determined the orientation of the P–P dipolar vector with respect to the principal axes system of the ^{31}P shielding tensor of the well known Lawesson's reagent $[p\text{-}MeOC_6H_4P(S)S]_2$, by dipolar NMR spectroscopy.

In this paper we present the isotropic chemical shifts δ_{iso} and the principal values σ_{ii} of the shielding tensor of six esters **1** of hexathiometadiphosphoric acid and compare them with results of *ab initio* calculations of $[MeSP(S)S]_2$ **1a**. For the methyl compound **1a** the orientation of the principal axes of the shielding tensor in the molecular frame has been provided from analysis of a static powder spectrum and from individual gauge for localized orbitals (IGLO)[5] calculations. To investigate the dependence of the principal values σ_{ii} on geometry changes at the P nucleus the crystal structures of compounds $[C_6H_{11}SP(S)S]_2$ **1c** and $[PhCH_2SP(S)S]_2$ **1d** have been determined. The structures of the other esters are known.[6–9]



1

	R
1a	Me
1b	Et
1c	cyclo-C_6H_{11}
1d	CH_2Ph
1e	Ph
1f	C_6H_4Me-*p*

Experimental

Syntheses.—Compounds **1a**–**1f** all crystallizing in the *trans* configuration were prepared by published standard procedures.[10–12]

Method A. A mixture of P_4S_{10} (0.05 mol), the appropriate alcohol (0.15 mol) and 1,2,4-trichlorobenzene (0.3 mol) was refluxed carefully. After heavy H_2S generation the mixture was stirred at 160 °C for 3–4 h. The clear yellow solution obtained was cooled to 80 °C, decanted, a slight excess of P_4S_{10} and insoluble by-products were filtered off, and **1a**–**1d** were recovered from the filtrate by further cooling.[10]

Method B. A mixture of P_4S_{10} (0.0315 mol), the appropriate thiol (0.15 mol), and 1,2,4-trichlorobenzene (0.3 mol) was refluxed for 30 min. The clear yellow solution was cooled to room temperature, and **1c**, **1e** and **1f** were obtained.[11]

Single crystals of compounds **1c** and **1d** were grown by slow cooling of hot-saturated 1,2-dichloroethane solutions to room temperature using sealed glass tubes. Both compounds crystallize as thin pale yellow plates.

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

NMR Spectroscopic Measurements.—Magic angle spinning (MAS) solid-state ^{31}P NMR spectra were recorded on a Bruker MSL 300 instrument at 121.495 MHz and spinning rates of 3.0–4.5 kHz. Typical conditions were: 5.0 μs 90° pulse, cross polarization (CP) and ^{1}H high power decoupling, 1 ms contact time, 10 s recycle delays, 100–1500 scans, multiple contact pulse sequence.[13] The static CP ^{31}P NMR spectra were acquired by a Hahn spin-echo experiment. Acquisition time 8.2 ms, 10 s recycle delay, 10 000–15 000 scans. The ^{31}P chemical shifts are referenced to 85% phosphoric acid (δ 0).

The principal components of the chemical shift tensor of the ^{31}P resonance for powdered samples were calculated from spinning sideband intensities using the programs MASNMR and WINMAS[14] based on the method of Herzfeld and Berger.[15] The ^{31}P chemical shifts were converted to shieldings using the data of Jameson *et al.*,[16] $\sigma(^{31}P)$ 328 for H_3PO_4. The data are reported following the convention $\sigma_{33} \geqslant \sigma_{22} \geqslant \sigma_{11}$.

The isotropic chemical shift is given by $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$ and the shielding anisotropy by $\Delta\sigma = \sigma_{33} - (\sigma_{11} + \sigma_{22})/2$.

Quantumchemical Calculations.—The IGLO method[5] is a coupled Hartree–Fock type method for the calculation of the nuclear magnetic shielding tensor σ and the magnetic susceptibility χ of a molecule. For each localized molecular orbital (MO) an individual gauge origin is chosen. The shielding is given as a sum of contributions of these localized molecular orbitals. These contributions provide additional insight and can be used to study the relation between structure parameters and the principal values in more detail.[17,18]

Basis II as described in ref. 5 was used for P, S and C, a DZ basis (see ref. 5) was employed for H. The experimental geometry[6] was used. Compound **1a** was calculated in C_{2h} symmetry whereas the crystal structure shows the lower C_i symmetry with two different P–S bonds in the PS_2P ring.

Crystal Structure Determination.—The measurements were carried out on an Enraf-Nonius four-circle CAD4 diffractometer with graphite-monochromated Mo-Kα radiation at 294 K. The crystals were selected using a polarization microscope, placed in glass capillaries and mounted on the CAD4 diffractometer. The monoclinic lattice constants of the cyclohexyl compound **1c** were determined using the automatic search and indexing routine of the CAD4 diffractometer (refined on 21 reflections in the range $4 < \theta < 12°$). For the benzyl compound **1d** the lattice constants were determined by a film technique on a Buerger precession camera and checked again on the CAD4 diffractometer by centring and indexing 11 reflections in the range $5 < \theta < 15°$. Details of the data collection are given in Table 2. For data reduction the program XCAD4[19] was used. Both compounds crystallize in the monoclinic space group no. 14 (ref. 20) with the unique axis *b* and different cell choice 2 and 3 (**1d**, $P2_1/n$; **1c**, $P2_1/a$) determined by reflection conditions. The programs employed were SHELXS 86[21] for the structure solution by direct methods and SHELXL 93[22] for the structure refinement.

For the intensity data of compound **1d** the reflections with unequal background were corrected or omitted. In this case only 633 reflections with $2\theta < 40°$ and $F_o > 4\sigma(F_o)$ were used. Both structures were refined using anisotropic thermal parameters for the non-hydrogen atoms.

For compound **1c** the hydrogen atoms were located by difference electron density synthesis and refined as isotropic free atoms in the program SHELXL 93.[22] For compound **1d** the difference electron density synthesis led only to the hydrogen atoms of the CH_2 group. The hydrogen atoms were therefore calculated with constraints and idealized coordinates. In spite of the high final *R* value no odd features were detected during the refinement. The high *R* value is probably the result of insufficient intensity data from the low quality crystals available.

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

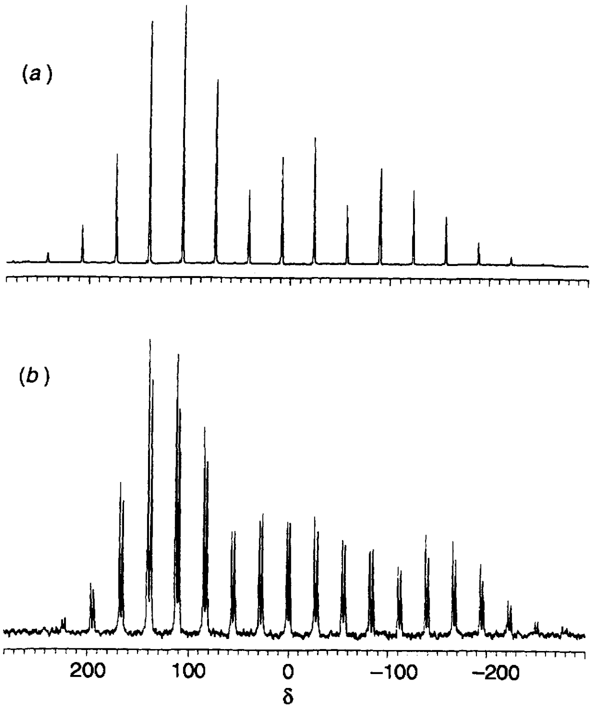

Fig. 1 The ^{31}P CP MAS NMR spectra of (*a*) 2,4-bis(methylsulfanyl)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane **1a** and (*b*) 2,4-bis(cyclohexylsulfanyl)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane **1c**

Results and Discussion

CP MAS Spectra.—Dithiadiphosphetanes $[RSP(S)S]_2$ exhibit anomalously low-frequency solution ^{31}P NMR chemical shifts (δ 21–26) compared with those of the corresponding tetrathiophosphoric acid triesters $P(S)(SR)_3$ which typically lie in the region δ 85–100. While the chemical shifts of compounds **1a**–**1f** in solution are very similar, the isotropic chemical shifts in the solid-state range from δ 25 to 44 depending on the substituent R (Table 1). The decrease of δ_{iso} from methyl *via* ethyl and benzyl to the cyclohexyl ester reflects the increasing shielding by bulky substituents. For compounds bearing sterically demanding substituents (C_1 tetrahedral, at least one C–C bond) smaller differences between δ_{soln} and δ_{iso} are observed compared to the methyl or phenyl compound. In contrast to the methyl compound **1a** (see ref. 6) it is probable that in solutions of **1b**, **1c** and **1d** the same conformation predominates as that found in the solid state.

Fig. 1 displays the ^{31}P MAS NMR spectra of the methyl and cyclohexyl compounds **1a** and **1c**. The spectra are typical of all the compounds investigated. They are characterized by a relatively large anisotropy Δσ [*cf.* P_4S_{10} 163 and 157 ppm,[23] $MeP(S)(SH)_2$ 92 ppm[24]] mainly caused by their common structural feature, a four-membered PS_2P ring (1,3,2,4-dithiadiphosphetane). Bond angles between 93.0 and 93.7° [endocyclic S(1)–P(1)–S(1′)] and 116.4 and 119.4° [S(1)–P(1)–S(2)] indicate that the tetrahedral geometry at the P atom is significantly distorted.

Except for the cyclohexyl ester **1c** all the compounds investigated show a single isotropic line. Thus, esters **1a**, **1b**, **1d**, **1e** and **1f** consist of one half molecule as an independent unit per unique volume. This is in agreement with the crystallographic data of these compounds.[6–9] For the cyclohexyl ester **1c** two isotropic lines are observed. The two crystallographically distinct phosphorus sites result from two different molecules 1 and 2 with crystallographically equivalent phosphorus nuclei. In the *para*-tolyl compound **1f** (C_i molecular symmetry)[9] the

Table 1 Phosphorus-31 chemical shift and nuclear magnetic shielding parameters (ppm), selected bond lengths (pm) and bond angles (°) of dithiadiphosphetanes **1**

R	δ_{soln}*	δ_{iso}	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$	P(1)–S(2)	S(1)–P(1)–S(1′)	S(1)–P(1)–S(2)
Me	23.6	42.1	134	198	526	360	191.9	93.0	118.5
Et	21.8	31.1	139	193	558	392	190.9	93.1	116.4
cyclo-C_6H_{11}	22.2	28.7	137	193	568	403	191.0	93.6	117.1
		25.7	136	201	570	402	191.2	93.2	117.0
$PhCH_2$	20.9	32.9	136	199	549	382	191	93.3	117.2
Ph	23.9	43.3	130	184	541	384	192.0	93.7	118.8
p-MeC_6H_4	25.5	43.6	130	185	538	380	191.7	93.7	119.4
Me (IGLO)		30	150	204	541	364			
Ag (ref. 2)		64.4	131	193	467	305			

* Chemical solution shifts in CS_2. Data in ref. 1: δ 22.6 (Me), 20.9 ($PhCH_2$), 23.3 (Ph).

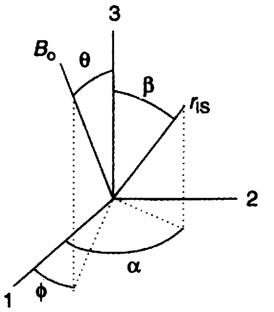

Fig. 2 Angles describing the orientation of the dipolar coupling vector r_{IS} in the principal axes system of the nuclear magnetic shielding tensor

tolyl groups are not strictly perpendicular to the S=P–S(3) plane. The corresponding torsion angles P(1)–S(3)–C(1)–C(2) and P(1)–S(3)–C(1)–C(6) deviate by 5.4 and 8.1°, respectively, from a perpendicular arrangement. Consequently, the six aromatic carbon atoms of one substituent R are chemically inequivalent, which has been confirmed by ^{13}C CP MAS NMR spectroscopy. Five signals appear well resolved in the region of aromatic C atoms [δ 143.9, 139.2, 137.2, 133.0 (2 C atoms), 127.4; Me δ 21.1]. A further interesting result is the extremely large linewidth (360 Hz) of the ^{31}P MAS spectrum of the benzyl compound in comparison to the other values which range from 60 (cyclo-C_6H_{11}) to 150 Hz (*p*-MeC_6H_4). This will be discussed later on the basis of the crystal structure.

Considering the principal values of the shielding tensor further information can be gained. As known the principal components σ_{ii} depend on the electronic structure in a plane perpendicular to the direction of the principal axis *i*.[25] Chemical bonds close to this plane cause a deshielding whereas bonds parallel to *i* have a shielding MO contribution. As can be seen from Table 1 the bond lengths and angles of compounds **1a**–**1f** differ only slightly and changes in the principal values are small, the largest being observed for σ_{33} (44 ppm). Relationships between σ_{ii} values and structure parameters can be discussed only qualitatively. Changes in the P=S bond length are reflected in σ_{11} and σ_{33}. The shorter the P=S bond the larger are σ_{11} and σ_{33}. The S–P–S bond angle of the four-membered ring is nearly constant (93.0–93.7°). When this angle increases σ_{22} becomes smaller, which corresponds to the correlation described for dithiadiphosphetanes $[RP(S)S]_2$ based on IGLO calculations.[17] The bond angle S(1)–P(1)–S(2) covers a wider range (116.4–119.4°) and if this angle increases a decrease of σ_{11} and σ_{33} is observed. As changes in the P=S bond length are accompanied by changes in the bond angle S(1)–P(1)–S(2) then changes in the magnitude of both σ_{11} and σ_{33} are reflected.

Phosphorus-31 *Static Powder Spectra*.—For further characterization of the phosphorus shielding tensor its orientation with respect to the molecular frame has been determined. Besides NMR investigations of single crystals,[26] in some cases dipolar NMR spectroscopy[27] can provide this information. For both methods the orientation of the molecules with respect to the crystal axes system available from diffraction techniques, *e.g.* X-ray crystallography, must be known.

By analysis of the NMR spectra resulting from a $S = \frac{1}{2}$ nucleus that is dipolar-coupled to a neighbouring spin the following information can be gained: the dipolar coupling constant of the spin pair, the three principal components of the shielding tensor and two of the angles required for specifying the orientation of the shielding tensor. The orientation dependence of the dipolar interaction[4] in the magnetic field relative to the principal axes system of the shielding tensor (see Fig. 2) is given by equation (1). The effective dipolar coupling constant R_{eff} =

$$\nu_D = R_{eff}[1 - 3(\sin\beta \sin\theta \cos(\phi - \alpha) + \cos\beta \cos\theta)^2] \quad (1)$$

$1.5R - \Delta J/3$ (homonuclear spin pair) depends on the direct dipolar coupling constant *R* and the anisotropy of the indirect spin–spin coupling tensor Δ*J*. So far little is known concerning the magnitude of Δ*J* for indirect P–P couplings.

The presence of a dipolar-coupled spin pair in **1** allows the determination of the orientation of the ^{31}P shielding tensor with respect to the P–P dipolar vector from a static powder spectrum. Compound **1a** has been investigated. Both P nuclei have the same isotropic chemical shift and are related by a $\bar{1}$ centre (A_2 spin pair). According to Eichele and Wasylishen[28] all combinations of angles α and β (see Fig. 2) consistent with the experimental dipolar splitting ratios of the principal components of the shielding tensor are obtained. Considering the molecular symmetry and/or the dipolar coupling constant computed from the interatomic distance of the spin pair investigated, the set of possible solutions becomes restricted. The three parameters R_{eff}, α and β are refined in an iterative manner to provide the best fit of a calculated spectrum to the experimental one.

In Fig. 3 the experimental and simulated static powder spectra of compound **1a** are shown. The dipolar splittings are $\Delta\nu_{11} = 2320$, $\Delta\nu_{22} = 1190$, $\Delta\nu_{33} = 1130$ Hz with an error of ±200 Hz resulting from the resolution and shape of the experimental spectrum. The dipolar coupling constant can be calculated according to equation (2). Using the atomic distance

$$R = \gamma_A^2(h/2\pi)(\mu_0/4\pi)\langle r_{AA}^{-3}\rangle \quad (2)$$

P···P of 291.9 pm as an approximate value for $\langle r_{AA}^{-3}\rangle$ a dipolar coupling constant *R* of 793 Hz is obtained.

It is a good approximation to consider the S=P–S(3) plane of compound **1a** as a mirror plane [the bond lengths P–S(1) and P–S(1′) are only slightly different]. Owing to the (local) C_s symmetry one principal axis has to be perpendicular to the mirror plane. Only the first of the two solutions (*i*) α = 0°, β = 82.5°, R_{eff} = 1190 Hz and (*ii*) α = 90°, β = 45.2°, R_{eff} = 2320 Hz corresponds to the calculated dipolar coupling

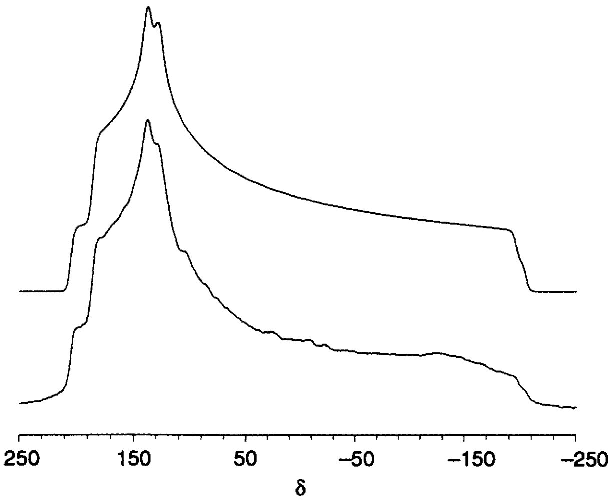

Fig. 3 Experimental (below) and calculated static powder spectrum (above) of **1a**

constant. Best fitting of the observed and calculated static lineshapes yields $\alpha = 0°$, $\beta = 75°$, $R_{eff} = 1275$ Hz with $\sigma_{11} = 133$, $\sigma_{22} = 195$ and $\sigma_{33} = 530$ ppm. This means that axis 2 is perpendicular to the mirror plane and the angle between axis 3 and the P $\cdots$ P vector amounts to 75°. The spectra are also consistent with the angle P $\cdots$ P–3 being 105°. As shown below IGLO calculations confirm the value of 105°.

With $R_{eff} = \pm 1275$ Hz, ΔJ is computed to be +255 or −7395 Hz. However, only the first solution seems reasonable but it cannot be evaluated as the value is within the experimental error of the measurement.

IGLO Calculations.—By means of the IGLO method the ^{31}P NMR chemical shifts δ_{iso} and the principal values σ_{ii} of the shielding tensor have been calculated. As the full tensors are calculated the orientation of the principal axes is directly available. This information has also been obtained experimentally from static powder spectra.

Comparing the computed and experimental data (see Table 1) the following conclusions may be drawn. For 2,4-bis(methylsulfanyl)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane **1a** the isotropic chemical shift as well as the calculated principal values agree well with the experimental data, all deviations being less than 20 ppm. Thus, the results of the calculations can be used to assign principal values and principal axes. As a result of the (local) C_s symmetry in the dithiadiphosphetanes **1** one principal axis has to be perpendicular to the mirror plane. The corresponding value is σ_{22}. The most shielded component σ_{33} is located in the mirror plane (see Fig. 4). Axis 3 is tilted by 26.3° from the P=S bond in the direction of a perpendicular to the PS$_2$P ring plane yielding the angle P $\cdots$ P–3 107.2°. Principal axis 1 lies in the mirror plane and intersects the S–P–S angle of both terminal S atoms.

In analogy to calculations on 2,4-dimethyl-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane[17] the P=S bond molecular orbitals dominate the shielding tensors of compounds **1**. As the P=S bond is nearly parallel to axis 3 no significant deshielding interactions occur in σ_{33}. The comparably large shielding along the bond axis has been discussed in connection with a semipolar bond character.[17]

Crystal Structures.—Both compounds **1c** and **1d** show a *trans* configuration for the different cyclohexyl and benzyl ligands in relation to the PS$_2$P ring and a *trans* conformation for S(2) and C(1). In comparison to other structures of the 2,4-bis(organosulfanyl)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes[6–9] the orientation of the ligands is as expected and similar for all compounds **1a**–**1f**. It is interesting that in all the structures only space groups with a $\bar{1}$ symmetry are realized. This symmetry is a direct requirement of the molecule, because in each structure the half molecule is repeated using the $\bar{1}$ centre in the plane of the phosphorus–sulfur ring.

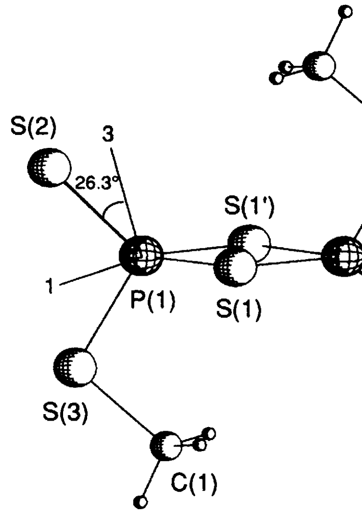

Fig. 4 Orientation of the principal axes of the nuclear magnetic shielding tensor of compound **1a** calculated by the IGLO method [axis 2 is perpendicular to the S=P–S(3) plane]

Table 2 Crystallographic and selected experimental data for compounds **1c** and **1d**

	1c	**1d**
Formula	$C_{12}H_{22}P_2S_6$	$C_{14}H_{14}P_2S_6$
M_r	420.6	436.6
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$ (no. 14)	$P2_1/n$ (no. 14)
a/pm	875.5(4)	649.6(20)
b/pm	2285.5(8)	609.5(7)
c/pm	964.8(6)	2435.3(60)
β/°	92.33(2)	91.34(10)
$U/10^{-30}$ m^3	1928.9	964
Z	4	2
D_c/g cm^{-3}	1.448	1.504
F(000)	880	448
Crystal size/mm	0.2 × 0.2 × 0.1	0.3 × 0.2 × 0.1
μ(Mo-Kα)/mm^{-1}	0.86	0.87
θ-Range for data/°	$1 \leqslant \theta \leqslant 28$	$1 \leqslant \theta \leqslant 32$
hkl Ranges	$-3 \leqslant h \leqslant 11$ $-20 \leqslant k \leqslant 12$ $-12 \leqslant l \leqslant 2$	$-4 \leqslant h \leqslant 9$ $-9 \leqslant k \leqslant 0$ $-10 \leqslant l \leqslant 36$
Scan angle	(0.9 + 0.35tan θ)	(1.0 + 0.35tan θ)
Scan mode	$\bar{\omega}$-scan	$\bar{\omega}$-scan
Reflections measured	6042	4452
Unique reflections	3231	799
Used reflections ($F_o > 4\sigma$)	2068	633
R_{int} (for merging)	0.0272	0.0215
Weighting scheme parameters[a]	$a = 0.0416, b = 0.67;$ $q = 1.0; f = 0.333\,33$	$a = 0.0978, b = 16.68;$ $q = 1.0; f = 0.0333\,33$
Extinction coefficient	0.000 26	Not refined
$R1$[b]	0.0346	0.0933
$wR2$[c]	0.0724	0.2666

[a] $w = q/[\sigma^2F_o + (aP)^2 + bP]$ with $P = f(\max.F_o^2 \text{ or } 0) + (1 - f)F_c^2$. [b] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [c] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}$.

In the cyclohexyl compound **1c** there are two independent molecules formed in this way with only small differences in their geometrical arrangement (see Table 3 and Fig. 5; atomic coordinates are in Table 4). The packing of the two different molecules in the unit cell is plotted in Fig. 6. There are two chains formed by the different molecules running along the *b* axis and alternately arranged in direction of axis *c*. Both molecules are characterized by the chair conformation of the

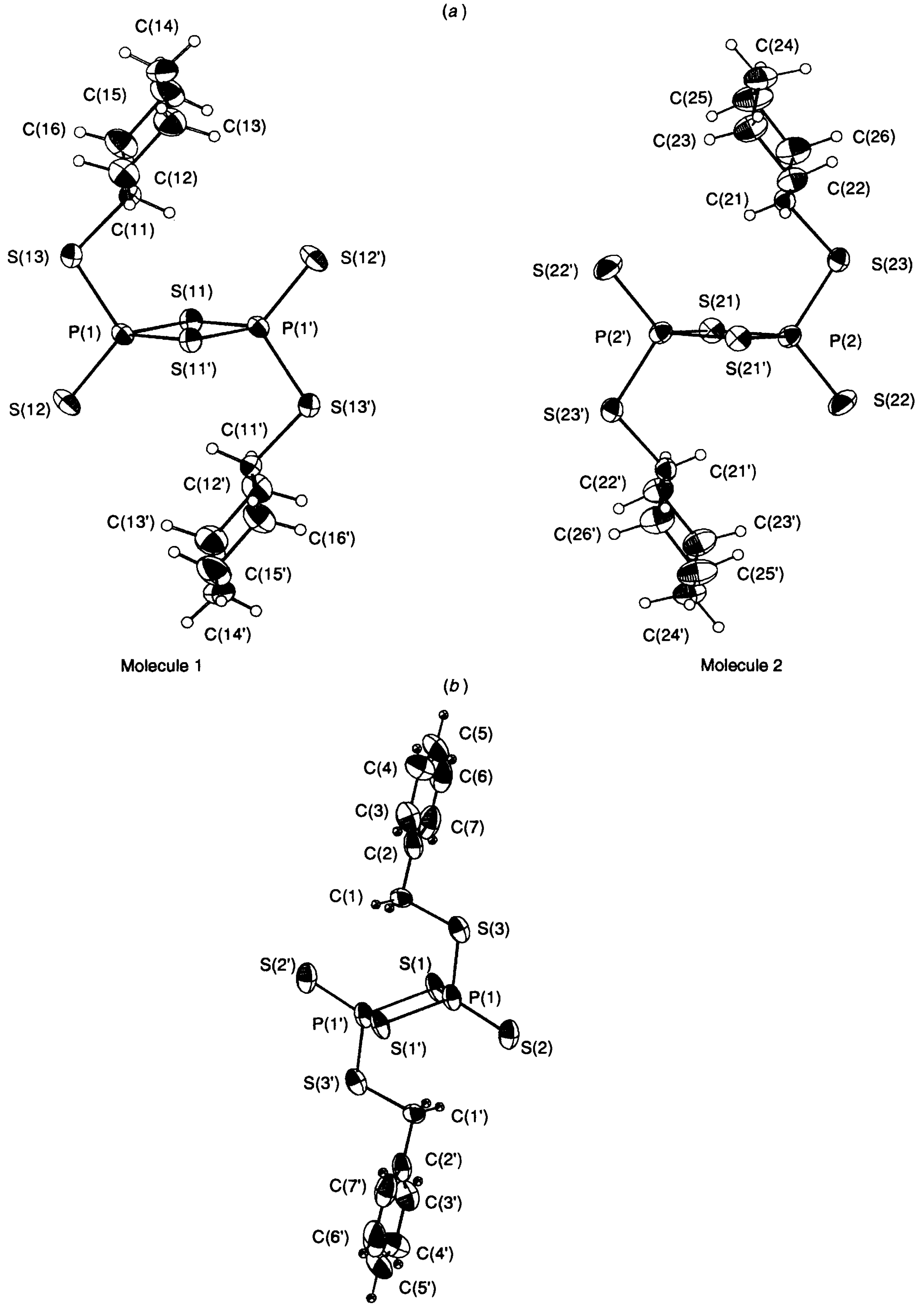

Fig. 5 ORTEP[29] drawings of the molecules of (*a*) 2,4-bis(cyclohexylsulfanyl)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane **1c** and (*b*) 2,4-bis(benzylsulfanyl)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane **1d**

cyclohexyl ligands. The exocyclic bridging sulfur occupies an equatorial position on the cyclohexyl ring. This leads to a nearly right-angled orientation of the ligand with respect to the planar PS_2P ring.

The torsion angle S=P–S–C in **1c** (molecule 1 −175.8°, molecule 2 177.2°) confirms the γ-*anti* arrangement of the cyclohexyl substituent and the S atom of the P=S group. Larger differences in torsion angles of both molecules are observed for P–S–C–C (see Table 3). The values reflect different large deviations from an eclipsed conformation of P(1) and the H atom attached to C(11) and P(2) and the H atom attached to C(21), respectively.

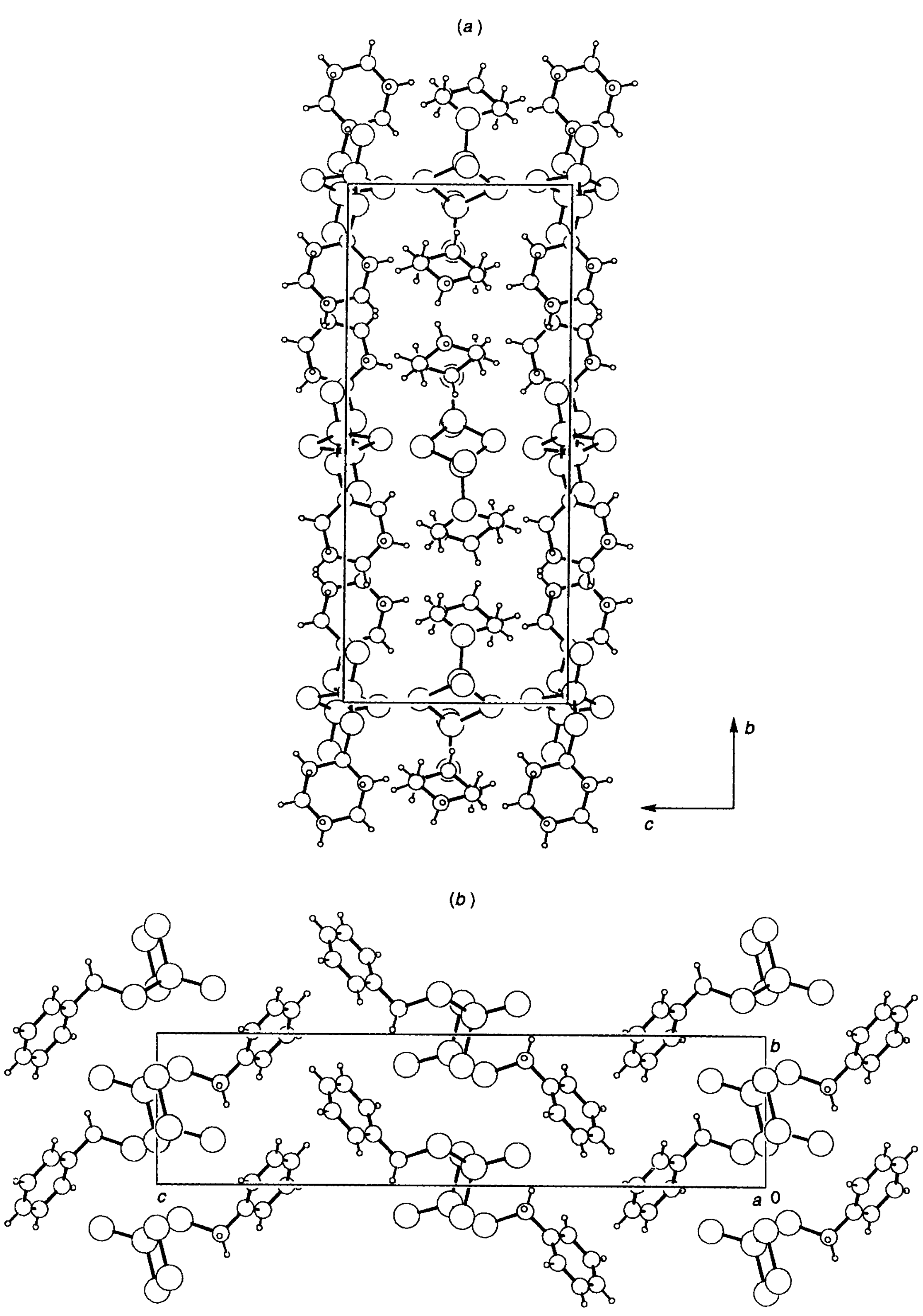

Fig. 6 Packing of the molecules (*a*) **1c** and (*b*) **1d** in the unit cell (viewed along the *a* axis, *b* vertical and *c* horizontal to the plane of the paper); program used PLUTON 89[30]

A further interesting result is obtained by comparing the angles between the PS_2P ring plane and the S–C bond for the different compounds. Only the cyclohexyl compound has a remarkably different value for this angle (Me, 43.2°; Et, 42.2°, $PhCH_2$, 42°; Ph, 41.6°; *p*-MeC_6H_4, 42.45°, cyclo-C_6H_{11}, 44.0°/45.0°).

The bond lengths and angles for the benzyl compound **1d** are given in Table 5 and atomic coordinates in Table 6. Although **1d** contains an aromatic system it is not comparable with the phenyl and *para*-tolyl compounds. The pure aromatic rings directly connected to the sulfur form more compact molecules. In this case there is no reason to expect any disorder for the ligands.

If the ligand is bonded *via* a sp^3-hybridized carbon, which is

Table 3 Selected bond lengths (pm), bond angles (°) and torsion angles (°) of **1c** with standard deviations in parentheses

Molecule 1		Molecule 2	
P(1)–S(11)	210.7(2)	P(2)–S(21)	211.3(2)
P(1′)–S(11)	211.6(2)	P(2′)–S(21)	210.8(2)
P(1)–S(12)	191.0(2)	P(2)–S(22)	191.2(2)
P(1)–S(13)	204.4(2)	P(2)–S(23)	204.5(2)
S(13)–C(11)	183.6(4)	S(23)–C(21)	182.6(4)
P(1)–S(11)–P(1′)	86.41(5)	P(2)–S(21)–P(2′)	86.79(5)
P(1)–S(13)–C(11)	105.13(13)	P(2)–S(23)–C(21)	105.42(13)
S(11)–P(1)–S(12)	117.07(6)	S(21)–P(2)–S(22)	116.61(7)
S(11)–P(1)–S(13)	110.12(6)	S(21)–P(2)–S(23)	109.64(6)
S(11)–P(1)–S(11′)	93.59(5)	S(21)–P(2)–S(21′)	93.21(6)
S(12)–P(1)–S(13)	109.70(6)	S(22)–P(2)–S(23)	109.42(7)
S(12)–P(1)–S(11′)	116.73(6)	S(22)–P(2)–S(21′)	116.98(7)
S(13)–P(1)–S(11′)	108.55(6)	S(23)–P(2)–S(21′)	110.00(6)
S(13)–C(11)–C(12)	109.40(30)	S(23)–C(21)–C(22)	110.80(30)
S(13)–C(11)–C(16)	109.50(30)	S(23)–C(21)–C(26)	108.70(30)

Molecule 1	
S(12)–P(1)–S(13)–C(11)	−175.8
P(1)–S(13)–C(11)–C(12)	110.4
P(1)–S(13)–C(11)–C(16)	−126.4
Molecule 2	
S(22)–P(2)–S(23)–C(21)	177.2
P(2)–S(23)–C(21)–C(22)	−101.5
P(2)–S(23)–C(21)–C(26)	134.8

Table 4 Fractional atomic coordinates for non-hydrogen atoms of compound **1c** with standard deviations in parentheses

Atom	*x*	*y*	*z*
Molecule 1			
P(1)	0.619 15(1)	0.457 23(0)	0.481 73(1)
S(11)	0.479 87(1)	0.506 26(0)	0.341 46(1)
S(12)	0.835 24(1)	0.465 66(0)	0.469 39(1)
S(13)	0.561 50(1)	0.370 64(0)	0.469 97(1)
C(11)	0.351 83(4)	0.369 29(2)	0.469 51(4)
C(12)	0.289 70(6)	0.350 63(3)	0.329 01(5)
C(13)	0.116 78(6)	0.346 89(3)	0.326 51(6)
C(14)	0.063 72(7)	0.307 15(3)	0.436 82(9)
C(15)	0.126 11(7)	0.324 87(3)	0.576 21(7)
C(16)	0.300 78(6)	0.329 20(3)	0.583 01(6)
Molecule 2			
P(2)	0.846 75(1)	0.519 21(0)	0.029 31(1)
S(21)	1.036 24(1)	0.492 69(0)	0.155 95(1)
S(22)	0.766 69(1)	0.595 64(0)	0.061 37(1)
S(23)	0.674 84(1)	0.458 92(0)	0.039 32(1)
C(21)	0.762 19(4)	0.388 77(2)	−0.001 31(4)
C(22)	0.722 84(6)	0.371 19(2)	−0.149 32(4)
C(23)	0.785 24(8)	0.311 33(2)	−0.180 03(6)
C(24)	0.730 67(8)	0.266 08(2)	−0.081 51(6)
C(25)	0.770 07(9)	0.283 50(2)	0.066 39(6)
C(26)	0.711 12(8)	0.343 81(2)	0.101 09(5)

realized for the ethyl and benzyl compounds, it is more probable that disorder occurs. For both structures **1b** and **1d** the hydrogen atoms of the complete ligands could not be located by difference electron density synthesis. Only the hydrogen atoms attached to the carbons directly bonded to sulfur could be located by this method. For all other hydrogen atoms the motion or vibration is too high to give a significant electron density peak.

If the ligands are disordered the ^{31}P MAS NMR spectrum would clearly show broad signals, because of small variations in the geometrical and electronic fields of the investigated phosphorus atom. Apart from other sources of error this effect may be one reason for the difficult measurements and insufficient intensity data for the benzyl compound.

Table 5 Selected bond lengths (pm) and angles (°) of **1d** with standard deviations in parentheses

S(1)–P(1)	212(1)	S(3)–P(1)	206(1)
S(1)–P(1′)	211(1)	S(3)–C(1)	184(2)
S(2)–P(1)	191(1)		
P(1)–S(1)–P(1′)	86.7(3)	S(2)–P(1)–S(3)	108.2(4)
P(1)–S(3)–C(1)	104.4(7)	S(2)–P(1)–S(1′)	119.9(4)
S(1)–P(1)–S(2)	117.2(4)	S(3)–P(1)–S(1′)	108.7(4)
S(1)–P(1)–S(3)	108.5(4)	S(3)–C(1)–C(2)	107(2)
S(1)–P(1)–S(1′)	93.3(3)		

Table 6 Fractional atomic coordinates of compound **1d** with standard deviations in parentheses

Atom	*x*	*y*	*z*
P(1)	0.826 2(1)	0.624 5(1)	0.019 9(0)
S(1)	0.867 3(1)	0.290 9(1)	−0.000 3(0)
S(2)	0.734 8(1)	0.703 2(1)	0.091 1(0)
S(3)	0.629 7(1)	0.764 6(9)	−0.037 6(0)
C(1)	0.726 7(3)	0.670 6(4)	−0.103 9(1)
C(2)	0.667 1(4)	0.842 0(4)	−0.145 3(1)
C(3)	0.482 0(5)	0.828 7(5)	−0.174 0(1)
C(4)	0.427 7(7)	0.991 7(7)	−0.212 5(1)
C(5)	0.556 4(11)	1.156 0(10)	−0.220 4(2)
C(6)	0.733 3(10)	1.170 1(8)	−0.193 6(2)
C(7)	0.792 5(5)	1.014 5(5)	−0.156 2(1)
H(11)	0.875 24(34)	0.654 03(36)	−0.101 92(8)
H(12)	0.665 95(34)	0.530 44(36)	−0.113 93(8)

Conclusion

Investigations of the ^{31}P nuclear magnetic shielding tensor of dithiadiphosphetanes of the general formula $[RSP(S)S]_2$ show good agreement between experimental results and IGLO calculations. Isotropic chemical shifts, principal values and the orientation of the shielding tensor in the molecular axes system have been determined. The most shielded component is approximately perpendicular to the PS_2P ring plane, hence the P=S bond axis is nearly parallel to principal axis 3. Changes in the substituent are reflected most by σ_{33}. Although only small differences in the structure parameters occur a dependence of σ_{ii} on P=S bond length, endocyclic S–P–S bond angle and S–P=S bond angle is observed. The results confirm that the nuclear magnetic shielding is a sensitive probe of the electronic structure of a given system and reflects slight changes of the molecular geometry at the observed nucleus.

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