^{31}P CP MAS NMR Studies of Bis(organothiophosphoryl) Disulfides. Correlation of Chemical Shift Tensors and Shielding Parameters to Molecular Structure

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The principal elements of the ^{31}P chemical shift tensors δ_{ii} for a series of bis(organothiophosphoryl) disulfides have been calculated by employing the graphical method of Berger and Herzfeld from spinning sideband intensities. The linear relationship between the S=P–S angle and anisotropy and asymmetry parameters has been shown. The orientation of the principal components δ_{ii} with respect to the molecular frame was postulated. It has been suggested that the δ_{22} component is oriented along the P–S bond, whereas δ_{11} is oriented approximately along the direction bisecting the S–P=S angle. Furthermore, the ^{31}P CP MAS NMR spectra provide information about the number of magnetically and crystallographically non-equivalent phosphorus centres.

Solid state NMR spectroscopy has recently become a very powerful tool in investigations of powder patterns.[1,2] Owing to the recent progress in high resolution cross polarization magic angle spinning (CP MAS) techniques, it is possible to obtain liquid-like spectra of the solids.[3] As the NMR experiment is a sensitive probe of the local environment, when combined with X-ray diffraction data it can provide complementary information into the contents and apparent symmetry of the crystallographic unit cell. Furthermore, the solid state NMR data can be used as a unique source of information about the static and dynamic properties of powders.[4,5] In particular, the ^{31}P nucleus, owing to its high sensitivity and large chemical shift anisotropy (CSA), is an excellent probe for such projects.

Phosphorus–sulfur systems have been attractive for investigators for many decades, but only very recently have they been used as models for solid state NMR studies.[6–8] These investigations have been mainly carried out for series of inorganic phosphorus sulfides with the general formula P_xS_y ($x = 4$, $y = 3, 4, 5, 7, 9, 10$). For instance, Eckert *et al.* in demonstrating the linear relationship between the S–P–S angle and asymmetry parameter, revealed that it is possible to correlate the ^{31}P chemical shielding tensor with local environments for this class of compounds.[9] Unfortunately, so far there have been no similar studies for organic dithiophosphates. In this paper, we wish to report the first attempt to correlate ^{31}P shielding parameters with the molecular structure of dithiophosphates employing the bis(organothiophosphoryl) disulfides as models. As shown in other papers the class of compounds in question shows a strong dependence of geometrical parameters on the S=P–S–S–P=S backbone conformation.[10] Since such parameters as S=P–S angle, P–S and P=S bond lengths vary in a broad range (from 101–116° and from 2.080–2.153 and 1.894–1.938 Å respectively) phosphoroorganic disulfides could be considered as excellent material for this work.

Experimental

NMR Spectroscopy.—Cross-polarization magic angle spinning solid state ^{31}P NMR spectra were recorded on a Bruker 300 MSL instrument with high-power decoupling at 121.49 MHz. Powder samples of disulfides were placed in a cylindrical rotor and spun at 3.0–4.2 kHz. For the ^{31}P NMR experiments, the field strength for ^{1}H decoupling was 1.05 mT with a contact time of 5 ms, a repetition time of 6 s and a spectral width of 20 kHz; 8 K data points represented the FID. Spectra were accumulated 12–500 times, which gave a reasonable signal-to-noise ratio. The ^{31}P chemical shifts were calibrated indirectly through the 85% phosphoric acid peak set at 0 ppm.

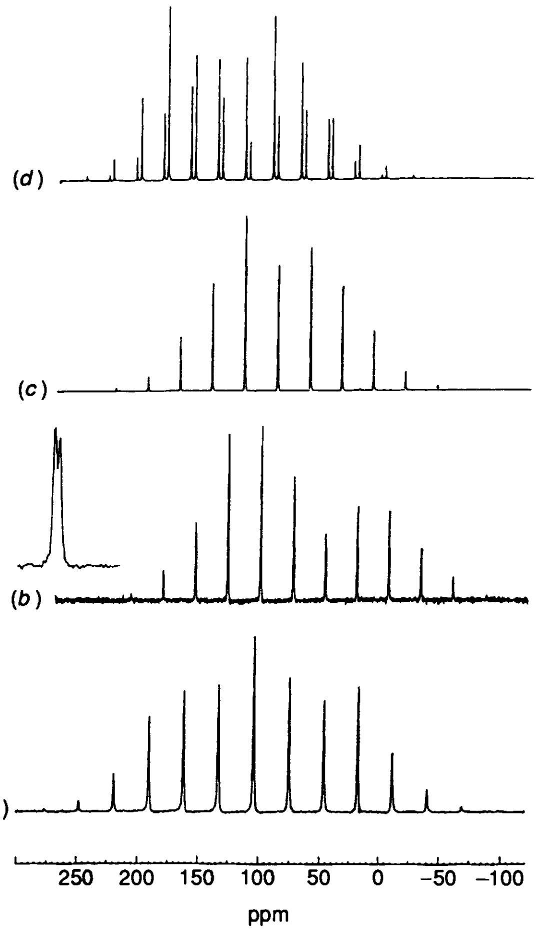

Fig. 1 121.49 MHz ^{31}P CP MAS spectra of bis(organothiophosphoryl) disulfides. (*a*) P-epimeric (S_p,S_p)-bis[(−)menthyloxy(phenyl)-thiophosphoryl] disulfide (**1**), (*b*) bis(diphenoxythiophosphoryl) disulfide (**2**), (*c*) bis[*tert*-butyl(phenyl)thiophosphoryl) disulfide (**3**), (*d*) bis[*tert*-butyl(methoxy)thiophosphoryl] disulfide (**4**). All spectra have 8 K data points, a contact time of 5 ms and 12–500 scans.

The principal elements of the chemical shift tensor of the ^{31}P resonance for powdered samples were calculated from spinning sideband intensities using the method of Berger and Herzfeld.[11]

Table 1 Selected geometrical parameters for the S=P–S unit in a series of bis(organothiophosphoryl)disulfides

Disulfide	P–S bond length/Å	S=P–S angle/°	P=S bond length/Å	Reference
Bis(diisopropoxythiophosphoryl) disulfide	2.085	104.8	1.920	24
Bis(dineopentoxythiophosphoryl)disulfide	2.088	106.6	1.911	25
Bis[(–)menthyloxy(phenyl)thiophosphoryl] disulfide	2.101	103.8	1.926	26
Bis(diphenoxythiophosphoryl) disulfide	2.080	107.7	1.900	10
Bis(dimethoxythiophosphoryl) disulfide	2.088	105.4	1.904	25
Bis[*tert*-butyl(methoxy) thiophosphoryl] disulfide	2.093	101.2	1.923	
	2.139	115.3	1.913	10
Bis[*tert*-butyl(phenyl)thiophosphoryl] disulfide	2.153	114.0	1.938	10
Bis(5,5′-dimethyl-2-thiono-1,3,2-dioxaphosphorinan-l-yl) disulfide	2.112	116.0	1.894	
	2.118	116.0	1.891	23

Table 2 ^{31}P Chemical shift parameters for a series of bis(organothiophosphoryl) disulfides[a]

Disulfide	δ_{33}	δ_{22}	δ_{11}	δ_{iso}	$\Delta\delta$	η	Reference
Bis[*tert*-butyl(methoxy)thiophosphoryl] disulfide	204.8	107.9	31.8	114.8	134.9	0.85	This work
	219.7	176.7	–4.7	133.7	193.5	0.33	
Bis[(–)menthyloxy(phenyl)thiophosphoryl] disulfide	184.8	95.9	–10.5	90.1	150.9	0.88	This work
Bis(diisopropoxythiophosphoryl) disulfide	178.4	79.4	–20.4	79.1	149.2	0.99	22
Bis(dimethoxythiophosphoryl) disulfide	199.8	90.4	–29.4	87.1	174.8	0.94	
	196.9	87.9	–32.4	84.1	174.8	0.94	22
Bis(dineopentoxythiophosphoryl) disulfide	185.8	98.7	–34.8	84.00	179.6	0.73	22
Bis(diphenoxythiophosphoryl) disulfide	177.7	98.3	–49.2	75.6	187.2	0.64	This work
Bis[*tert*-butyl(phenyl)thiophosphoryl] disulfide	222.3	122.8	–41.6	102.1	216.7	0.65	This work
Bis(5,5′-dimethyl-2-thiono-1,3,2-dioxaphosphorinan-1-yl) disulfide	181.5	149.7	–83.4	82.6	249.1	0.19	
	182.1	140.0	–107.8	71.4	268.8	0.23	23

[a] Errors in the experimental principal components of the chemical shift tensor are ±2 ppm.

Employing the commonly used notation, the isotropic chemical shift is given by eqn. (1),

$$\delta_{iso} = (1/3)(\delta_{11} + \delta_{22} + \delta_{33}). \qquad (1)$$

The asymmetry parameter, η, is given by eqn. (2)

$$\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso}). \qquad (2)$$

The anisotropy parameter, $\Delta\delta$ is defined as eqn. (3) with

$$\Delta\delta = \delta_{33}{}^{-} (1/2)(\delta_{11} + \delta_{22}) \qquad (3)$$

principal elements δ_{ii} defined by eqn. (4)

$$|\delta_{33} - \delta_{iso}| \geqslant |\delta_{11} - \delta_{iso}| \geqslant |\delta_{22} - \delta_{iso}|. \qquad (4)$$

Results and Discussion

Selected geometrical parameters of the S=P–S unit are shown in Table 1. Fig. 1 displays the ^{31}P CP MAS NMR spectra of the P-epimeric (S_p,S_p)-bis[(–)menthyloxy(phenyl)thiophosphoryl] disulfide **1** (*a*), bis(diphenoxythiophosphoryl) disulfide **2** (*b*), bis[*tert*-butyl(phenyl)thiophosphoryl] disulfide **3** (*c*), and bis[*tert*-butyl(methoxy)thiophosphoryl] disulfide **4** (*d*), recorded at room temperature. In the spectra, each sample shows a number of spinning sidebands due to the large shielding anisotropy. Since all adjacent atoms in the tetrahedral arrangement are zero spin nuclei, the phosphorus can be considered as an isolated nucleus. The dipolar coupling from the protons of the alkyl and aryl groups was eliminated by proton decoupling during data acquisition. Non-zero spin isotopes of sulfur and oxygen show only minute coupling with the phosphorus and were below the detectable limits. Since the experimental procedure ensured that the phosphorus resonances were governed only by the chemical shift interactions, it was possible to obtain the shielding anisotropy ($\Delta\delta$), the asymmetry parameter (η) and the isotropic values (δ_{iso}) using MAS lineshape analysis. The calculated values of the principal elements of the chemical shift tensors and shielding parameters obtained from the graphical methods of Berger and Herzfeld are given in Table 2.[11]

The ^{31}P CP MAS NMR spectra are consistent with the crystallographic data and can be used to establish the number of the crystallographically non-equivalent sites. The observed singular isotropic line symmetrically flanked by spinning sidebands shows that both disulfides **1** and **3** consist of one half molecule as independent unit per unique volume. Moreover, these results provide unambiguous evidence that both phosphorus centres of the disulfide have the same absolute configuration. As recently shown by Jakobsen and co-workers, the ^{31}P nucleus is a very sensitive probe of the local environment and can even be employed to establish the enantiomeric purity of optically active compounds.[12]

Two lines appear in the spectrum of disulfide **2** [Fig. 1(*b*)] because the unit cell consists of one molecule per unique volume as an independent unit. The crystallographically non-equivalent phosphorus centres are clearly assigned. Judging from the spinning sideband intensities and small differences in isotropic chemical shifts, it can be concluded that both phosphorus sites P-1 and P-2 for disulfide **2** are in identical environments. The most spectacular result was obtained when bis[*tert*-butyl(methoxy)thiophosphoryl] disulfide **4** was investigated [see Fig. 1(*d*)]. The rough analysis of ^{31}P spectra shows that intensities of appropriate spinning sidebands differ significantly. The difference in chemical shifts of isotropic lines was found to be 18.9 ppm. Furthermore, the shielding parameters: anisotropy $\Delta\delta$ and asymmetry η calculated from spinning sideband intensities show dramatic differences for both phosphorus centres (Table 2). From X-ray studies it is known that both P-1 and P-2 phosphorus atoms have the same absolute configuration, hence the observed discrepancies cannot be

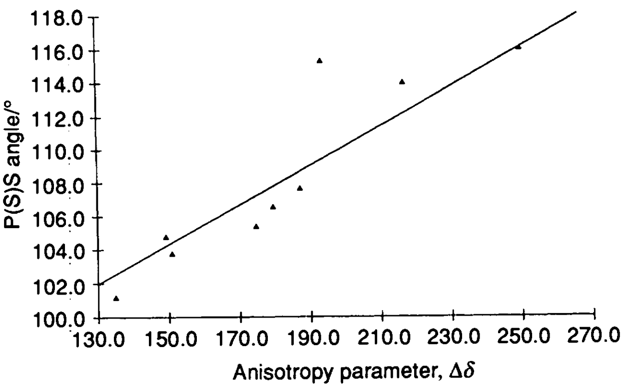

Fig. 2 The relationship between the S=P–S angles and anisotropy parameters Δδ for series of bis(organothiophosphoryl) disulfides with a correlation coefficient of 0.91

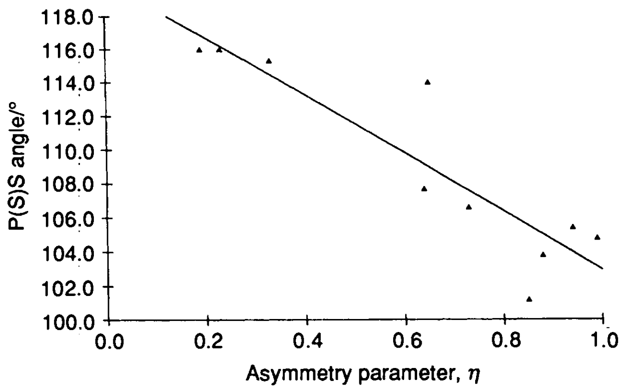

Fig. 3 The relationship between the S=P–S angles and asymmetry parameters η for a series of bis(organothiophosphoryl) disulfides with a correlation coefficient of 0.90

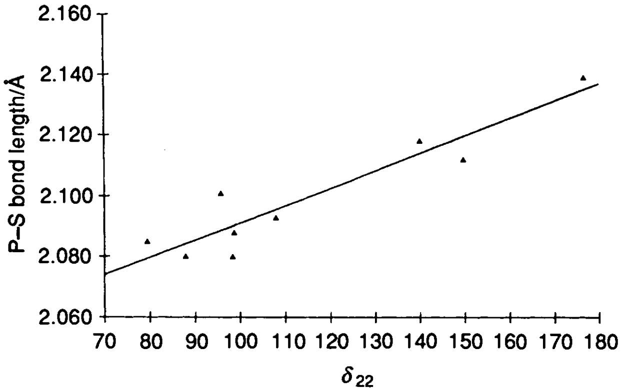

Fig. 4 The relationship between the P–S bond length and the δ_{22} component of the chemical shift tensor for series of bis(organothiophosphoryl) disulfides. The correlation coefficient is 0.94 with data (filled circle) for bis[*tert*-butyl(phenyl)thiophosphoryl] disulfide (3) omitted (see text).

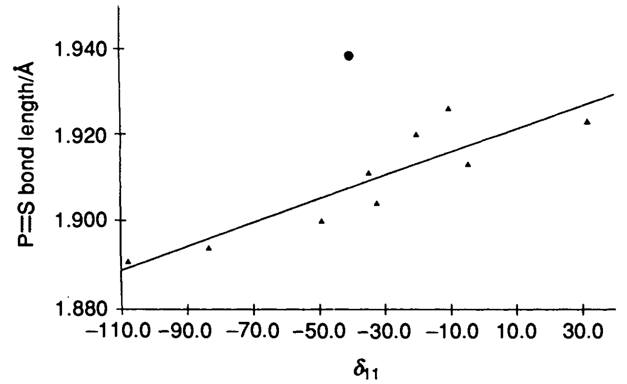

Fig. 5 The relationship between the P=S bond length and the δ_{11} component of the chemical shift tensor for a series of bis(organothiophosphoryl) disulfides. The correlation coefficient is 0.89 with data (filled circle) for bis[*tert*-butyl(phenyl)thiophosphoryl] disulfide (3) omitted (see text).

explained in terms of different stereochemistry. On the other hand, the crystallographic data clearly indicate that both centres have apparently different local environments. The appropriate S=P–S angles and P–S bonds were found to be 101.2°, 115.3° and 2.093 Å, 2.139 Å, respectively. From these results, it was obvious that changes of shielding parameters reflect the degree of distortion of the S=P–S unit for bis(organothiophosphoryl) disulfides and further, these parameters can be correlated with molecular structure.

It is commonly known that ^{31}P shielding paramers can be considered as a source of unique information about the molecular structure of the phosphorus moieties and some useful correlations have been shown.[13] For instance, a linear relationship between the asymmetry parameters and intracyclic O–P–O bond angles for a series of cyclic thioxophosphates was found by Dutasta *et al.*[14] Grimmer observed a linear relationship between the chemical shift anisotropy and P–O bond length for various axially symmetric halogenophosphates.[15]

More general conclusions given by Herzfeld *et al.*, combined chemical shift anisotropy with the degree of departure from cubic symmetry and are consistent with the recent paper of Turner and co-workers who confirmed that ^{31}P CSA increases linearly with the deviation of O–P–O angle from the tetrahedral value.[16,17]

Shown in Fig. 2 is the relationship between the S=P–S angles and anisotropy parameters Δδ. As in the case of the phosphates the changes of ^{31}P anisotropy Δδ *vs.* the geometrical parameters are apparent, although the experimental points are slightly scattered (the correlation coefficient is 0.91). A similar trend was observed for correlation of S=P–S angles *vs.* the asymmetry parameter. This relationship displayed in Fig. 3 shows that with increasing S=P–S angle there is a decrease in asymmetry, η. The correlation coefficient was found to be 0.90.

The orientation of the chemical shift tensor with respect to the molecular frame can be completely specified from single crystal NMR studies. Kohler,[18] Herzfeld[16] and Burlinson[19] have shown that the orientation of the ^{31}P chemical shift tensors of phosphates and phosphate esters are relatively constant and principal axes of the tensors are oriented roughly along the P–O bond directions. As there are no similar monocrystal studies for dithiophosphates, from our investigation of powder patterns only hypothetical orientations of chemical shift tensor *vs.* dithiophosphate units could be obtained.

Shown in Fig. 4 is the correlation of P–S bond length *vs.* δ_{22} chemical shift tensor component. δ_{22} increases linearly with P–S bond length for all cases with the exception of bis[*tert*-butyl(phenyl)thiophosphoryl] disulfide 3 in which this relationship is not obeyed. The correlation coefficient, with data for disulfide 3 omitted (shown as filled circle), was found to be 0.94. Fig. 5 displays the correlation of P=S bond length with most upfield δ_{11} chemical shift tensor component. As in the previous case, the data for disulfide 3 differs significantly from other experimental points (correlation coefficient of 0.89 with data for disulfide 3 omitted).

It can be postulated from these results that for O–P–O and C–P–O disulfides the δ_{22} component is oriented roughly in the P–S bond direction, whereas the δ_{11} is oriented approximately along the direction bisecting the S–P=S angle.

The bis[*tert*-butyl(phenyl)thiophosphoryl] disulfide **3** [where, contrary to other cases, phosphorus is directly bonded to alkyl and aryl residues (P–C bonds) and the S=P–S–S–P=S unit represents a *syn–syn* arrangement] is presumably characterized by its different orientation of the chemical shift tensor with respect to the molecular frame when compared with other disulfides.

As seen in Table 2, appropriate disulfides show a large disparity in the values of isotropic chemical shifts, from 71 to 134 ppm. From semiempirical studies of Van Wazer and Lechter, it has been shown that the ^{31}P chemical shift is influenced by three main factors;[20,21] the number and electronegativity of the nearest-neighbour ligands, the bond angles about the phosphorus atom and the occupation of the π-bonding orbitals on the phosphorus atom. In discussion of the isotropic chemical shifts for disulfides no factors can be ignored and considered separately. For instance, the shielding effect of the *tert*-butyl group directly bonded to phosphorus is apparent (disulfides **3** and **4**). Furthermore, analysis of the bis[*tert*-butyl(methoxy)thiophosphoryl] disulfide provides straightforward evidence that a change of S=P–S bond angle about the phosphorus can cause a difference of up to *ca.* 19 ppm in the isotropic values.

Conclusions

We have investigated the series of bis(organothiophosphoryl) disulfides by ^{31}P CP MAS technique in order to establish the relationship between the geometrical and NMR parameters. The ^{31}P solid state NMR studies show that it is possible to correlate the anisotropic chemical shift information with the molecular structure of the dithiophosphates. As shown, both anisotropy and asymmetry parameters can be correlated with the S=P–S angle. Since different types of models with O–P–O, O–P–C and C–P–C fragments were employed in this project the experimental points were not ideally fitted, but both relationships are obvious. Hence, it can be concluded that changes of shielding parameters are caused by distortion of the S=P–S unit.

Furthermore, the orientation of the principal elements of the chemical shift tensor with respect to the molecular frame has been postulated. On the basis of relationships between δ_{11} and δ_{22} components and geometrical parameters it has been postulated that the δ_{22} component is oriented along the P–S bond whereas the upfield δ_{11} component is oriented along the direction of the angle bisecting the S=P–S fragment. However it should be stressed that unambiguous assignment of the orientation of the principal components of the chemical shift tensor can be obtained only from monocrystal NMR studies. Further investigations, including assignment of the principal elements of the chemical shift tensor δ_{ii} to molecular structure, are in progress.

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References

1 C. A. Fyfe, *Solid State NMR for Chemists*, C.F.C. Press, Guelph, Ontario, 1983.
2 C. S. Yannoni, *Acc. Chem. Res.*, 1982, **15**, 201.
3 M. Mehring, *Principles of High Resolution NMR in Solids*, 2nd edn., Springer, Berlin, 1983.
4 *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*, ed. R. A. Komoroski, VCH Publishers Inc., Deerfield Beach, Florida, 1986.
5 M. J. Potrzebowski, *Magn. Reson. Chem.*, 1992, **30**, 35.
6 T. Bjorholm and H. J. Jakobsen, *J. Am. Chem. Soc.*, 1991, **113**, 27.
7 T. Bjorholm, *Chem. Phys. Lett.*, 1988, **143**, 259.
8 H. J. Jakobsen, V. Langer and P. J. Daugaard, *J. Magn. Reson.*, 1988, **76**, 162.
9 H. Eckert, C. S. Liang and G. D. Stucky, *J. Phys. Chem.*, 1989, **93**, 452.
10 P. Knopik, L. Łuczak, M. J. Potrzebowski, J. Michalski, J. Błaszczyk and M. W. Wieczorek, manuscript in preparation.
11 J. Herzfeld and A. E. Berger, *J. Chem. Phys.*, 1980, **73**, 1021.
12 K. V. Andersen, H. Bildsoe and H. J. Jakobsen, *Magn. Reson. Chem.*, 1990, **S47**, 28.
13 S. Un and M. P. Klein, *J. Am. Chem. Soc.*, 1989, **111**, 5119.
14 J. P. Dutasta, J. B. Roberts and L. Wiesenfeld, *Phosphorus Chemistry*, eds. L. D. Quinn and J. G. Verkade, American Chemical Society, Washington D.C., 1981.
15 A. R. Grimmer, *Spectrochim. Acta, Part A*, 1978, **34**, 941.
16 J. Herzfeld, R. G. Griffin and R. A. Haberkorn, *Biochemistry*, 1978, **17**, 2711.
17 G. L. Turner, K. A. Smith, R. J. Kirkpatrick and E. Oldfield, *J. Magn. Reson.*, 1986, **70**, 408.
18 S. J. Kohler, J. D. Ellet and M. P. Klein, *J. Chem. Phys.*, 1976, **50**, 4451.
19 N. E. Burlinson, B. A. Dunnell and J. A. Ripmeister, *J. Magn. Reson.*, 1986, **67**, 217.
20 J. H. Lechter and J. R. Van Wazer, *Top. Phosphorus Chem.*, 1967, 75.
21 J. H. Lechter and J. R. Van Wazer, *J. Chem. Phys.*, 1965, **44**, 815.
22 P. J. Chu and M. J. Potrzebowski, *Magn. Reson. Chem.*, 1990, **28**, 477.
23 G. Grossmann, personal communication.
24 S. Lawton, *Inorg. Chem.*, 1970, **9**, 2269.
25 M. Potrzebowski, J. H. Reibenspies and Z. Zhong, *Heteratom. Chem.*, 1991, **2**, 455.
26 A. Łopusiński, L. Łuczak, J. Michalski, A. E. Kozioł and M. Gdaniec, *J. Chem. Soc., Chem. Commun.*, 1991, 889.

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