Synthesis, Structure and Solid-state Nuclear Magnetic Resonance Studies of P-Chiral (Dicyclohexylaminosulfanyl)-[(−)-*p*-menthan-3-yloxy]phenylthioxophosphorane†

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P-Chiral (R_P) (dicyclohexylaminosulfanyl)[(−)-*p*-menthan-3-yloxy]phenylthioxophosphorane **1** was synthesized by condensation of (S_P) (−)-*p*-menthan-3-yl phenylthiophosphinate **2** and $(H_{11}C_6)_2NSBr$. The reaction proceeds with retention of configuration at the chiral phosphorus centre. Compound **1** crystallized from chloroform–acetone or chloroform as two polymorphs in proportions depending on the solvent. X-Ray crystallography revealed that in the asymmetric part of the unit cell polymorph **1** contains two independent molecules with *anti* and *syn* geometry of the S=P–S–N fragment and polymorph **1′** contains only one independent molecule with *anti* geometry. Preliminary structural results were obtained by analysis of ^{31}P cross-polarization magic angle spinning NMR spectra. The S=P–S bond angles, P–S and P=S bond lengths were established from the anisotropy $\Delta\delta$ and principal components of the chemical shift tensor, δ_{22} and δ_{33}, respectively. Comparison of geometrical parameters obtained from solid-state NMR spectroscopy with those from X-ray diffraction analysis of single crystals confirms the accuracy of this approach. For the *anti* S=P–S–N conformation the S=P–S bond angle is smaller than the tetrahedral value, and the P–S bond length is 2.09 Å. The *syn* geometry is associated with a larger S=P–S valence angle and longer P–S bond. The trend towards planarity is explained in terms of a π contribution to the P–S single bond.

Our ongoing interests in pseudohalogen chemistry prompted us to deal with P-chiral species with general formula R′R″P(S)SX where X = Br, Cl, NR_2 or R′R″P(S)S (R,R′,R″ = alkyl or aryl).[1] Such compounds are potentially useful as models for mechanistic studies in electrophilic processes, *e.g.* addition of thioxophosphorane sulfenyl halides RR′P(S)SX to unsaturated systems, new strategy for (*Z*)-olefin synthesis as well as understanding the stereochemistry of nucleophilic substitution at two-co-ordinate sulfur.[2–5] The stereospecific synthesis of P-epimeric (S_P, S_P)-bis[(−)-menthyloxy(phenyl)thiophosphoryl] disulfide and an unusual case of steric selection was recently published.[6] In this paper we report the synthesis and intriguing properties in the solid phase of the P-chiral (dicyclohexylaminosulfanyl)[(−)-*p*-menthan-3-yloxy]phenylthioxophosphorane **1** investigated by means of X-ray diffraction and high-resolution solid-state NMR spectroscopy.

Solid-state NMR spectroscopy has become a very powerful tool in the investigation of powdered samples.[7,8] Owing to progress in high-resolution cross-polarization magic angle spinning (CP MAS) techniques it is possible now to obtain liquid-like spectra of solids.[9] In particular, ^{31}P CP MAS NMR spectroscopy, owing to the 100% natural abundance and high sensitivity of the phosphorus-31 nucleus, can provide unique information about the structure, dynamics and properties of materials in easy experiments and reasonable time periods.[10] Moreover in combination with X-ray methods, NMR provides complementary information on the contents and apparent symmetry of the crystallographic unit cell and contributes to an understanding of the phenomenon of polymorphism.

The question of the polymorphism of bulk materials and ambiguity of the space group *versus* solid-state NMR parameters has attracted the attention of several research groups. Penner and Wasylishen,[11] employing ^{31}P CP MAS, found more signals than expected from X-ray diffraction results for a commercial sample of trimesitylphosphine, owing to the presence of two polymorphs in the bulk material. Davies and Dutremez[12] showed that for transition-metal phosphine complexes the results obtained from single-crystal X-ray diffraction are not always consistent with NMR data for powdered samples. Recent ^{31}P CP MAS NMR studies on series of bis(organothiophosphoryl) dichalcogenides reported by Potrzebowski *et al.*[13,14] provide further information in this respect.

The present work reveals another example of polymorphism and describes the influence of changes on the local geometry of the S=P–S–N unit on bond lengths and angles and the relationship between the molecular structure and ^{31}P chemical shift parameters.

Results and Discussion

Synthesis.—The chemistry of organic and heteroorganic sulfenamides was recently reviewed by Craine and Raban.[15] The synthesis of organophosphorus sulfenamides with chiral substituents on the phosphorus centre was developed by Michalski and co-workers.[1,16–19]

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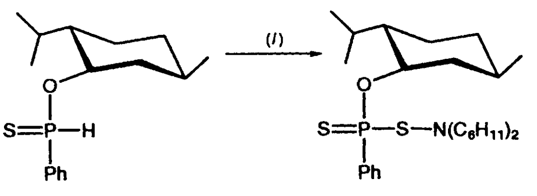
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



2 **1**

Scheme 1 (*i*) $(H_{11}C_6)_2NSBr$, NEt_3

P-Chiral diastereomeric phosphorane sulfenamides $R'R''P(S)SNR_2$ are available in two major ways. First, by condensation of P-chiral phosphorane sulfenyl halides $R'R''P(S)SX$ (X = Br or Cl) with secondary amines [equation (1)], secondly, by condensation of $R'R''P(S)H$ compounds with sulfenamoyl halides R_2NSX [18] [equation (2)]. The latter method was used in this work to synthesize the P-chiral compound **1**.

$$R'R''P(S)SX + NHR_2 \longrightarrow R'R''P(S)SNR_2 \qquad (1)$$

$$R'R''P(S)H + XSNR_2 \longrightarrow R'R''P(S)SNR_2 \qquad (2)$$

Crystalline P-chiral (–)-*p*-menthan-3-yl phenylthiophosphinate **2** is readily available. The *S* absolute configuration at phosphorus in **2** has been deduced by chemical correlation [19] and is here confirmed by X-ray studies. The compound $(H_{11}C_6)_2NSBr$ was prepared by bromolysis of the corresponding disulfide according to the established procedure.[20] The crude bromide was found to be pure enough to obtain a high yield and purity of the sulfenamide **1** prepared by reaction shown in Scheme 1. This reaction proceeds with retention of configuration at the chiral phosphorus centre as unambiguously revealed by X-ray diffraction analysis.

Solid-state ^{31}P *CP MAS NMR Studies.*—Fig. 1 displays the ^{31}P CP MAS spectrum of the P-chiral compound **1** recorded at room temperature. It shows a number of spinning sidebands due to the large chemical shielding anisotropy. The phosphorus can be considered as an isolated nucleus, because the adjacent atoms in tetrahedral arrangement are zero-spin nuclei. The interactions with active isotopes of sulfur, carbon and oxygen at natural abundance are below the detectable limit and were neglected. The dipolar coupling from the protons was eliminated by proton decoupling during data acquisition.

A sample of compound **1** analysed by means of mass spectrometry, elemental analysis and NMR techniques in solution was found to be analytically pure. Surprisingly, for the solid phase crystallized from chloroform–acetone, the ^{31}P CP MAS spectrum shows three different spinning-sideband patterns. Jakobsen and co-workers [21] have reported that the phosphorus nucleus is a very sensitive probe of the local environment and can be employed to establish the enantiomeric purity of optically active compounds. The pure diastereoisomers and the racemic mixture should be distinguishable by solid-state NMR spectroscopy owing to differences in molecular packing. Careful inspection of ^{31}P chemical shift parameters indicates that this is not the case for the sulfenamide **1**. The principal components of the ^{31}P chemical shift tensors δ_{ii} were calculated from the intensities of the spinning sidebands by employing the program MASNMR which is based on the Berger–Herzfeld algorithm.[22,23] The calculated values of the principal tensor elements δ_{ii} and shielding parameters are given in Table 1. The accuracy of the calculations was confirmed by comparison with the theoretical spectrum shown in Fig. 1(*b*).

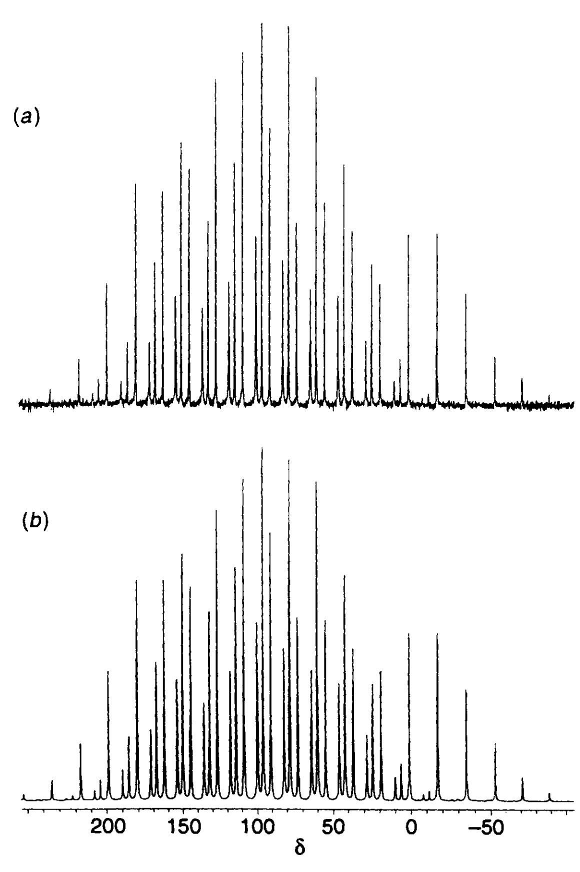


Fig. 1 The ^1H–^{31}P CP MAS NMR spectra of a mixture of polymorphs **1** and **1'**: (*a*) experimental, 8 K data points with 10 Hz line broadening, contact time 1 ms, 100 scans and ν_{rot} = 2100 Hz; (*b*) theoretical, calculated using the MASNMR program (Bruker)

In our recent papers it was shown that ^{31}P CP MAS is a very powerful technique for studying the structural properties of thiophosphorylorganic compounds.[10,24] From an analysis of the shielding parameters and ^{31}P principal components of the chemical shift tensor, δ_{ii}, for bis(organothiophosphoryl) disulfides, conclusions regarding the geometry of the molecule may be drawn. In particular, linear relationships between the S=P–S angles and anisotropy parameters $\Delta\delta$ were found to be useful in the analysis of the class of compounds in question.

The $|\Delta\delta|$ values for the present two high-frequency systems (δ_{iso} 99.0 and 95.1, see Table 1) are similar (*ca.* 140 ppm), whereas the low-frequency system (δ_{iso} 89.8) is characterized by $|\Delta\delta|$ 229 ppm. These differences indicate that the molecular structures of the crystallographic modifications, in particular the S=P–S angles are different. Assuming that the relationships between the molecular structure of a S=P–S–S–P=S backbone and the ^{31}P shielding parameters and δ_{ii}, published previously,[24] are also valid for the present S=P–S–N unit, we conclude that for both high-frequency spinning-sideband systems the S=P–S bond angles are *ca.* 105° whereas for the low-frequency system the S=P–S angle is 114°. Moreover, it is noteworthy that the principal components of the ^{31}P chemical shift tensors δ_{22} and δ_{33} can be correlated to the P–S and P=S bond lengths, respectively. Thus, it is further concluded that the high-frequency systems represent polymorphs with slightly shorter P–S bond lengths (2.08, 2.09 Å) compared to the low-frequency system (P–S *ca.* 2.11 Å). A similar conclusion can be drawn for the P=S bond lengths where it is predicted that for the low-frequency system this distance is about 0.015 Å shorter compared to that of the high-frequency systems.

Fig. 2 displays the spectrum of compound **1** after recrystallization from chloroform of the above sample. The recrystallization procedure was repeated several times. It is interesting that the melting points for the two samples are very different; 375 K before and 360 K after recrystallization. The analysis of the ^{31}P CP MAS results reveals apparent differences between spectra 1 (Fig. 1) and 2 (Fig. 2). The latter contains one spinning-sideband system with traces of two others which are

Table 1 The ^{31}P chemical shift parameters for the polymorphs of compound **1**

Polymorph	Conformation	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	$\lvert\Delta\delta\rvert$ (ppm)	Ω (ppm)	η	κ
1a	*anti*	95.1	189	84	12	141	177	0.76	−0.06
1b	*syn*	89.8	218	114	−63	229	281	0.68	0.11
1′	*anti*[a]	99.0	193	93	11	141	182	0.87	−0.03
	anti[b]	99.0	193	93	11	141	182	0.087	−0.03

[a] Parameters taken from spectrum 1 (Fig. 1). [b] Parameters taken from spectrum 2 (Fig. 2). Estimated errors in δ_{11}, δ_{22}, δ_{33} and $\Delta\delta$ are ± 5 ppm; errors in δ_{iso} are ±0.2 ppm. The principal components of the chemical shift tensor are $\delta_{11} > \delta_{22} > \delta_{33}$. The isotropic chemical shift is given by $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$.

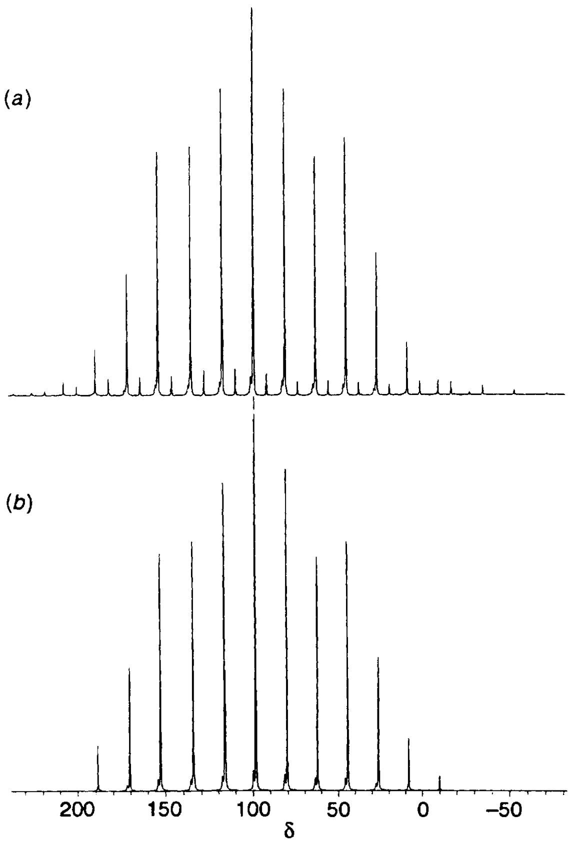


Fig. 2 The ^{1}H–^{31}P CP MAS NMR spectra of polymorph **1′**: (*a*) experimental; (*b*) theoretical. Details as in Fig. 1

from the crystallographic modification observed as the major product in Fig. 1. From a comparison of the chemical shift parameters and ^{31}P principal elements δ_{ii} it is obvious that the main spinning sideband system from spectrum 2 corresponds to the higher-frequency spinning sideband system from spectrum 1.

From NMR studies it is concluded that compound **1** forms at least two polymorphs in the solid phase. The presence of three individual molecules is apparent from the analysis of the ^{31}P CP MAS spectra. Two have very similar molecular structures with respect to the S=P–S unit. The molecular structure of the third is very different. It should be stressed that despite several attempts we were unable to grow polymorphs of **1** in pure form. However, we were able to select from the mixture of crystallographic modifications single crystals suitable for X-ray diffraction studies.

Crystallographic Studies.—Crystallographic data and experimental details for compounds **1** and **2** are shown in Table 2, selected geometrical parameters in Table 3. Fig. 3 shows the ORTEP[25] plot of the thiophosphinate **2**, Fig. 4 that for polymorph **1** with the atom numbering scheme.

Polymorph **1**, crystallized from acetone–chloroform, contains two molecules (**a** and **b**, Table 2) in the asymmetric part of the unit cell. The molecular structures of the two are very different, the S=P–S–N torsion angles being 167.9(2) for **a** and 59.2(3)° for **b**. The *anti* and *syn* arrangement of the S=P–S–N backbone causes significant differences in bond lengths and angles. For the *syn* conformation the P–S bond length is 2.129(3) Å whereas for the *anti* it is 2.090(2) Å. Differences are also seen in the S=P–S valence angles: 115.3(1)(*syn*) and 107.6(1)° (*anti*). The P=S bond of molecule **b** is somewhat shorter compared to that of **a**. The influence of the S=P–S–N conformation on the molecular structure of sulfenamide **1** is thus apparent.

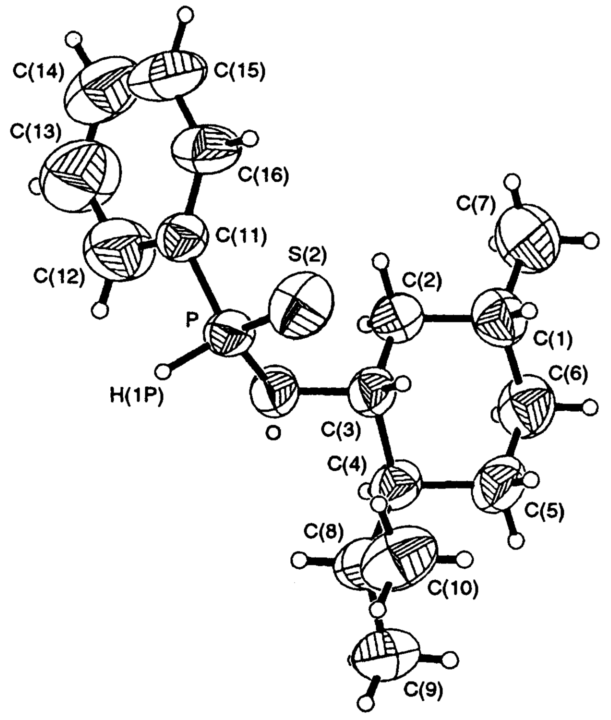


Fig. 3 An ORTEP plot of compound **2**

Similar observations for S=P–S–S systems in series of bis(organothiophosphoryl) disulfides were reported by Gallacher and co-workers[26–28] and Potrzebowski and co-workers.[29,30] This work shows that the explanation proposed for the S=P–S–S–P=S skeleton is also valid for the present S=P–S–N unit. The maximum overlap between the p orbital of sulfur and the d_{xz} and d_{yz} on phosphorus (in ideal point symmetry C_s) takes place when the S=P–S–N fragment is planar (torsion angle 180 or 0°), see Scheme 2. In the *anti* conformation the S=P–S valence angle is smaller than tetrahedral and the P–S bond is short. At low S^1=P^2–S^3–N^4 torsion angle, owing to $S^1 \cdots N^4$ steric interaction, the molecule approaches the eclipsed conformation. Steric interaction results in lengthening of the P–S bond and opens up the S=P–S valence angle by 8° with respect to the *anti* geometry. The differences in S=P–S valence angles and change in P–S bond distances for the two conformations give some measure of the driving force required

Table 2 Crystal data and experimental details *

	1	**1′**	**2**
Molecular formula	$C_{28}H_{46}NOPS_2$	$C_{28}H_{46}NOPS_2$	$C_{16}H_{25}OPS$
M	507.77	507.77	296.41
Space group	$P2_12_12_1$	$P2_12_12_1$	$P1$
a/Å	9.810(1)	9.830(2)	5.833(2)
b/Å	10.821(2)	10.195(1)	8.493(2)
c/Å	56.206(3)	30.430(1)	8.899(3)
α/°			87.56(3)
β/°			77.50(3)
γ/°			83.09(3)
U/Å^3	5966(1)	3049.7(6)	427(3)
Z	8	4	1
D_c/g cm^{-3}	1.131	1.106	1.157
F(000)	2272	1104	160
μ/cm^{-1}	22.4	21.9	24.7
Crystal dimensions/mm	0.2 × 0.4 × 0.4	0.2 × 0.3 × 0.3	0.3 × 0.4 × 0.4
Scan width/°	1.30 + 0.14 tan θ	0.68 + 0.14 tan θ	1.38 + 0.14 tan θ
hkl ranges	0–12, 0–13, 0–70	−12 to 0, −12 to 0, −38 to 0	−7 to 7, −10 to 10, 0–11
No. unique reflections	6124	3247	1928
Decay correction minimum	1.000 07	1.000 09	—
maximum	1.122 37	1.076 27	—
average	1.054 96	1.038 94	—
No. reflections refined [$I \geqslant 3\sigma(I)$]	5172	2904	1891
No. of parameters refined	597	300	175
R	0.0706	0.0525	0.0581
R'	0.0867	0.0560	0.0602

* Details in common: maximum 2θ 150°; scan mode ω–2θ.

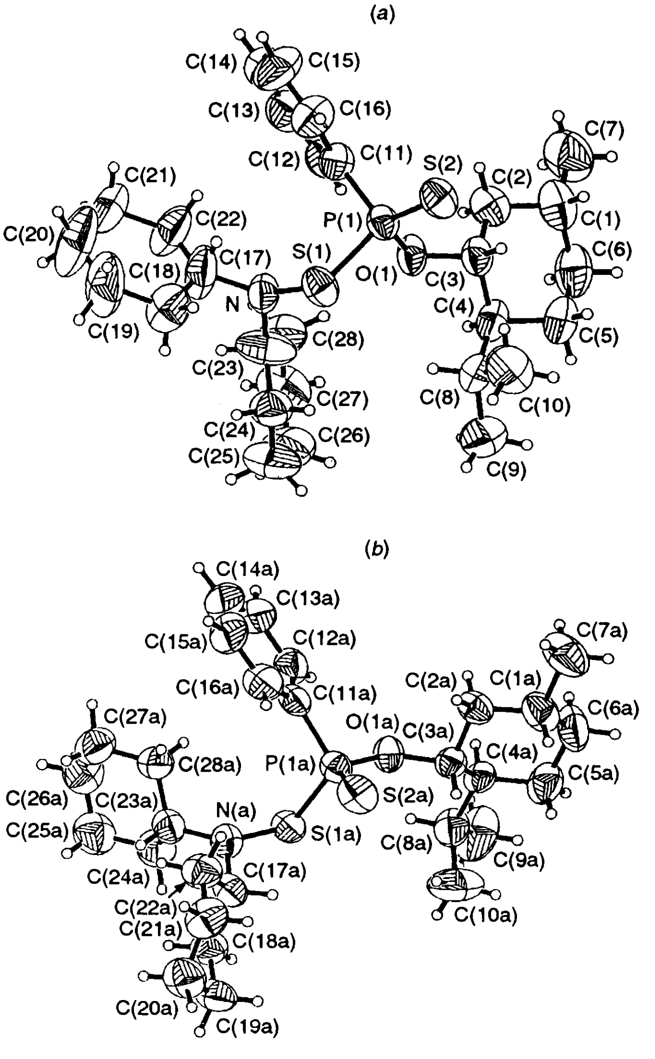
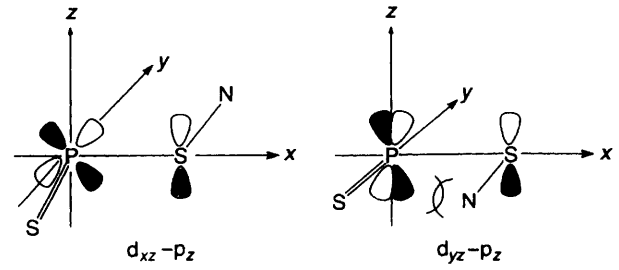


Fig. 4 The ORTEP plots of polymorph **1**: (*a*) molecule with *anti* geometry, (*b*) molecule with *syn* geometry



Scheme 2

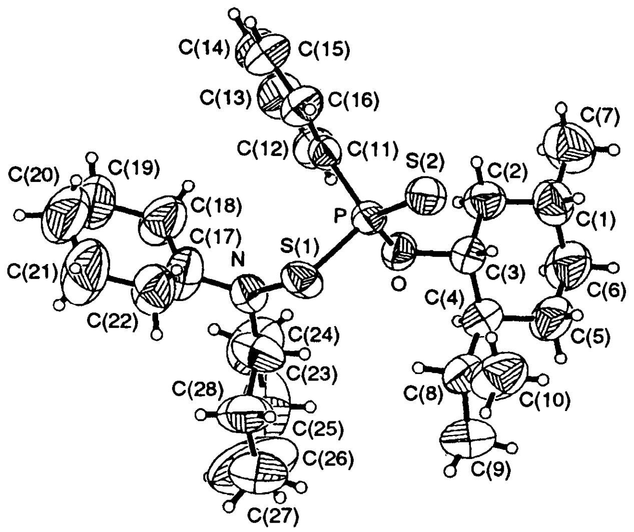


Fig. 5 An ORTEP plot of polymorph **1′**

Table 3 Selected bond lengths (Å) and angles (°)

	1a	**1b**	**1′**	**2**
P–S(1)	2.090(2)	2.129(3)	2.086(1)	1.20(4)*
P–S(2)	1.932(3)	1.921(2)	1.935(1)	1.932(2)
P–O	1.586(5)	1.596(5)	1.566(3)	1.584(3)
P–C(11)	1.817(6)	1.784(9)	1.805(3)	1.795(3)
S(1)–N	1.675(6)	1.676(7)	1.682(4)	—
O–C(3)	1.466(8)	1.453(8)	1.468(5)	1.455(4)
C(1)–C(7)	1.501(16)	1.527(14)	1.536(9)	1.532(9)
C(4)–C(8)	1.526(16)	1.527(11)	1.530(8)	1.533(6)
C(8)–C(9)	1.547(15)	1.493(13)	1.513(10)	1.523(9)
C(8)–C(10)	1.547(15)	1.525(15)	1.542(10)	1.523(9)
N–C(17)	1.399(14)	1.509(11)	1.424(7)	—
N–C(23)	1.438(12)	1.460(12)	1.431(7)	—
Averages in six-membered rings				
C(1)–C(6)	1.522(36)	1.515(17)	1.516(10)	1.526(17)
C(11)–C(16)	1.373(29)	1.353(46)	1.370(32)	1.376(26)
C(17)–C(22)	1.498(6)	1.513(26)	1.488(11)	—
C(23)–C(28)	1.502(4)	1.498(33)	1.500(7)	—
S(1)–P–S(2)	107.6(1)	115.3(1)	105.4(1)	112(2)*
S(1)–P–O	105.4(2)	96.5(2)	106.1(1)	104(2)*
S(1)–P–C(11)	107.1(2)	107.9(3)	108.0(1)	100(2)*
S(2)–P–O	117.1(2)	117.8(2)	117.5(1)	117.3(1)
S(2)–P–C(11)	115.7(2)	114.2(3)	115.5(1)	114.8(1)
O–P–C(11)	103.2(3)	103.2(3)	103.7(2)	106.7(2)
P–S(1)–N	104.4(2)	103.1(2)	105.2(1)	—
P–O–C(3)	125.3(5)	124.7(4)	126.0(3)	123.0(2)
C(2)–C(1)–C(7)	112.3(10)	111.6(9)	111.1(5)	111.6(4)
C(6)–C(1)–C(7)	112.4(10)	109.7(9)	112.3(5)	113.4(5)
O–C(3)–C(2)	108.0(7)	109.2(6)	108.3(4)	110.3(3)
O–C(3)–C(4)	108.4(7)	106.8(5)	109.4(4)	107.6(3)
C(3)–C(4)–C(8)	115.0(7)	113.7(6)	113.1(5)	113.5(3)
C(5)–C(4)–C(8)	115.0(8)	115.3(6)	114.0(5)	113.9(3)
C(4)–C(8)–C(9)	113.4(8)	111.1(8)	113.5(5)	111.6(4)
C(4)–C(8)–C(10)	111.8(8)	114.4(8)	113.1(5)	113.7(5)
C(9)–C(8)–C(10)	112.1(9)	109.9(9)	110.1(5)	111.3(5)
P–C(11)–C(12)	121.8(6)	120.9(7)	122.3(4)	119.7(4)
P–C(11)–C(16)	119.6(6)	121.3(7)	118.1(3)	121.4(3)
S(1)–N–C(17)	116.2(6)	117.7(5)	116.8(4)	—
S(1)–N–C(23)	119.0(5)	119.1(5)	115.6(3)	—
C(17)–N–C(23)	113.7(7)	117.9(6)	116.5(4)	—
N–C(17)–C(18)	119.4(9)	115.5(7)	116.1(5)	—
N–C(17)–C(22)	118.3(9)	109.1(7)	120.1(5)	—
N–C(23)–C(24)	120.2(7)	116.1(7)	114.4(6)	—
N–C(23)–C(28)	114.0(7)	113.4(7)	119.8(5)	—
Averages in six-membered rings				
C(1)–C(6)	110.0(38)	109.6(25)	110.6(26)	110.0(28)
C(11)–C(16)	119.7(10)	120.5(28)	120.0(6)	120.0(12)
C(17)–C(22)	118.3(33)	111.8(23)	115.6(18)	—
C(23)–C(28)	118.0(22)	111.2(36)	117.6(32)	—

* In compound **2** atom S(1) = H(1P).

to obtain a completely planar geometry and of the strength of the p_π–d_π interaction.

Polymorph **1**′, recrystallized from chloroform, contains only one molecule in the asymmetric part of the unit cell. The corresponding ORTEP thermal ellipsoidal plot with atom numbering scheme is shown in Fig. 5. The molecular structure is very similar to that of molecule **a** of polymorph **1**. The torsion angle S=P–S–N is 175.4(1)°. The P=S and P–S bond distances and S=P–S valence angle have values characteristic of *anti* geometry (Table 3).

The absolute configurations at the phosphorus centre for polymorphs **1** and **1**′ are the same and were established to be *R*, that for **2** is *S*. They were assigned on the basis of the Hamilton test and calculations of the η parameters [for **1**, *R* ratio = 1.068 : 1, $\alpha < 10^{-9}$ and η = 1.02(8); for **1**′, *R* ratio = 1.81 : 1, $\alpha < 10^{-9}$ and η = 0.99(8); for **2**, *R* ratio = 1.068 : 1, $\alpha < 10^{-9}$ and η = 1.29(10)].[31,32]

Conclusion

This work shows the power of high-resolution solid-state NMR spectroscopy in structural studies of dithiophosphoryl organic compounds. The ^{31}P CP MAS technique, in simple experiments, allows one to recognize different crystallographic modifications and explain the nature of the polymorphism phenomenon. Moreover, NMR can be used as a preliminary test for selection of suitable crystallographic forms before single-crystal studies.

The selected geometrical parameters of the S=P–S unit can be obtained from analysis of the ^{31}P chemical shift parameters. Recently published relationships between the molecular

Table 4 Non-hydrogen atomic coordinates (× 10^4) for compound **1**

Atom	Molecule **a**			Molecule **b**		
	x	*y*	*z*	*x*	*y*	*z*
P	9 229(2)	6 670(2)	9 402(1)	980(2)	5 454(2)	8 108(1)
S(1)	10 557(2)	7 291(2)	9 137(1)	2 847(2)	5 985(2)	7 945(1)
S(2)	7 399(2)	7 068(2)	9 302(1)	1 159(2)	4 561(2)	8 402(1)
O	9 580(4)	5 250(4)	9 438(1)	329(5)	6 806(4)	8 118(1)
C(1)	7 342(11)	2 882(10)	9 752(2)	−2 166(9)	7 746(9)	8 592(2)
C(2)	8 334(9)	3 951(8)	9 712(2)	−1 590(7)	7 074(7)	8 379(2)
C(3)	8 580(7)	4 245(7)	9 451(2)	−134(7)	7 414(6)	8 334(1)
C(4)	9 131(8)	3 151(6)	9 316(2)	40(7)	8 795(5)	8 295(1)
C(5)	8 157(10)	2 060(8)	9 351(2)	−497(11)	9 445(8)	8 518(2)
C(6)	7 911(11)	1 771(9)	9 606(2)	−1 982(11)	9 146(9)	8 565(2)
C(7)	7 174(15)	2 577(16)	10 011(2)	−3 670(10)	7 446(12)	8 629(3)
C(8)	9 521(9)	3 415(8)	9 058(2)	1 476(9)	9 165(7)	8 219(2)
C(9)	10 284(14)	2 333(11)	8 937(2)	1 529(15)	10 495(9)	8 148(3)
C(10)	8 284(11)	3 853(14)	8 910(2)	2 573(11)	8 897(13)	8 404(2)
C(11)	9 778(7)	7 369(7)	9 680(1)	−27(7)	4 685(6)	7 889(2)
C(12)	10 563(8)	6 736(8)	9 841(2)	−580(9)	5 332(7)	7 698(2)
C(13)	10 993(10)	7 318(10)	10 051(2)	−1 320(10)	4 679(12)	7 528(2)
C(14)	10 591(11)	8 482(12)	10 097(2)	−1 456(11)	3 476(12)	7 531(3)
C(15)	9 814(13)	9 103(9)	9 939(3)	−951(12)	2 792(9)	7 723(2)
C(16)	9 420(10)	8 556(8)	9 730(2)	−235(9)	3 409(7)	7 897(2)
N	12 102(6)	7 200(6)	9 262(1)	3 636(7)	4 629(6)	7 901(1)
C(17)	12 792(14)	8 320(11)	9 294(1)	4 525(7)	4 141(7)	8 099(2)
C(18)	13 271(12)	9 031(8)	9 080(2)	5 994(8)	4 459(7)	8 081(2)
C(19)	13 955(17)	10 252(11)	9 127(2)	6 791(8)	3 922(8)	8 293(2)
C(20)	14 586(17)	10 542(11)	9 363(2)	6 581(11)	2 540(9)	8 318(2)
C(21)	13 997(12)	9 849(8)	9 570(2)	5 076(10)	2 265(9)	8 336(2)
C(22)	13 299(14)	8 629(8)	9 537(2)	4 253(9)	2 793(7)	8 131(2)
C(23)	12 978(12)	6 184(8)	9 200(1)	3 945(8)	4 240(6)	7 658(2)
C(24)	13 167(10)	5 826(8)	8 944(1)	4 678(10)	5 191(9)	7 502(2)
C(25)	14 117(13)	4 758(10)	8 899(2)	5 021(11)	4 673(11)	7 262(2)
C(26)	14 356(17)	3 812(9)	9 090(2)	3 806(12)	4 239(12)	7 136(2)
C(27)	14 041(11)	4 148(10)	9 343(2)	2 996(10)	3 288(10)	7 278(2)
C(28)	13 130(11)	5 235(7)	9 393(2)	2 701(8)	3 791(10)	7 521(2)

Table 5 Non-hydrogen atomic coordinates (× 10^4) for compound **1′**

Atom	*x*	*y*	*z*
P	5 017(1)	2 523(1)	8 863(1)
S(1)	6 212(1)	3 651(1)	8 441(1)
S(2)	3 154(1)	2 942(1)	8 713(1)
O	5 492(3)	1 069(3)	8 799(1)
C(1)	3 462(7)	−1 904(6)	9 146(2)
C(2)	4 326(6)	−679(5)	9 183(2)
C(3)	4 600(5)	−71(4)	8 737(2)
C(4)	5 259(6)	−1 020(5)	8 420(2)
C(5)	4 358(7)	−2 235(5)	8 390(2)
C(6)	4 105(8)	−2 874(6)	8 829(2)
C(7)	3 197(8)	−2 511(7)	9 600(2)
C(8)	5 593(6)	−401(6)	7 975(2)
C(9)	6 446(9)	−1 273(8)	7 682(2)
C(10)	4 320(8)	73(8)	7 725(2)
C(11)	5 513(4)	2 898(4)	9 420(1)
C(12)	6 347(6)	2 094(6)	9 659(2)
C(13)	6 691(6)	2 439(8)	10 091(2)
C(14)	6 215(7)	3 548(7)	10 269(2)
C(15)	5 397(8)	4 361(7)	10 033(2)
C(16)	5 017(6)	4 040(5)	9 608(1)
N	7 825(4)	3 378(4)	8 601(1)
C(17)	8 568(8)	4 480(5)	8 759(2)
C(18)	8 778(9)	4 542(6)	9 239(2)
C(19)	9 657(8)	5 623(7)	9 412(2)
C(20)	9 504(12)	6 902(7)	9 174(2)
C(21)	9 430(11)	6 813(7)	8 683(2)
C(22)	8 503(8)	5 751(5)	8 521(2)
C(23)	8 568(7)	2 449(6)	8 343(2)
C(24)	9 336(9)	1 457(7)	8 605(3)
C(25)	10 099(9)	446(7)	8 341(3)
C(26)	10 554(13)	832(13)	7 890(3)
C(27)	9 694(10)	1 748(8)	7 624(3)
C(28)	9 004(7)	2 800(7)	7 888(2)

Table 6 Non-hydrogen and H(1P) atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*
P	3 637(1)	6 858(1)	7 527(1)
S	6 062(3)	5 835(2)	8 528(1)
O	4 010(5)	6 636(3)	5 728(3)
C(1)	9 705(8)	7 697(6)	3 163(5)
C(2)	7 260(7)	7 954(5)	4 229(4)
C(3)	6 334(6)	6 385(4)	4 713(4)
C(4)	6 110(7)	5 421(4)	3 353(4)
C(5)	8 577(9)	5 179(5)	2 276(5)
C(6)	9 563(9)	6 735(6)	1 804(5)
C(7)	10 728(13)	9 270(8)	2 702(9)
C(8)	5 009(10)	3 877(5)	3 833(6)
C(9)	4 707(12)	2 998(7)	2 444(8)
C(10)	6 309(17)	2 791(6)	4 860(7)
C(11)	2 912(7)	8 945(4)	7 868(4)
C(12)	973(13)	9 726(8)	7 451(9)
C(13)	364(19)	11 342(9)	7 698(13)
C(14)	1 646(19)	12 141(7)	8 443(8)
C(15)	3 607(17)	11 401(7)	8 854(7)
C(16)	4 254(12)	9 775(6)	8 601(5)
H(1P)	1 754(72)	6 411(46)	8 049(46)

structure of bis(organothiophosphoryl) disulfides and phosphorus shielding parameters and principal elements of the chemical shift tensors, δ_{ii}, are applicable also to other dithiophosphorylorganic compounds. The P=S and P–S bond distances and S=P–S valence angles were determined from ^{31}P NMR parameters with sufficient accuracy. Comparing the X-ray data for single crystals and NMR results for powders, the discrepancies in bond distances and angles were 0.02 Å and 2°, respectively.

The results obtained from X-ray diffraction are in excellent agreement with those from solid-state NMR spectroscopy. The two techniques provide complementary information on the question of the polymorphism of compound **1**. Analysis of the molecular structures of the *anti* and *syn* polymorphs provides unambiguous evidence that π interaction contributes to the P–S single bonds at tetrahedral phosphorus.

Experimental

Synthesis of Compound **1**.—Freshly prepared $(H_{11}C_6)_2NSBr$[20] (0.02 mol) in dry hexane (20 cm^3) was added dropwise to a stirred solution of thiophosphinate **2** (0.02 mol) and triethylamine (0.02 mol) in hexane (30 cm^3) at 243 K. Stirring was continued for a few minutes at 243 K and then the mixture was allowed to warm to room temperature. It was filtered through a sintered funnel and the triethylamine hydrobromide sludge rigorously washed with dry hexane (three times with 10 cm^3). The solvent was removed under reduced pressure and the crude product purified by crystallization from acetone–chloroform. Yield 92%; $\delta(^{31}P)$ ($CDCl_3$) 97.4.

NMR Measurements.—Cross-polarization magic angle spinning ^{31}P NMR spectra were recorded on a Bruker MSL 300 instrument at 121.49 MHz in the presence of high-power proton decoupling. Powder samples of compound **1** were placed in cylindrical rotor and spun at 2.0–4.5 kHz. For the ^{31}P experiments the field strength for ^1H decoupling was 1.05 mT, contact time 5 ms, repetition rate 6 s and spectral width 50 kHz and 8 K data points represented the free induction decay. Spectra were accumulated 100 times which gave a reasonable signal-to-noise ratio. The ^{31}P chemical shifts were calibrated indirectly through bis(dineopentoxythiophosphoryl) disulfide (δ 84.0).

The principal elements of the ^{31}P chemical shift tensor δ_{ii} and shielding parameters were calculated employing the MASNMR program. Details of the method and accuracy of calculations are exhaustively discussed elsewhere.[22,23] The δ_{ii} values were used for calculation of the shielding parameters, *i.e.* anisotropy $\Delta\delta$, asymmetry η, span Ω and skew κ.[33] If $|\delta_{11} - \delta_{iso}| > |\delta_{33} - \delta_{iso}|$ and $\delta_{11} > \delta_{22} > \delta_{33}$ then equations (3) and (4) are applicable. If $|\delta_{11} - \delta_{iso}| < |\delta_{33} - \delta_{iso}|$ and $\delta_{11} > \delta_{22} > \delta_{33}$ then the corresponding expressions are (5) and (6). Moreover equations (7) and (8) are also applicable.

$$\Delta\delta = \delta_{11} - [(\delta_{22} + \delta_{33})/2] \tag{3}$$

$$\eta = (\delta_{22} - \delta_{33})/(\delta_{11} - \delta_{iso}) \tag{4}$$

$$\Delta\delta = \delta_{33} - [(\delta_{11} + \delta_{22})/2] \tag{5}$$

$$\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso}) \tag{6}$$

$$\Omega = \delta_{11} - \delta_{33} \tag{7}$$

$$\kappa = 3(\delta_{22} - \delta_{iso})/\Omega \tag{8}$$

Crystallography.—The crystal and molecular structures of compounds **1**, **1′** and **2** were determined using data collected on a CAD4 diffractometer. Polymorphs **1** and **1′** formed crystals in the orthorhombic system, space group $P2_12_12_1$, **2** crystallized in the triclinic system, space group $P\bar{1}$. Crystal data and experimental details are given Table 2. Intensity data for all compounds were collected at room temperature using graphite-monochromatized Cu-Kα radiation (λ = 1.541 78 Å). Lattice constants were refined by least-squares fit of 25 reflections in the range θ 21.7–27.9 for **1**, 20.1–27.2 for **1′** and 10.5–26.8° for **2**. The decrease in intensities of three standard reflections was 20.6 (**1**), 13.7 (**1′**) and 2.9% (**2**) during 106.0, 48.9 and 28.0 h of exposure, respectively. A decay correction was applied for **1** and **1′**. The structures were solved by direct methods and refined by full-matrix least squares on F. Hydrogen atoms were placed geometrically and allowed to ride with fixed thermal parameters equal to 1.3 times that of the equivalent isotropic thermal parameter of the parent atom, except for the H(1P) phosphoryl hydrogen in compound **2** which was found in a Fourier-difference map and refined isotropically. Anisotropic thermal parameters were refined for all non-hydrogen atoms in each structure.

The final refinement converged to $R = 0.0706$, $R' = 0.0867$ with $w = 1/[\sigma^2(F) + 0.005\,254F^2]$ for **1**, $R = 0.0525$, $R' = 0.0560$ with $w = 1/[\sigma^2(F) + 0.000\,2276F^2]$ for **1′** and $R = 0.0581$, $R' = 0.0602$ with $w = 1/[\sigma^2(F) + 0.012\,041F^2]$ for **2**. The largest shift/e.s.d. in the last cycle was 0.005 for **1**, 0.001 for **1′** and 0.005 for **2**. The largest residual peaks in the final Fourier difference map were 0.527 for **1**, 0.294 for **1′** and 0.459 e Å^{-3} for **2**.

Structure solutions were carried out with the SDP crystallographic computing package[34] and SHELXS 86 program,[35] structure refinement with the SHELXTL package.[36] Scattering factors were taken from ref. 37. Final atomic coordinates are given in Tables 4–6.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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