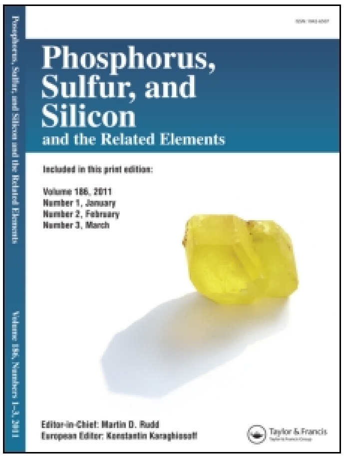

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METHYLTRITHIOPHOSPHONIC ACID AND RELATED COMPOUNDS - SYNTHESIS, SOLUTION, AND SOLID-STATE NMR SPECTROSCOPY AS WELL AS SHIELDING TENSOR CALCULATIONS

J. Hahn[a]; U. Drexler[a]; S. Oimann[a]; G. Grossmann[b]; G. Ohms[b]; K. Krüger[b]
[a] Institut für Anorganische Chemie der Universität zu Köln, Köln, Germany [b] Institut für Analytische Chemie der Technischen Universität Dresden, Dresden, Germany

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METHYLTRITHIOPHOSPHONIC ACID AND RELATED COMPOUNDS - SYNTHESIS, SOLUTION, AND SOLID-STATE NMR SPECTROSCOPY AS WELL AS SHIELDING TENSOR CALCULATIONS

J. HAHN[a,*], U. DREXLER[a], S. OIMANN[a], G. GROSSMANN[b,*], G. OHMS[b] and K. KRÜGER[b]

[a]*Institut für Anorganische Chemie der Universität zu Köln, Greinstraße 6, D-50939 Köln, Germany;* [b]*Institut für Analytische Chemie der Technischen Universität Dresden, Mommsenstraße 13, D-01062 Dresden, Germany*

Dedicated to Prof. Dr. Marianne Baudler on the occasion of her seventy-fifth birthday.

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Methyltrithiophosphonic acid (**1**) has been prepared in a pure state. The thermal decomposition of **1** into 2,4-dimethyl-2,4-dithio-1,3,2,4-dithiadiphosphetane (**3**) proceeds via dimethylpentathiodiphosphonic acid (**2**), which has been characterized by its ^1H and ^{31}P high resolution NMR parameters and by a derivatization reaction with norbornadiene. Solid-state ^{31}P CP MAS spectra of **1**, **3**, and the related compounds, 3,5-dimethyl-3,5-dithio-1,2,4,3,5-trithiadiphospholane (**4**), and 3,6-dimethyl-3,6-dithio-1,2,4,5,3,6-tetrathiadiphosphorinane (**5**), have been measured. The experimentally determined phosphorus anisotropic shielding tensors are compared with results of IGLO calculations. From a comparison of the experimental values with those calculated for different geometry optimized conformations of **1**, **4**, and **5** structural assignments became possible: In the solid state **1** most probably shows a trans orientation of the H-S-P=S unit, **4** probably realizes a half-chair and **5** a chair conformation, both with bisaxial orientation of the methyl groups. Using the orientation of the shielding tensor in the molecular framework obtained from IGLO calculations and the experimentally determined σ_{ii} values, the calculated shielding ovaloids have been plotted in order to visualize the variation of the shielding value in dependence on the molecule orientation relative to the magnetic field direction. The shielding or deshielding contributions of localized molecular orbitals (LMO) available from IGLO calculations have also been inspected: Principal axis 3, corresponding to the most shielding value σ_{33}, nearly coincides with the P=S double bond for all molecules. In

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*Corresponding authors.

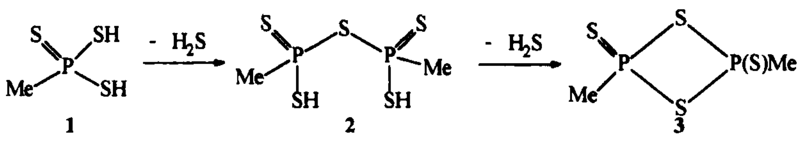
spite of large deshielding contributions from P-C and P-S single bonds the high shielding along this axis results from the very low P═S LMO contribution.

Keywords: methyltrithiophosphonic acid; dimethylpentathiodiphosphonic acid; addition reaction; phosphorus sulfur heterocycles; high resolution NMR; solid state NMR; chemical shift anisotropy; IGLO calculations

INTRODUCTION

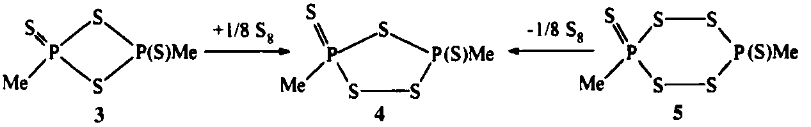
Because of their high versatility the esters and thioanhydrides of organotrithiophosphonic acids have intensively been studied for many decades. Recently it has been found that these compounds also represent interesting objects for solid state NMR investigations since they exhibit strong anisotropic shielding.[1] It must be expected that the anisotropic shielding tensors provide much more structural information than can be extracted from the isotropic value. However, to understand the meaning of these parameters it is necessary to develop correlations between shielding tensors and structural properties from appropriate model compounds. In this work methyltrithiophosphonic acid (**1**)[2] and three related compounds, the *trans*-form of 2,4-dimethyl-2,4-dithio-1,3,2,4-dithiadiphosphetane (**3**),[3] 3,5-dimethyl-3,5-dithio-1,2,4,3,5-trithiadiphospholane (**4**),[4] and the trans configurated chair form of 3,6-dimethyl-3,6-dithio-1,2,4,5,3,6-tetrathiadiphosphorinane (**5**),[4,5] have been chosen as models. These compounds offer the advantage of showing identical substitution patterns at the phosphorus atoms. Furthermore their molecular weights do not exceed the limit, which prohibits the calculation of reliable nuclear magnetic shielding tensors. Theoretical calculations are needed because they provide the correlation between the orientation of the principal axes of the shielding tensors and the molecular geometry. This information is mostly not available from the solid-state MAS NMR spectra.

From a chemical point of view the trithiophosphonic acid **1** is of special interest since it represents the parent compound of many well known thioesters MeP(S)(SR)$_2$ and of the phosphorus sulfur heterocycles **3**–**5**. Thus the dithiadiphosphetane **3** may be understood as the thioanhydride of **1** (see equation 1)



(1)

and the tetrathiadiphosphorinane **5** is the hypothetical oxidation product of the acid (in fact **5** is obtained from the disilylester of **1** by ringclosing oxidation reactions[4,5]). The five-membered heterocycle **4** can be synthesized either by the sulfurization of **3** or by sulfur elimination of **5**[6] (equation 2).



(2)

In contrast to its cyclic thioanhydride **3** and the related esters mentioned above, the acid **1** is quite unstable. It readily reacts with water (oxygen) to the corresponding oxoacids and dihydrogensulfide (sulfur). It has also been reported[2] that the acid thermally loses dihydrogensulfide even at low temperatures. Although it may be assumed, that this decomposition proceeds according to equation (1), the reaction has not yet been studied nor has the intermediate **2** been observed so far. During our solid-state NMR measurements of the acid **1**, signals with chemical shifts appropriate for compound **2** have been detected. Thus reaction (1) has been studied in more detail.

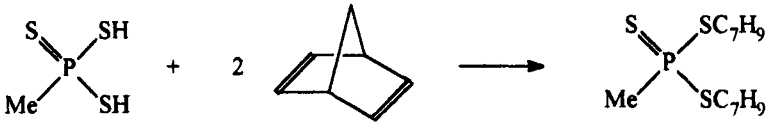
RESULTS AND DISCUSSION

Preparative Results

Of the two reactions, which have been reported for the synthesis of organotrithiophosphonic acids, the conversion of the sodium salts into the acids via ion exchange[7] and the hydrolysis of the corresponding silylesters,[2] only the latter can be applied to generate the extremely reactive methyl compound. In order to get **1** in very high purity the original synthetic procedure was slightly modified: The hydrolysis was carried out in toluene solution at −40°C (instead of −30°C) using a mixture of water/acetonitrile (1/1) (instead of pure water). Under these conditions a quasi homogeneous solvent-reactant-mixture is obtained and the reaction is finished before the separation of water can be observed. Thus the reaction rate could be increased considerably and less by-products were produced. Recrystallization from toluene yielded a white microcrystalline powder of pure methyltrithiophosphonic acid. At the melting point of −4°C, which could be determined for the first time, decomposition under dihydrogensulfide elimination is observed. Very slow decomposition of the solid begins at −10°C (not at −30°C, as reported earlier[2]).

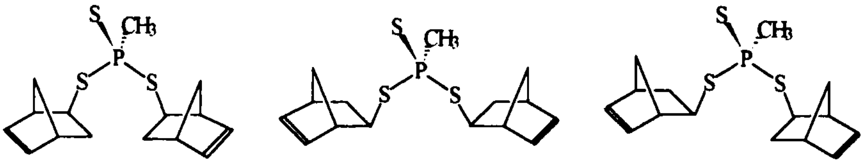
Dihydrogensulfide elimination from the acid leads to the condensation products **2** and **3** [see equation (1)]. Although extreme care was taken to protect the acid from water and oxygen small amounts of by-products probably resulting from oxoacids could not be avoided. After 3–4 h at −4°C about 70% of the acid was converted into dimethylpentathiodiphosphonic acid **2**. Prolongation of the reaction time did not lead to considerable amounts of **3** but only increased the formation of by-products. 2,4-Dimethyl-2,4-dithio-1,3,2,4-dithiadiphosphetane **3** (cis and trans isomer in the ratio 1/5) was formed on further stirring of the melt at room temperature.

The diphosphonic acid **2**, which could be observed for the first time as an intermediate of the condensation reaction (1) was characterized by its ^1H and ^{31}P NMR spectra (see below). Because of the low stability of **2** further characterization was only possible by derivatization. Since the SH functional group of thiophosphonic acids readily adds to alkenes,[8] this type of addition reaction was expected to be also appropriate for the formation of pentathiodiphosphonic acid derivatives. In order to avoid decomposition of the acid, the addition must be carried out at −30 to −20°C. Thus, the reactivity of the system was first checked by reacting the more easily available trithiophosphonic acid **1** with a series of different unsaturated hydrocarbons: trimethylvinylsilane, cyclopentadiene, norbornene, norbornadiene, bis(trimethylsilyl)-ethine, and phenylethine. Only norbornadiene was found to react quantitatively to the diester under the required conditions and only one of the two double bonds was involved in the addition reaction (equation 3).



1 **6** (3)

As could be expected, a large number of isomers is produced by the addition to norbornadiene. The trithiophosphonate anion may attack the double bond from above or from below, from the right or from the left side leading to four different configurations at the norbornenyl group (exo/R, exo/S, endo/R, endo/S). Since also the P atom may become asymmetric, in general $2^5 = 32$ different isomers of **6** are possible. However, for symmetry reasons only 10 pairs of diastereomers or meso-forms can be distinguished by NMR: three exo-exo-forms (R-R/S-S, RrS = SrR, SsR = RsS; statistical probability 2:1:1), three endo-endo-forms (R-R/S-S, RrS = SrR, SsR = RsS; statistical probability 2:1:1), and four exo-endo-forms (RRR/SSS, RRS/SSR, SRR/RSS, RSR/SRS; statistical probability 2:2:2:2). In the notation characterizing the diastereomers (for example RRS/SSR) a sequence of three letters (RRS) indicates the configuration of the two sulfur substituted carbon atoms (first and last letter) and of the P atom (letter in the middle). If the two norbornenyl substituents of a molecule show identical configuration (R-endo) the P atom is not asymmetric as indicated by the notation R-R.


SrR RsS R-R

exo-exo-isomers of trithiophosphonic acid bis(norbornenyl) ester (**6**)

Even though the addition reaction should be thermodynamically controlled, a strong effect disturbing the product distribution resulting from statistical considerations is only expected for endo- and exo-orientation. Since it may be assumed that the exo-form is favoured over the endo-form the three exo-exo-diastereomers (relative abundance ≅ 2 : 1 : 1) should represent the main products followed by the four exo-endo-forms (relative abundance ≅ 1 : 1 : 1 : 1). The lowest concentration must be expected for the three endo-endo-diastereomers (relative abundance ≅ 2 : 1 : 1). This assumption is in agreement with the ^{31}P NMR spectrum of the product mixture (Figure 1) showing three strong signals (g, d, i;

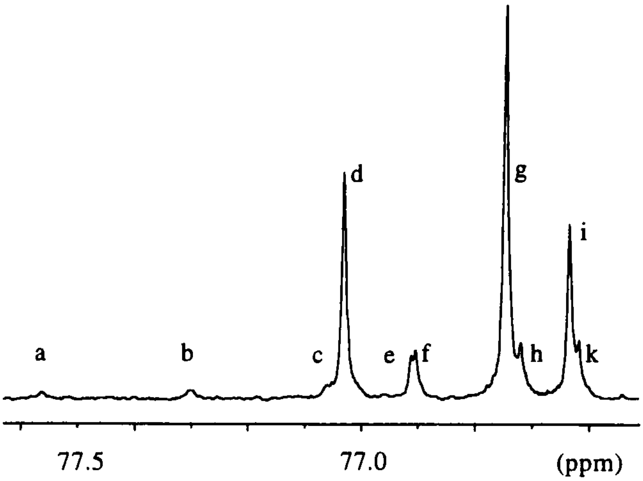
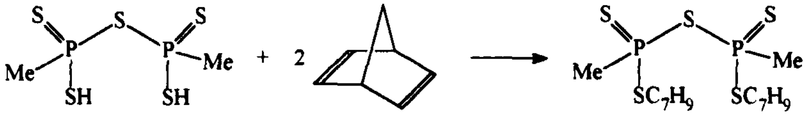


FIGURE 1 ^{31}P{^{1}H}-NMR spectrum of methyltrithiophosphonic acid bis(norbornenyl) ester (**6**) in $CDCl_3$ at 23°C, frequency: 81.02 MHz; exo-exo-isomers: d, g, i; endo-endo-isomers: a, b, c; exo-endo-isomers: e, f, h, k.

relative intensities ≅ 2:1:1), four smaller signals of nearly identical intensities (e, f, h, k), and three very small signals (b, a, c; relative intensities ≅ 2:1:1). Apart from the number of the signals and their relative intensities the formation of the addition products is indicated by the observed chemical shifts (16 ppm downfield from the signal of the acid **1**). Further evidence for the formation of the expected products is given by the ^{13}C NMR (DEPT 135) and mass spectrum (see experimental).

Since a slight excess of norbornadiene quantitatively transfers the phosphonic acid **1** into the dinorbornenyl ester **6** a similar result was expected for the reaction with the diphosphonic acid **2** (equation 4).


(4)

2 **7**

The ^{31}P NMR spectrum of the product mixture confirmed that **2** was quantitatively transferred into the dinorbornenyl ester **7**. However, in consequence of a large number of possible isomers, the addition product shows a spectrum of many overlapping singlets (centred at 95–98 ppm, 10 ppm downfield from the signal of the diphosphonic acid **2**) which could not be assigned to single isomers. The higher stability of the ester allowed the characterization by mass spectroscopy, which was not possible in the case of the rather reactive parent compound **2**. The mass spectrum, which is not influenced by the presence of the complex isomeric mixture, clearly indicates the identity of **7** (see experimental). This result indirectly confirms the existence of the diphosphonic acid **2**.

High Resolution NMR Spectroscopy

The ^{1}H and ^{31}P NMR parameters of methyltrithiophosphonic acid **1** were found to be identical with those reported in the literature.[2] On diluting a saturated solution of **1** in chloroform (concentration about 10%, $\delta = 60.6$) by the factor two a high field shift of 0.6 ppm was observed. This effect is in agreement with the finding that the isotropic δ-value of the solid-state spectrum (see below) shows a low field shift relative to the value found in solution. Dimethylpentathiodiphosphonic acid (**2**) shows the following significant structural features deducible from its NMR spectra:

- the presence of two chemically equivalent Me-groups and of two chemically equivalent P atoms connected by a $^{2}J(PSP)$ coupling constant
- CH_3- and SH-protons in the ratio 3:1.

Since the acidic protons of pentathiodiphosphonic and trithiophosphonic acid, the latter was present as by-product in the sample studied by proton NMR (either **1** or **3** must be accepted as by-product), undergo rapid exchange, they do not show separate resonance signals. Nevertheless the ratio of the CH_3- and SH-protons could be calculated from the integrals of the two methyl resonances (^{31}P-decoupled) of the mono- and diphosphonic acid and the integral of their common SH signal. The experimental result of 2.8 : 1 is sufficiently close to the theoretical value.

The more important structural information is provided by the undecoupled ^1H and ^{31}P NMR spectra. The signals of the methyl groups and of the phosphorus atoms can be assigned to an $A_3A'_3XX'$-system and thus indicate the presence of two chemically equivalent Me-groups and of two chemically equivalent P atoms. However, the information about the P,P-coupling constant was only available from very weak outer lines of the A- or X-part of the spectrum. Although

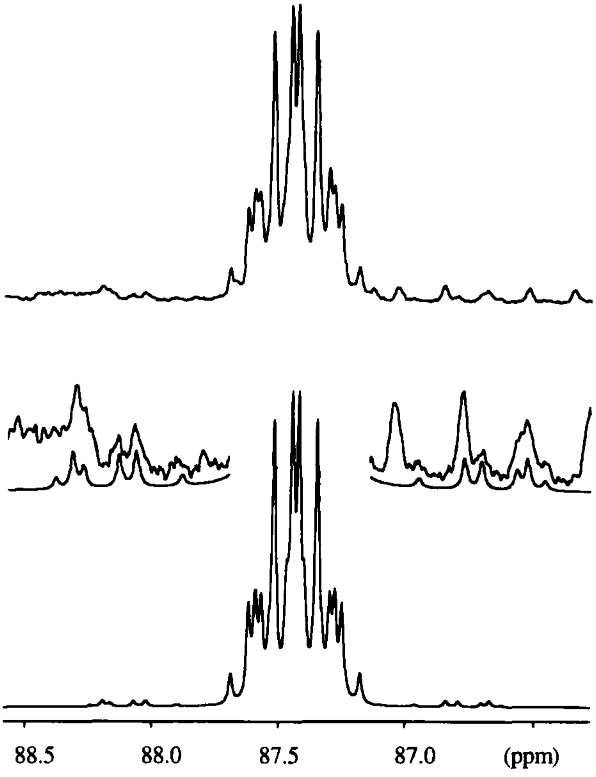


FIGURE 2 Experimental (top) and calculated (bottom) ^{31}P NMR spectrum of dimethylpentathiodiphosphonic acid (**2**) in CS_2/C_6D_6 (5/1) at −30°C, frequency: 81,02 MHz.

TABLE I NMR parameters of the $A_3A_3'XX'$ spin system of dimethylpentathiodiphosphonic acid **2** in CS_2/C_6D_6 at −30°C.

$\delta(^{31}P)$	$^2J(P\text{-}S\text{-}P)$	$^2J(P\text{-}C\text{-}H)$	$^4J(P\text{-}S\text{-}P\text{-}C\text{-}H)$	$\delta(CH_3)$
87.4 ppm	50.7 Hz	−14.4 Hz	0.6 Hz	2.12 ppm

these outer lines were partly hidden by the signals of small amounts of impurities they could be identified in the ^{31}P part by the comparison of two spectra run at 121 and 81 MHz, respectively. Only the line distance to signals resulting from impurities is influenced by the field difference. Within the X-(or A-)part the lines of the $A_3A'_3XX'$-system merely depend on coupling constants and are therefore not shifted with respect to each other when the field is changed. The simulated spectrum (obtained with the iterative computer program "PERCH"[9]) fits very well to the main lines of the spectrum as well as to the small ones identified by the method just described (see Figure 2). The NMR parameters of the simulated spectrum (Table I) agree very well with the structure of the diphosphonic acid **2**. Especially the $^2J(PP)$ coupling constant of 50.7 Hz is indicative of the formation of a P-S-P structure unit of an acyclic compound.

The $A_3A'_3$-part of the spectrum calculated with the parameters of Table I also fits the experimental NMR lines of the methyl groups very well (though partial overlapping with the methyl signal of the monomeric acid **1** occurs). The weak outer lines of the experimental spectrum, which were assigned by comparison with the calculated ones, could be confirmed by selective population transfer (SPI) experiments.

^{31}P Solid-State NMR and IGLO Calculations

^{31}P CP MAS spectra of methyltrithiophosphonic acid have been measured in the crystalline state at −40°C. Figure 3a presents the sideband spectrum of the pure sample.

Immediately after increasing the sample temperature to −20°C first traces of decomposition and oxidation products could be detected as sideband-free signals of a fluid layer, when a single-scan spectrum was measured. Through accumulation the new signals became saturated and were suppressed in the spectrum. After the temperature had been kept at −20°C for 50 minutes and for further 70 minutes at −10°C a CP MAS sideband spectrum could no longer be detected, since the sample had molten. A spectrum reflecting this state is shown in Figure 3b. Since the heterocycles **4** and **5** are much more stable than the acid the corresponding ^{31}P CP MAS spectra have been measured at room temperature. The analysis of the sideband spectra obtained from the three compounds (**1**, **4**,

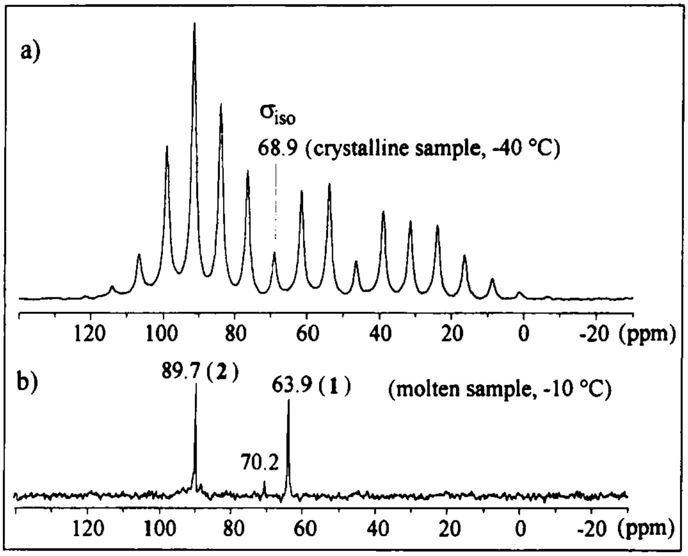


FIGURE 3 a) ^{31}P CP MAS spectrum of methyltrithiophosphonic acid **1**, ν_{rot} = 915 Hz, b) ^{31}P spectrum after the degradation of **1** due to formation of **2**.

and **5**) resulted in the experimental principal values σ_{11}, σ_{22}, σ_{33} of the nuclear magnetic shielding tensors and the isotropic chemical shifts σ_{iso} presented in Table II.

In addition the parameters of **3**[10] are also given. Obviously the two phosphorus atoms of the heterocycle **4** experience slightly different surroundings in the solid state, which results in two sets of shielding tensors (the same phenomenon is observed for **5**). The mean value of the two σ_{iso} values of **4** is in very good agreement with $\sigma_{solution}$. In contrast to **4**, showing only one isomer which is present in solution and in the solid state, the solution of **5** contains four different isomers.[5] The σ_{iso} value of the solid state corresponds to $\sigma_{solution}$ of the chair form with bisaxial orientation of the methyl groups. Thus it can be concluded, that the trans-chair-form of **5** (Me = axial) is present in the solid state. This is confirmed by the results of the theoretical calculations (see below).

In contrast to the heterocycles **4** and **5** the isotropic value σ_{iso} of the acid **1** shows a low-field shift of ca. 8 ppm relative to the solution shift. This difference indicates the existence of short intermolecular S...S distances in the crystal packing of the trithiophosphonic acid. This can be concluded by analogy with the findings of several dithiadiphosphetanes[11,12] and of 2,4-dimethyl-2,4-dithio-

TABLE II Experimental and calculated ^{31}P nuclear magnetic shielding data of compounds **1**, **3**, **4** and **5**

								Angles (in °)					
Comp. No.	*Conformation or configuration*	*Method*[a]	σ_{11}	σ_{22}	σ_{33}	δ_{iso}	$\delta_{solution}$	*S═P-1*	*C-P-1*	*S-P-1*	*S═P-3*	*C-P-3*	*S-P-3*
1	unknown	CP MAS NMR	224	232	322	68.9	60.6[b]						
	HSP═S *trans*	TM-IGLO	203	218	360	(68)		86.8	22.4	63.9	3.2	67.6	67.0
		GDF-IGAIM	204	213	403	(55)		88.3	24.6	63.9	1.7	65.4	67.4
	HSP-Me *trans*	TM-IGLO	171	223	377	(72)		76.3	13.3	71.5	13.7	76.7	60.0
		GDF-IGAIM	155	214	435	(61)		79.9	17.5	70.9	10.1	72.5	60.8
	HSP-S-*trans*	TM-IGLO	181	219	382	(68)		78.4	35.6	56.8	11.6	54.4	70.6
		GDF-IGAIM	154	201	465	(55)		76.6	37.3	55.3	13.3	52.7	70.3
3	Me *trans*	CP MAS NMR[c]	131	220	486	49.5	23.7						
		TM-IGLO[c]	152	228	554	(17)		68.8	46.5	50.0	21.2	43.5	75.2
		CS-IGLO[d]	139	216	533	(32)		69.5	44.1	50.7	20.5	45.9	76.1
4	unknown	CP MAS NMR	105	210	329	113.9	111.3[e]						
			102	210	345	109.4							
	half-chair; Me, Me; *ax*, *ax*[f]	TM-IGLO	121	226	376	(87)		87.2	25.0	72.1/52.7	7.3	65.9	61.5/70.5
5	chair; Me, Me; *ax*, *ax*[e]	CP MAS NMR	193	233	403	52.2	48.2[e]						
			196	239	400	50.0							
		TM-IGLO	215	246	407	(39)		67.6[g]	50.1[g]	53.3[g]	22.4	39.9	84.3

[a] TM-IGLO: Abbreviation for TURBOMOLE Hartree-Fock calculation with geometry optimization followed by calculations with the DIGLO program. GDF-IGAIM: Abbreviation for GAUSSIAN density functional theory calculation with geometry optimization followed by tensor calculations with the IGAIM program.

[b] δ of **1** is equal 63.9 ppm in a mixture of molten **1** and **2**.

[c] Data from the Reference [10].

[d] CS: Abbreviation for use of molecular coordinates from crystal structure data without geometry optimization.

[e] Data from Reference [5]

[f] For this compound the S═P-C plane does not coincide with the *1*-P-*3* plane, the centres of S and C atoms have a normal distance of 0.23 and 0.21 Å, respectively.

[g] For **5** the angles X-P-*2* are given because, principal axis *1* is perpendicular to the symmetry plane S═P-C.

1,3,2,4-dithiadiphosphetane **3**. Using the crystal structure data of Daly[13] a reconstruction of the crystal packing of **3** shows short intermolecular S···S distances of 3.36 Å (Figure 4).

These distances are smaller than 3.6 Å, the sum of the Van der Waals radii. They should primarily result in a changed distribution of the electron density at the sulfur lone pairs and as a consequence, the nuclear magnetic shielding tensor of the investigated phosphorus atom should also change. In solution the interaction of the P-S compounds with solvent molecules is much smaller because the molecular motion averages these interactions. The short intermolecular S···S distances in **3** result in an unusually large low-field shift of about 26 ppm relative to the value found in solution (see Table II). In the trithiophosphonic acid the low-field shift is smaller, probably, since two of the sulfur atoms are bonded to a hydrogen atom and the four bonds to the phosphorus atom are more flexible. Hence, there is less intermolecular interaction between the S atoms than in the rigid four-membered ring system of some dithiadiphosphetanes.

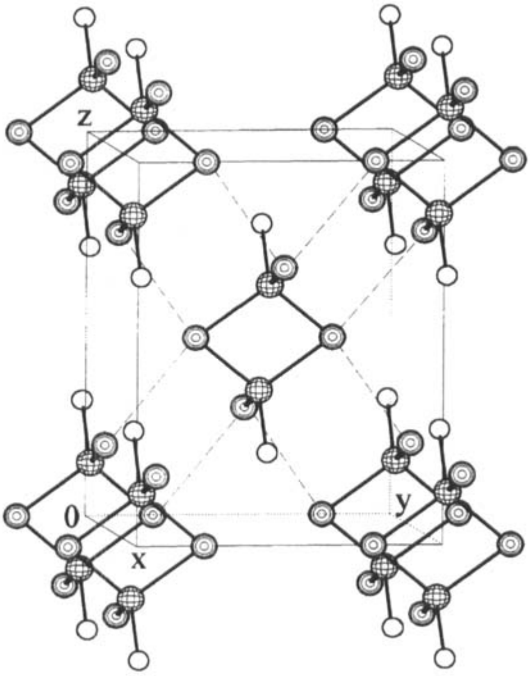


FIGURE 4 The molecular packing of *trans*-2,4-dimethyl-2,4-dithio-1,3,2,4-dithiadiphosphetane **3** according to the crystal structure determination of Daly and Wheatley.[13] The short intermolecular S···S distances of 3.36 Å are marked by dash lines.

An inspection of the experimental values presented in Table II shows quite similar σ_{22} values for the investigated compounds while the other values differ considerably. This indicates that the distribution of the valence electrons in the vicinity of the phosphorus atom and perpendicular to the principal axis *2* varies only slightly for the investigated compounds. From IGLO calculations of compound **3** published in a previous paper[10] it is known that the axis *2* is perpendicular to the mirror plane S═P-C. The experimental σ_{22} data of the investigated compounds allow the assumption that also in the compounds **1**, **4**, and **5**, the principal axes *2* are nearly or completely perpendicular to the planes S═P-C. Theoretical calculations of the shielding data for **1** and **4** corroborate this assumption.

For the compounds **1**, **4**, and **5** the crystal structure data are unknown, therefore, the theoretical calculations were started with standard geometry data and proposed configurations and conformations followed by a geometry optimization process and finally, by calculation of the nuclear magnetic shielding tensor. Shielding data obtained by selected calculation methods and some angles characterizing the orientation of the principal axes are summarized in Table II. The calculated optimized molecular structure of the assumed configuration and conformation represent model structures for the crystalline compounds **1**, **4**, and **5**. These structures are shown on the left side of Figure 5 together with the experimental molecular structure[13] of **3**.

Considering only the large differences of calculated (see Table II, values in brackets) and experimental isotropic chemical shift values the quality of the calculations seems to be not satisfactory. But supposed the three σ_{ii} values have distinctly different values the calculated orientation of the principal axes can be used for further discussions. The calculated shielding data of **1** and **4** confirm the assumption that the principal axis *2* is perpendicular to the S═P-C plane, whereas for **5** axis *1* has this orientation. As can be seen, the calculated and the experimental σ_{ii} values of the axis *i* being perpendicular to the S═P-C plane show a minimal variation, that means σ_{22} of **1**, **3**, and **4**, and σ_{11} of **5** are similar. In the compounds **1**, **3**, and **5** calculated with C_s or C_{2h} symmetry, these principal axes are strongly perpendicular to the S═P-C planes. Although compound **4** in the half chair conformation with bisaxial methyl groups possesses C_2 symmetry without a mirror plane, the axis *2* shows only a slight declination of 6.5° from the normal to the S═P-C plane.

For **1** the trans conformation *H*SP═**S** is in best accordance with the experimental σ_{11} and σ_{33} values. Since the calculations are carried out for an isolated molecule the influence of the above mentioned intermolecular S···S interactions is not considered. The two methods of the calculations (TM-IGLO and GDF-

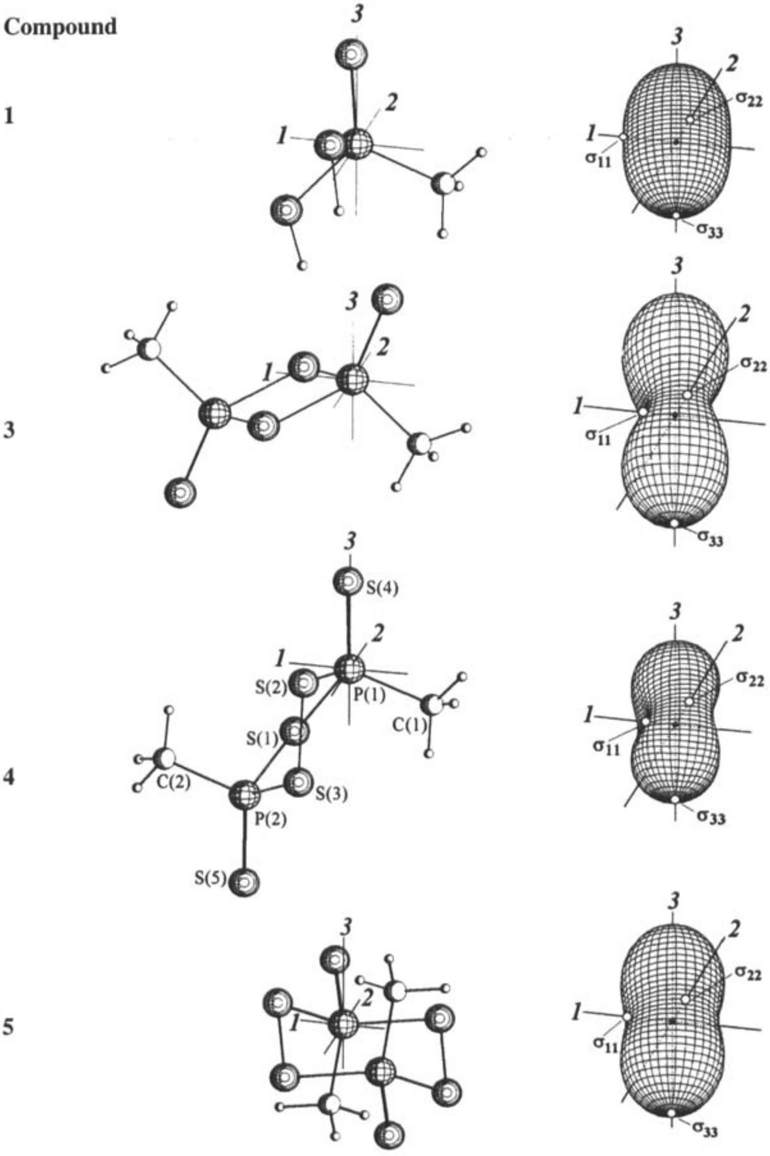


FIGURE 5 Molecular structures and calculated orientations of the principal axes *1*, *2* and *3* (on the left) and ovaloids (on the right) of the phosporus nuclear magnetic shielding tensors. The molecular structures of **1**, **4**, and **5** are calculated by TURBOMOLE geometry optimization of a probable configuration and conformation, the structure of **3** results from x-ray diffraction analysis.[13] In the ovaloids the "distance" from the origin to the surface in any chosen direction is proportional to the value of the measurable shielding if the magnetic field has this direction.

IGAIM)[14–16] of the conformers **1** give some different results being of the same order as the deviations from the experimental values.

For compound **3** Table II contains in addition to the geometry optimized IGLO calculations published earlier[10] those results obtained when the experimentally determined molecular geometry[13] has been used. The sensitivity of the calculated σ_{ii} values is remarkable if changing the molecular geometry (see Table I in Reference[10]) but the location of the principal axes changes only slightly.

As already mentioned the experimental spectrum of **4** shows two isotropic lines. Therefore, structures with chemically non-equivalent P atoms seem reasonable: a *trans* envelope conformer or a *cis* half-chair conformer. The calculation started with a *trans* envelope conformation lead by geometry optimization to the half-chair conformer with bisaxial methyl groups. For the *cis*-configurated half-chair the calculated isotropic shieldings of the two P atoms differ by 12 ppm. As in the experimental spectrum the two lines are separated by only 4.5 ppm we reject this structure assumption. Such a small difference can be caused by a slightly disturbed C_2 or C_s symmetry of the possible two *trans* half-chair or two *cis* envelope conformers due to crystal packing effects. The calculations of these four structures with chemically equivalent P atoms show similar shielding values. The results for the two *trans* half-chairs are in better accordance with the experimental values than the results for the *cis* envelope conformers. In Table II only the results of one structure are given: the *trans* half-chair with bisaxial methyl groups having the lowest SCF total energy of all five calculated conformers.

In the case of the tetrathiadiphosphorinane **5** configuration and conformation differences result in rather different shielding data. The calculated anisotropy value σ_{33}–σ_{11} of the chair form with bisequatorial methyl groups is significantly larger than that of the chair form with bisaxial methyl groups: 390 and 192 ppm respectively. Since the experimental anisotropy values are 210 and 204 ppm, the most probable molecular structure is the *chair* conformation with bisaxial orientation of the methyl groups. This structure gives the lowest SCF total energy of all computed models for **5**. In the crystal the C_{2h} symmetry of the chair should be slightly disturbed giving two experimental isotropic shifts for the two phosphorus atoms.

The differences of the shielding situation in the investigated compounds can be visualized by drawing the shielding ovaloids[17] as shown on the right side of Figure 5. These ovaloids show the variation of the shielding value in dependence on the location of the molecule with respect to the magnetic field direction. If the direction of the magnetic field is parallel to one of the principal axes *1*, *2*, or *3* the nuclear magnetic shielding is equal to σ_{11}, σ_{22}, or σ_{33}, respectively. The distances between the origin of the principal axes (the phosphorus nucleus) and certain points on the ovaloid's surface correspond to the possible shielding values for all orientations of the molecule in the spherical space about the phosphorus nucleus. For ovaloid calculations the theoretically calculated orientations of the principal axes and the experimental values σ_{ii} were used. In the drawings of the ovaloids the proportionality of surfaces to the σ_{ii} values has been considered. That means, magnitude and shape of the ovaloids correspond to the solid-state experimental shieldings for all locations of phosphorus containing molecules in the magnetic field, whereas the orientation of the principal axes to the molecular geometry may somewhat differ from the orientation in the solid state (see Figure 5, left side). For better comparison all ovaloids are drawn on the same scale.

In contrast to other methods IGLO calculations allow an inspection of the principal shielding or deshielding contributions of the localized molecular orbitals σ_{ii}(LMO) in terms of "chemical bonds" and "lone-pairs". In Table III the main LMO contributions for the investigated compounds are summarized. The core electrons of phosphorus atoms show a very similar large shielding while the contributions of the valence electrons usually have deshielding values.

TABLE III LMO contributions to the principal values σ_{ii} of the compounds **1**, **3**, **4** and **5**

	σ_{11}(LMO)				σ_{22}(LMO)				σ_{33}(LMO)			
LMO	*1*[a]	*3*[b]	*4*	*5*	*1*[a]	*3*[b]	*4*	*5*	*1*[a]	*3*[b]	*4*	*5*
Core P[c]	770	764	762	770	769	767	768	775	791	809	791	800
P=S	−319	−336	−363	−284	−287	−264	−275	−278	10	−25	8	−33
P-S	−96	−59	−110[d]	−37	−42	−54	−22[d]	−44	−156	−126	−145[d]	−170
P-S	−96	−59	−88[e]	−37	−42	−53	−62[e]	−44	−156	−129	−148[e]	−169
P-C	−29	−146	−38	−185	−168	−152	−167	−150	−194	−121	−210	−89
3 lp S=[f]	−7	−18	−19	3	1	0	2	−6	108	131	128	108
4 lp S-[g]	−20	−9	−16/−5	−3	−6	−21	1/−7	−4	−30	12	−11/−11	−45
Σ[h]	203	137	123	227	225	223	238	249	373	551	402	402
Total[i]	203	139	121	215	218	216	226	246	360	533	376	407

[a] Data for *trans* conformation HSP=S.

[b] Crystal structure data of Reference [3] were used.

[c] Core P are the contributions of the K and L shells of the considered phosphorus.

[d] Data for P-S(1).

[e] Data for P-S(2).

[f] 3 lp S = denotes the sum of contributions of the three lone-pair LMOs of the sulfur atom with coordination number one.

[g] 4 lp S- denotes the sum of contributions of the lone-pair LMOs of the both sulfur atoms with coordination number two.

[h] Σ is the sum of the considered LMO contributions.

[i] Total is the sum of all LMO contributions.

Some conclusions can be drawn from the location of the principal axes and from typical LMO contributions. It is well known that the principal values mainly depend on the electronic situation in the plane perpendicular to this axis and close to this plane,[18] the so-called study plane. As found for some four-coordinated thiophosphoryl compounds,[10,11,12] axis *3* corresponding to the most shielding value σ_{33} nearly coincides with the P═S bond. The highest shielding results, in spite of large deshielding contributions from the P-S and the P-C bonds, from the very low P═S LMO contribution to this value and the additional shielding from the S═lone pairs which possess almost cylindrical symmetry with respect to the P═S bond and, therefore, to axis *3*. Probably, this cylindrical symmetry will be disturbed by intermolecular S···S interactions in the crystalline state, which causes an increasing deshielding for the S═lone pairs. This is the reason for the nearly equal isotropic chemical shifts of **3** and **5** in the solid state ($\Delta\sigma$ = 0.5 and 2.7 ppm) while in solution the absence of special intermolecular S...S interactions leads to distinctly different chemical shifts ($\Delta\sigma$ = 24.5 ppm).

All LMO contributions to σ_{22} are rather similar for the investigated compounds as could be expected from the similarity of the experimental principal values σ_{22}. Large deshielding contributions result from the P═S and P-C bonds. For the most deshielding principal value σ_{11} large deshielding contributions can be expected from the following bonds lying in or close to the study plane (this condition is governed by the angles X-P-1): P═S for all compounds, P-C for **3** and **5**, and on the other hand P-S for **1** and **4**. Although for all compounds the angles C-P-1 are smaller than S-P-1, the P-C LMOs contribute an unexpected higher deshielding value than the P-S LMOs. Further, it must be mentioned that the contributions of the different LMOs depend not only on the position of the bonded atoms X with respect to the study plane but also on the energy difference between occupied and low-lying virtual orbitals of proper symmetry.

CONCLUSION

The preparative investigations for the first time resulted in the synthesis of pure methyltrithiophosphonic acid (**1**). In the absence of oxygen **1** thermally decomposes into 2,4-dimethyl-2,4-dithio-1,3,2,4-dithiadiphosphetane (**3**). It has been proved that the formation of this dimeric thioanhydride of **1** proceeds via dimethylpentathiodiphosphonic acid (**2**) as an intermediate. The addition reaction with norbornadiene revealed a suitable method of forming stable derivatives of the highly reactive monomeric and dimeric perthiophosphonic acids.

The solid-state NMR investigations of the four structurally similar compounds also allow some conclusions. The ring compounds are characterized by larger anisotropy values of the ^{31}P nuclear magnetic shielding than the acyclic compound. The strong deformation of the endocyclic S-P-S bond angle in the four-membered ring in comparison to the other ring compounds leads to the highest anisotropy value. The largest shielding occurs almost in direction of the P═S bond. Two of the principal values (σ_{33} and to a lesser extent σ_{11}) show a sensitive and complex response to the geometry around the P atom. The five-membered ring represents the exception of this series with its significant smaller σ_{11} and σ_{33} values and hence, the largest δ_{iso} value.

Since structural changes in most cases result in strong alteration of the anisotropy parameters, a comparison between the experimental and calculated principal values permits reliable conclusions about the solid state structure. Specially in the case of the tetrathiadiphosphorinane **5** a comparison between the experimental parameters and those calculated for different configurational and conformational isomers revealed that the chair conformation showing bisaxial orientation of the methyl groups is the most probable solid state structure. This result clearly confirms that the anisotropic shielding tensors provide valuable structural information which is not available from high resolution spectra.

EXPERIMENTAL

Preparation: All compounds were handled in an atmosphere of dry nitrogen. The solvents, toluene and pentane, were dried with potassium and lithium aluminum hydride, respectively, before use. 2,4-Dimethyl-2,4-dithio-1,3,2,4-dithiadiphosphetane (**3**),[3] 3,5-dimethyl-3,5-dithio-1,2,4,3,5-trithiadiphospholane (**4**),[4] 3,6-dimethyl-3,6-dithio-1,2,4,5,3,6-tetrathiadiphosphorinane (**5**),[4,5] and methyltrithiophosphonic acid bis(trimethylsilylester)[2] were prepared and purified as described in literature.

Methyltrithiophosphonic acid (1): 2.88 g (10 mmol) of methyltrithiophosphonic acid bis(trimethylsilylester)[2] are dissolved in 6 ml toluene and cooled to −40°C. Then a mixture of 0.36 ml (20 mmol) of water and 0.36 ml of acetonitrile is added under vigorous stirring. After 30 min the reaction mixture is cooled to −78°C resulting in the crystallization of a white precipitate. The solvent is removed through a cannula. At the temperature of −78°C the crystals are washed twice with toluene and pentane and dried in the vacuum. The product melts at −4°C showing decomposition at the melting point. The NMR parameters of the product are identical with those reported in literature.[2]

Dimethylpentathiodiphosphonic acid (2): 2.0 g (14 mmol) methyltrithiophosphonic acid (**1**) are slowly heated from −30°C to room temperature (heating rate: 2 K/min.). Above the melting point the sample is stirred by a magnetic stirrer. After 3–4 h at room temperature the sample has completely reacted to dimethylpentathiodiphosphonic acid (**2**) and dithiadiphosphetane **3** (product ratio about 4:1). The ^{31}P and ^{1}H NMR parameters of **2** are given in Table I.

Methyltrithiophosphonic acid bis(norbornenyl) ester (6): 1.4 g (10 mmol) of solid trithiophosphonic acid (**1**) is caused to react at −30°C with 2.2 g (20 mmol) of norbornadiene. While reacting a clear fluid is obtained. The reaction mixture is stirred at −30°C for 30 min and subsequently warmed to room temperature. According to the ^{31}P NMR spectrum (Figure 1) the acid is quantitatively transferred into the norbornenyl ester **6**.

Molar mass: 328 (determined by mass spectroscopy)– $^{13}C\{^{1}H\}$NMR (ca. 10 vol% in CS_2/C_6D_6 = 3/1, 22°C): δ = 138.26, 138.19 (=CH); δ = 134.67 − 134.57 (4 signals, =CH); δ = 49.87 − 49.37 (8 signals, SCH); δ = 46.51, 46.41 (CH_2-bridge; for comparison: CH_2-bridge of norbornadiene δ = 45.20, same conditions); δ = 45.90 − 41.70 (8 signals, 2CH); δ = 35.68 − 35.45 (3 signals $\underline{C}H_2$-CHS).

Dimethylpentathiodiphosphonic acid bis(norbornenyl) ester (7). 2.5 g dimethylpentathiodiphosphonic acid (**2**), prepared as described above, are caused to react at room temperature with 2.2 g norbornadiene. The reaction is complete after 5 min.

Molar mass: 438 (determined by mass spectroscopy) - $^{31}P\{^{1}H\}$NMR (ca. 10 vol% in CS_2/C_6D_6 = 3/1, 22°C): δ = 97.03 − 96.90 (4 singlets) 96.35 − 96.15 (4 singlets) 95.78, 95.60 (2 broad singlets).

High Resolution and Solid State NMR Spectroscopy: The high resolution NMR spectra were measured at 200.13 MHz (^{1}H), 81.02 MHz (^{31}P), and 50.32 MHz (^{13}C), using a Bruker AC 200 spectrometer; the solid-state NMR spectra were recorded with a Bruker MSL 300 (121.50 MHz for ^{31}P). The ^{31}P chemical shifts are relative to 85% phosphoric acid. For the determination of the anisotropy parameters ^{31}P CP MAS spectra were measured at spinning frequencies of 1–3 kHz using cross polarization with a pulse sequence containing two contact pulses.[19] The spinning sideband systems were computed by means of the program WIN-MAS.[20] The standard deviations of the isotropic chemical shifts are 0.1 ppm and those of the principal values of the chemical shift tensors caused by phase and base line correction are 2 ppm while the systematical deviations are estimated to 5 ppm. The principal values of the shielding tensors were calculated from the chemical shift tensors[21] with $\sigma_{ii} = 328$ ppm $- \delta_{ii}$ and have been labeled according to the convention $\sigma_{33} \geq \sigma_{22} \geq \sigma_{11}$.

IGLO calculation: The electronic ground state calculations were started with standard geometries using the TURBOMOLE package[14] or the GAUSSIAN 94 density functional theory program[16] for geometry optimization. The TURBOMOLE calculations (TM) were carried out with dzp basis sets and the GAUSSIAN optimizations (GDF) with a B3LYP density functional and 6-31G(d) basis sets. For **3** the coordinates from the X-ray diffraction studies[13] were used without geometry optimization.

The ^{31}P shielding tensors were calculated in the first case with the direct IGLO program (DIGLO)[15] (abbreviation TM-IGLO for these calculations in Table II) and in the second case with the GAUSSIAN IGAIM program[16] using atomic centres as gauge origins (abbreviation GDF-IGAIM for these calculations in Table II). For the DIGLO calculations of **1** the Huzinaga basis sets[22] were used: (6s 2p) contracted to [3 1 1 1, 1 1] with p exponents of 0.33 and 1.3 for H, (11s 7p 2d) contracted to [5 1 1 1 1 1 1, 2 1 1 1 1 1, 1 1] with d exponents of 0.35 and 1.4 for C, (12s 8p 3d) contracted to [5 1 1 1 1 1 1 1, 2 1 1 1 1 1 1, 1 1 1] with d exponents of 0.25, 0.8, and 2.5 for P and S. For calculations of **3**, **4**, and **5** following Huzinaga basis sets were used: (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 [5 1 1 1 1 1 1, 2 1 1 1 1 1, 1 1] with d exponents of 1.40 and 0.35 for P and 1.60 and 0.40 for S. The latter basis sets were also used for **3**, but for H an extended basis set (5s 1p) contracted to [3 1 1, 1] with a p exponent of 0.65 was applied. The GAUSSIAN IGAIM calculations were performed with a 6-31+G** basis set.

Acknowledgments

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