8 and 16-Membered Ring Phosphorus Compounds. Ring Size Dependence of the NMR Parameters

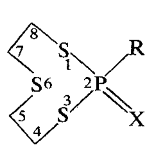
J. Martin and J. B. Robert*
Laboratoire de Chimie Organique Physique, Equipe de Recherche Associée au CRNS n° 674, Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, 85 X, F.38041 Grenoble Cédex, France

The ^1H NMR spectral analysis of four 8-membered rings, 2-thioxo- (or 2-oxo-) 2-R-1,3,6,2-trithiaphosphocane, is reported. The stereochemistry of the 8-membered ring is discussed. The ^{31}P NMR spectral parameters [$\delta^{31}P$, $^1J(PC)$] obtained on several cyclic 1,3,2-dithiaphospha compounds of variable size (5, 6, 8, 12 and 16-membered rings) are discussed as a function of the ring size and of the geometry of the molecule.

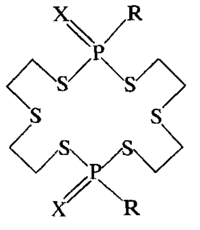
INTRODUCTION

In previous studies we reported that, in the synthesis of cyclic organophosphorus molecules such as the 6-membered rings 1,3,2-dioxaphosphorinanes or 1,3,2-dithiaphosphorinanes, the corresponding 12-membered ring dimers are also obtained. 10,[1] 12,[2,3] 14[4] and 16-membered rings[5,6] have thus been obtained. In addition to the chemical problem of the formation of these dimers, and the study of their stereochemistry which may be highly dependent upon transannular interactions,[7–9] this family of compounds is interesting from the NMR point of view. It offers a good opportunity to examine the variation of the NMR spectral parameters (spin–spin coupling and chemical shift) as a function of the ring size and of the geometrical parameters when structural data are available.

The NMR data obtained on several 1,3,2-dithiaphosphorus 5, 6, 8, 12 and 16-membered ring compounds containing the  fragment (X = O, S) have been analysed in this work. The results of the NMR spectral analysis of 2-thioxo- and 2-oxo-2-R-1,3,6,2-trithiaphosphocanes (**1**) and the corresponding dimers (**2**), together with a discussion on the stereochemistry of the 8-membered ring in solution, are first discussed.

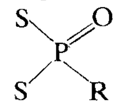
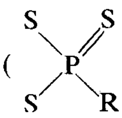


1



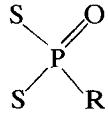
2

NMR STUDY OF 2-THIOXO- AND 2-OXO-2-R-1,3,6,2-TRITHIAPHOSPHOCANES

The 8-membered rings under study are first obtained as three co-ordinated phosphorus compounds by reacting the 2-mercaptoethyl sulphide $S(CH_2CH_2SH)_2$ with the appropriate alkyl dichlorophosphane ($RPCl_2$) and then oxidizing with hydrogen peroxide or elemental sulphur into the oxo () or thioxo () compounds.

The ring protons of the 8-membered rings were analysed as ABCDX (X, phosphorus) systems, the spectra being recorded at 250 MHz both with and without phosphorus decoupling. The results obtained using the LAOCOON III iterative program are presented in Table 1. Figure 1 shows an example of the agreement between the experimental and calculated spectra in the case of 2-thioxo-2-*t*-butyl-1,3,6,2-trithiaphosphocane.

Before examining the conclusions which can be drawn from the NMR spectral analysis on the stereochemistry of the molecule, the conformation of 2-thioxo-2-*t*-butyl-1,3,6,2-trithiaphosphocane as determined by X-ray diffraction will be briefly discussed.[10] In the solid state, the 8-membered ring adopts an asymmetric conformation which is best characterized by the torsional dihedral angles shown in Fig. 2. The ring shape can be described as a carbon edge boat-chair (BC) conformation.[11] From the solid state structure, and using standard H—C—H bond angles, all the H—C—C—H and P—S—C—H dihedral angles of the ring hydrogen atoms can be calculated. The values obtained are quoted in Table 2.

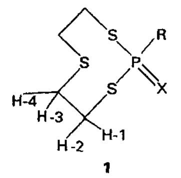
The results of the proton NMR spectral analysis given in Table 1 show that the $^3J(HH)$ coupling constants of the oxo compounds () have very

---

* Faculty member of the Université Scientifique et Médicale de Grenoble and author to whom correspondence should be addressed.

CCC-0030-4921/81/0015-0087$03.50

Table 1. ^{1}H NMR spectral parameters of 2-oxo- and 2-thioxo-2-R-1,3,6,2-trithiaphosphocanes



1

		Solvent	Chemical shifts[a] H-1	H-2	H-3	H-4	Spin–spin couplings (Hz)[b] H-1,H-2	H-1,H-3	H-1,H-4	H-1,P	H-2,H-3	H-2,H-4	H-2,P	H-3,H-4	H-3,P	H-4,P
R = CH_3	X = O	C_6D_6	2.98	2.40	2.44	2.11	−14.7	3.9	7.5	16.7	8.0	3.9	19.1	−15.1	−0.4	0.0
	X = S	$CDCl_3$	3.53	3.22	3.19	2.92	−14.9	4.1	6.6	16.8	8.8	4.2	24.6	−15.1	−0.5	0
R = *t*-Bu	X = O	C_6D_6	3.08	2.51	2.54	2.22	−14.6	3.8	7.4	16.8	8.2	4.0	19.4	−15.2	−0.5	0.1
	X = S	C_6D_6	3.15	2.64	2.75	2.28	−14.8	3.4	5.8	14.5	9.9	3.8	22.1	−15.4	−0.5	0

[a] The chemical shifts are given in ppm with respect to TMS as internal reference.
[b] The spin–spin couplings are given in hertz with an uncertainty of ±0.1 Hz.

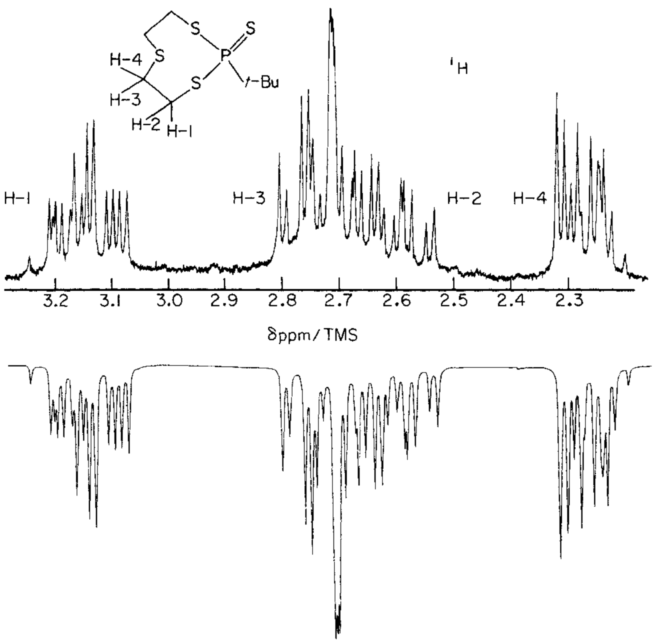
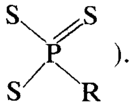


Figure 1. Observed and calculated ^{1}H NMR spectrum (250 MHz) of the methylenic protons of 2-thioxo-2-*t*-butyl-1,3,6,2-trithiaphosphocane.

similar values and exhibit only small differences compared with those in the thioxo compounds (). The existence of only one ABCDX spin system in the ^{1}H NMR spectrum shows that the two

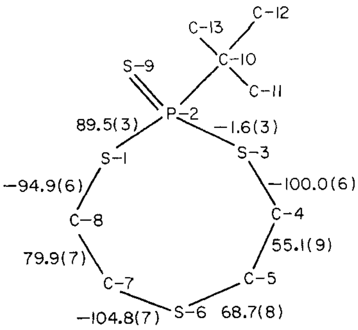


Figure 2. Ring torsional angles (°) obtained by X-ray diffraction in the solid state of 2-thioxo-2-*t*-butyl-1,3,6,2-trithiaphosphocane.[10] The uncertainty of the last digit is given parentheses.

–S—CH_2—CH_2 ring fragments are equivalent on the NMR time scale. Thus, the molecule exists in solution either as a unique conformation of C_s symmetry or as a mixture of two or several enantiomeric conformers in rapid equilibrium.

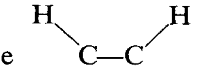
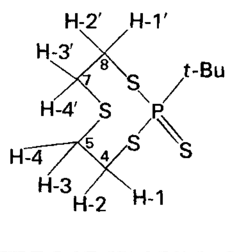
The C_s symmetry conformations which can be considered are the boat-chair (BC), chair-boat (CB), boat-boat (BB) and chair-chair (CC) conformers (Scheme 1). (The BC and CB forms depend upon the position of the phosphorus atom which may be either in the chair or in the boat moiety.) From examination of Dreiding models, the BC and BB conformers show three  dihedral angles close to 60° and

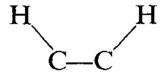
Table 2. Calculated[a] values of the H—C—C—H and P—S—C—H dihedral angles of 2-thioxo-2-*t*-butyl-1,3,6,2-trithiaphosphocane as obtained from X-ray structural data

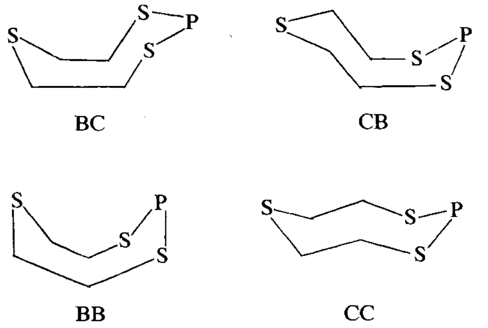


Dihedral angles around the C-4—C-5 bond H-1,H-3	H-1,H-4	H-2,H-3	H-2,H-4	Dihedral angles around the C-7—C-8 bond H-1′,H-3′	H-1′,H-4′	H-2′,H-3′	H-2′,H-4′
57°	52°	168°	58°	82°	165°	35°	78°

Dihedral angles around C-4,S P,H-1	P,H-2	Dihedral angles around C-8,S P,H-1′	P,H-2′
138°	22°	29°	142°

[a] The calculations are made assuming a standard H—C—H bond angle of 109.5°.

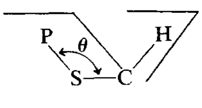
the fourth close to 180°. In the CB and CC conformers, three  $\overset{H\quad\;\; H}{C—C}$ angles are close to 120° and one close to 0°. The ^3J(HH) values corresponding to the 60° and 180° dihedral angles would be 4.5 Hz and 12 Hz, respectively, as observed in the 6-membered ring 1,3,2-dithiaphosphorinanes[12] which exist in a rigid chair conformation. Thus, the ^3J(HH) values reported in Table 1 are incompatible with an unique C_s symmetry conformation for the 8-membered ring trithiaphosphocane under study. The



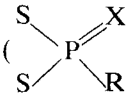
presence of two ν(P=O)[13] IR stretching frequencies of equal intensity at 1199 cm^{-1} and 1188 cm^{-1} for R = CH$_3$, and at 1204 cm^{-1} and 1182 cm^{-1} for R = *t*-butyl, supports this conclusion for the oxo compounds. The assignment of the IR frequencies to the P=O group has been confirmed by observing a low frequency shift ($\Delta\nu \sim 100$ cm^{-1}) by complexing the 2-oxo-2-R-1,3,6,2-trithiaphosphocanes with uranyl nitrate [UO$_2$(NO$_3$)$_2$, 6H$_2$O].[14] The small difference which exists between the two ν(P=O) values observed in the non-complexed molecules ($\Delta\nu < 20$ cm^{-1}) cannot be due to the presence of two conformations corresponding to the axial and equatorial orientations of the P=O bond, respectively, which would result in a difference of about 50 cm^{-1}.[15–17]

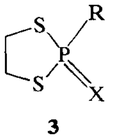
A definite conclusion concerning the 8-membered ring conformation in solution could probably be obtained from a low temperature NMR study, which has as yet been precluded owing to solubility problems. However, the existence of two ν(P=O) stretching frequencies of equal intensity strongly suggests the existence of a 1:1 equilibrium. As the solid state conformation reported for 2-thioxo-2-*t*-butyl-1,3,6,2-trithiaphosphocane[10] satisfies the staggered disposition around the C—C bonds and shows no intermolecular interactions, we suggest that one of the conformations observed in solution is similar to the one observed in the solid state (carbon edge boat-chair conformation). A pseudorotation process changing this asymmetric conformation to its mirror image will make the two CH$_2$—CH$_2$ spin systems equivalent on the NMR time scale. However, this conclusion on the ring conformation must be considered with caution as in a closely related compound, 2-oxo-2-phenyl-1,3,2-dithiaphosphorinane, different conformations have been observed in the solid state (twist form) and in the liquid state (chair form).[18]

An interesting fact should be noted concerning the ^3J(PSCH) coupling constants. For the 6-membered 2-thioxo-2-R-1,3,2-dithiaphosphorinane rings, with R = CH$_3$ or R = *t*-butyl, which exist in solution in a rigid chair conformation, the ^3J(PSCH) values of the equatorial protons are equal to 21.0 Hz and 21.5 Hz, respectively.[12] These values correspond to a 180° P—S—C—H dihedral angle. In the corresponding 2-thioxo-2-R-1,3,6,2-trithiaphosphocane (R = CH$_3$, R = *t*-butyl) where, according to our conclusions on the conformation, the average value of the P—S—C—H dihedral angle must be lower than 180°, the observed ^3J(PSCH) values are larger than in the 6-membered ring dithiaphosphorinanes (24.6 Hz vs 21 Hz for R = CH$_3$; 22.1 Hz vs 21.5 Hz for R = *t*-butyl). This fact, as already reported in the case of the P—O—C—H fragment,[19,20] strongly suggests that the ^3J(PH) coupling constant is not only dependent on the P—X—C—H dihedral angle and on the nature of the chemical groups attached to the phosphorus but also on the P—S—C bond angle, θ, which changes from 101° to 105° on going from a 6[21] to an 8-membered ring. Thus, care must be exercised when applying a simple Karplus-like relationship for a P—X—C—H fragment (X = O, S), especially when changes must exist in the P—O—C or P—S—C bond angle. Such large variations are, for example, observed when going from a 5-membered ring (POC = 111°[22]) to a 7-membered ring (POC = 127°[19]).

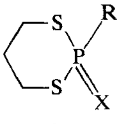


VARIATION OF THE NMR PARAMETERS WITH THE RING SIZE

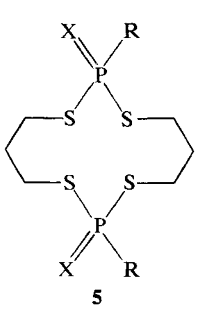
Having available a family of 1,3,2-dithiaphospha ring compounds of different size (5,[23] 6,[12] 8,[6] 12[3] and 16-membered rings[6]), and which have the same R groups attached to the phosphorus atom ( $\mathrm{S_2P(X)R}$ X=O, S; R = CH$_3$, *t*-butyl), it is interesting to examine the variation of the NMR parameters [δ^{31}P, ^1J(PC), ^3J(PSCH)] as a function of the ring size.



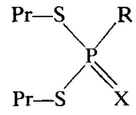
3



4



5

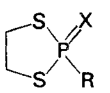
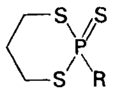
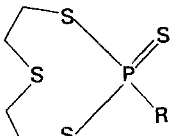
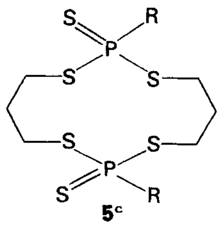
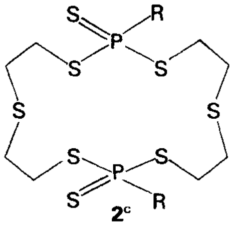
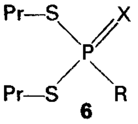


6

Phosphorus chemical shift

The ^{31}P chemical shift measured in solution of several 1,3,2-dithiaphospha rings of various sizes are reported in Table 3, together with the value measured in an

Table 3. ^{31}P NMR chemical shifts[a] in benzene solution of 2-thioxo- and 2-oxo-2-R-1,3,2-dithiaphospha ring compounds of various sizes

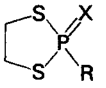
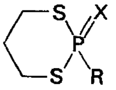
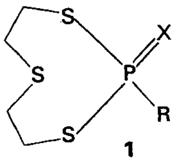
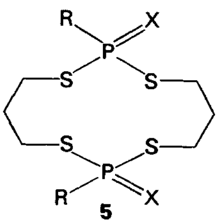
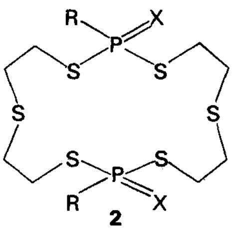
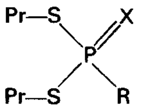
	R = CH_3		R = t-Bu	
	X = O	X = S	X = O	X = S
 3	96.4	97.6	107.4	129.0
 4	46.6	59.1 (105.6°)[b]	—	100.8
 1	57.1	77.4	83.0	112.4 (108.9°)[b]
 5[c]	—	76.3	—	116.1 120.2
 2[c]	62.0 61.7	80.6 80.1	83.8 83.5	117.0 118.5 (101°)[b]
 6	56.0	77.6	—	—

[a] Given in ppm with positive values downfield from 85% H_3PO_4 as external reference.

[b] The S—P—S bond angles obtained from X-ray diffraction in the solid state are given in parentheses.

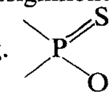
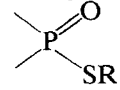
[c] For the 12 and 16-membered rings two diastereoisomers exist, which differ in the relative orientation of the R groups with respect to the mean plane of the ring.

Table 4. Values of the ^{1}J(PC) spin–spin coupling (Hz)

	R = CH_3		R = t-Bu	
	X = O	X = S	X = O	X = S
 3	—	56.7	72.5	46.3
 4	76.3	58.5	—	50.1
 1	78.5	63.7	72.0	51.6
 5	—	—	—	51.4 50.5
 2	76.4[a]	61.7[a]	69.9[a]	50.3[a]
 6	76.9	61.3	—	—

[a] The two isomers show the same ^{1}J(PC) value.

open-chain molecule. All the measurements have been made in the same solvent (C_6D_6). As we wish to examine the influence of the geometrical parameters on the NMR data the S—P—S bond angle values, when they have been determined by X-ray diffraction, are also reported in the table. These structural data correspond to solid state values but the NMR measurements have been carried out in solution. However, as no packing effects have been noticed in the X-ray work, one can safely assume that the bond angles measured in the solid state are close to the values which exist in the molecule in solution.

Several conclusions can be drawn from the examination of these chemical shift values. In the oxo compounds when R = CH_3, a change of chemical shift as large as 50 ppm is observed on changing the ring size. Such a variation is of the same order of magnitude as the change observed in going from an oxo compound [$CH_3P(O)(OCH_3)_2$ $\delta^{31}P = 30$ ppm] to the corresponding thioxo compound [$CH_3P(S)(OCH_3)_2$ $\delta^{31}P = 80$ ppm].[24] Thus, formula assignment based on phosphorus chemical shifts (e.g.  vs ) must be carried out with caution and by reference to rings of similar size.

The results in Table 3 show that for a given R substituent attached to the phosphorus, one observes a large high field shift on going from a 5-membered to a 6-membered ring. A low field shift of smaller amplitude is then observed from the 6-membered ring to the higher sized rings. A plot of the ^{31}P chemical shift, δ, as a function of the ring size is shown in Fig. 3.

Results on the phosphorus chemical shift, δ^{31}P, in cyclic organophosphorus compounds of various sizes have already been reported. In the case of cyclic derivatives of phosphorus oxy-acids[25] the ^{31}P NMR signals move to lower field in the order 6-membered ring > acyclic > 5-membered ring, as observed here for the 1,3,2-dithiaphospha compounds. Conversely, for

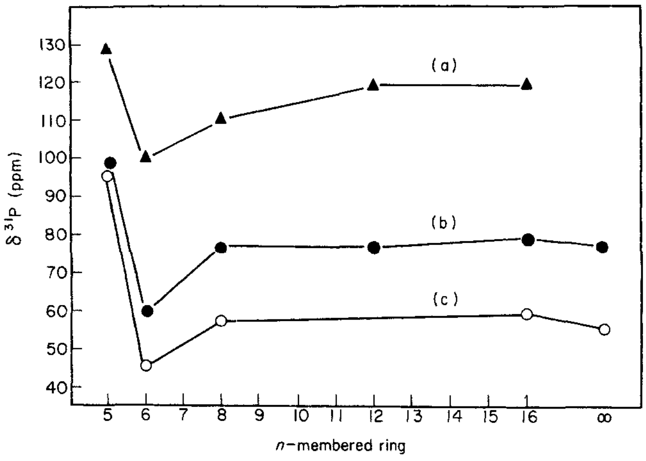
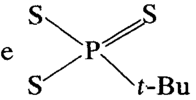
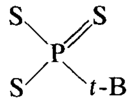


Figure 3. Variation of $\delta^{31}P$ (given with positive values downfield from H_3PO_4) as a function of the ring size of 2-X-2-R-1,3,2-dithiaphospha compounds: (a) X = S, R = *t*-Bu, (b) X = S, R = Me; (c) X = O, R = Me.

cyclopolyphosphanes, a monotonic low field shift is observed as the ring size increases.[26,27] For a better understanding of the factors on which the phosphorus chemical shift is dependent, it is more interesting to examine the $\delta^{31}P$ values as a function of the S—P—S bond angle. The influence of the O—P—O bond angle on the $\delta^{31}P$ has been examined for phosphate molecules from the theoretical[24,28] and experimental point of view.[29]

The value of the S—P—S bond angle is not available for all the compounds under study. For the molecules containing the  moiety, this angle has been determined by X-ray diffraction in the solid state for the 8[10] and 16-membered rings.[30] In the 6-membered ring 2-thioxo-2-R-1,3,2-dithiaphosphorinane[21] and for a given R group, the S—P—S bond angle is about 2° larger than in the corresponding 1,3,2-dioxaphosphorinane.[31] Thus, a value of 103° can be assumed in 2-thioxo-2-*t*-butyl-1,3,2-dithiaphosphorinane from the 101°9 measured in 2-thioxo-2,5-di-*t*-butyl-1,3,2-dioxaphosphorinane.[32] Only two 2-thioxo-2-R-1,3,2-dithiaphospholanes have been reported, which correspond to R = Cl (S—P—S = 100°5)[33] and R = C_6H_5 (S—P—S = 98°5).[34] As a *t*-butyl substituent tends to decrease the cyclic bond angle around the phosphorus atom, one can conclude that in 2-thioxo-2-*t*-butyl-1,3,2-dithiaphospholane the S—P—S angle will be equal to or smaller than the 98°5 obtained in the corresponding 2-phenyl compound.

In the 2-thioxo-2-*t*-butyl compounds (), from the measured or estimated S—P—S bond angle, α, and using the ^{31}P chemical shift values quoted in Table 3, it is possible to plot $\delta^{31}P$ as a function of α as shown in Fig. 4. A similar non-monotonic variation of δ vs α has already been proposed in the case of esters

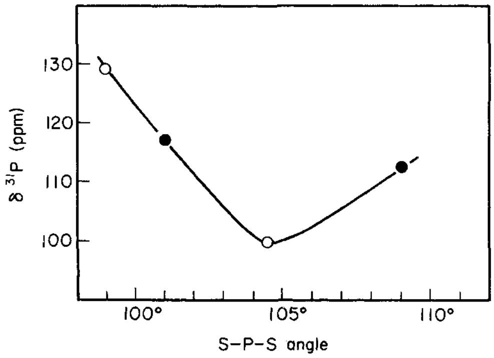
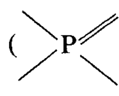


Figure 4. Variation of $\delta^{31}P$ (given with positive values downfield from H_3PO_4) as a function of the S—P—S bond angle in 2-thioxo-2-*t*-butyl-1,3,2-dithiaphospha compounds: ● = measured S—P—S bond angles; ○ = estimated values.

of phosphoric acids.[29,35] However, it must be pointed out that as suggested from theoretical data,[36] the phosphorus chemical shift in phosphates must be dependent upon two geometrical factors, namely the O—P—O angle and the torsional angle around the P—O bond. Similar effects must probably be taken into account here.

It is interesting to note that for the cyclopolyphosphanes,[26,27] phosphanes,[37,38] phosphane oxide[39] and sulphide,[40] one observes a monotonic high field shift when the bond angles around the phosphorus atom decrease.

^1J(PC) spin–spin couplings

Another spectral parameter which is interesting to examine as a function of the ring size is ^1J(PC), and values are reported in Table 4. The ^1J(PC) couplings are assumed to be positive, as shown in the tetracoordinated phosphorus compounds.[41] For the thioxo compounds ( one observes an increase of ^1J(PC) from the 5-membered to the 8-membered ring. For larger rings, ^1J(PC) remains about constant. A similar observation has been reported for cyclic phosphonates[5] and cyclic phosphane oxides,[42] where ^1J(PC) exhibits a large increase from the 3-membered ring to the 4-membered ring (ΔJ = 10 Hz) and remains approximately constant for the larger rings.

If one examines the ^1J(PC) spin–spin coupling as a function not of the ring size but of the S—P—S valence bond, α, one observes an increase of ^1J(PC) with α. It is noteworthy that the reasoning often made which considers that a decrease of the α angle will result in an increase of the *s* character of the exocyclic P—C bond, thus involving an increase in ^1J(PC), does not apply here.

A similar reasoning, which can be applied to the ^1J(CH) couplings,[43] also fails in explaining the ^1J(PH) trend observed in phosphanes where the following values are observed: phosphacyclopropane 155 Hz,[44] phosphacyclohexane 200 Hz,[45] diethylphosphane 190 Hz.[46] The failure of this simple reasoning, based on the *s* character of the bond, is perhaps due to the fact that the Fermi contact term is not the only one which contributes to the ^1J(PC) and ^1J(PH) spin–spin couplings.

Thus, it clearly appears from this study of 2-thioxo- and 2-oxo-2-R-1,3,2-dithiaphospha rings of various sizes that the NMR spectral parameters are highly dependent upon the ring size, the largest changes being observed on going from the 5 to the 6-membered ring. However, it must be pointed out that the chemical shift screening constant, σ, and the spin–spin coupling, J, are tensors of which only the trace can be obtained from NMR experiments in isotropic phases. The variations reported here, therefore, only concern the traces of these tensors. It is possible that even bigger variations could be observed if the individual components of the tensors were measured, as previously noted for several organophosphates where the components of the ^{31}P chemical shift tensor are significantly more sensitive to the stereochemical environment than their isotropic counterparts.[47]

EXPERIMENTAL

NMR spectra

The ^{1}H NMR spectra were recorded at 20 ± 2 °C in the continuous wave mode, with and without phosphorus decoupling, on a Cameca 250 spectrometer operating at 250 MHz. TMS was used as internal lock and as the reference signal. The phosphorus decoupling frequency was provided by an Adret Electronique 6100 frequency synthesizer and is amplified by an ENI 360 L RF power amplifier.

The ^{13}C and ^{31}P proton noise decoupled spectra were obtained in the Fourier transform mode on a Varian XL 100 spectrometer operating at 25.2 MHz and 40.5 MHz, respectively. The field frequency lock was provided by C_6D_6 used as solvent. The chemical shifts are given from internal TMS for the ^{13}C spectra and external 85% H_3PO_4 for the ^{31}P spectra. The concentration corresponds to approximately 0.1 M solutions.

IR spectra

The IR spectra were obtained for Nujol mulls between NaCl plates, using a Perkin Elmer 221 spectrometer.

Materials

Compounds of type 1 and 2. A benzene solution of 2-mercaptoethyl sulphide (1 M) [$S(CH_2CH_2SH)_2$, Aldrich] was added dropwise to a benzene solution of *t*-butyldichlorophosphine (1 M) or methyldichlorophosphine (1 M) in the presence of pyridine (2 M) at room temperature. After completion of the sulphide addition the solution was refluxed for 10 h for the *t*-butyl compound and for 1 h for the methyl compound. The reaction mixture was then split into two parts A and B.

Half a mole of elemental sulphur was added to part A and the solution refluxed for 1 h. The residue obtained after solvent evaporation, and after chromatographic elution on a silica column with a 1:1 hexane–benzene mixture, allowed the separation of the thioxo (P=S) monomers of type **1** and of the thioxo dimers of type **2**.

An acetone solution of half a mole of H_2O_2 was added slowly to part B at 0 °C. The oxidation reaction was immediate. The solution was then dried over anhydrous sodium sulphate. Silica column chromatography with a 4:1 chloroform-acetone mixture then allowed the separation of the oxo (P=O) monomers of type **1** and of the oxo dimers of type **2**.

Compounds of type 3. The compound bearing the P—CH_3 group has been described previously.[23] For the *t*-butyl compound the three co-ordinate phosphorus compound was first synthesized[48] and the preparation of the oxo and thioxo derivatives conducted as described for compounds of type **1** and **2**.

Compounds of type 4. The preparation of the thioxo compound (P=S) has been described in Ref. 12. The oxo compound was obtained as described previously by oxidation with H_2O_2 of 2-methyl-1,3,2-dithiaphosphorinane.[49]

Compounds of type 5. These compounds are described in Ref. 3.

Compounds of type 6. The oxo compound was obtained by reacting 1-propanethiol (2 M) with methyldichlorophosphine oxide [$CH_3P(O)Cl_2$] (1 M) in the presence of triethylamine (2 M) in benzene at room temperature. The compound was purified by silica column chromatography with a 5:1 chloroform–acetone mixture as eluent.

To obtain the thioxo compound (P=S) methyldipropyldithiophosphite [$CH_3P(SPr)_2$] was first synthesized by reacting 1-propanethiol (1 M) and methyldichlorophosphine (1 M) in the presence of triethylamine (2 M) in benzene at room temperature. The oxidation by elemental sulphur and the purification was performed as previously described for compounds **1** and **2**.

Acknowledgements

It is a pleasure to acknowledge many helpful discussions with J. P. Dutasta and A. Grand. The aid of M. Aubert, R. Nardin and R. Reutenauer in recording some of the spectra is also greatly acknowledged.

REFERENCES

1. J. P. Dutasta, A. Grand, A. C. Guimaraes and J. B. Robert, *Tetrahedron* **35**, 197 (1979).
2. J. P. Albrand, J. P. Dutasta and J. B. Robert, *J. Am. Chem. Soc.* **96**, 4584 (1974).
3. J. P. Dutasta, J. Martin and J. B. Robert, *J. Org. Chem.* **42**, 1662 (1977).
4. J. P. Dutasta, A. C. Guimaraes and J. B. Robert, *Tetrahedron Lett.* 801 (1977).

5. J. P. Dutasta and J. B. Robert, *J. Am. Chem. Soc.* **100**, 1925 (1978).
6. J. Martin and J. B. Robert, *Nouv. J. Chim.* accepted for publication.
7. M. Dräger, *Chem. Ber.* **107**, 2601 (1974).
8. M. Dräger and M. Engler, *Z. Anorg. Allg. Chem.* **405**, 183 (1974).
9. A. E. Kalinin, V. G. Andrianov and Y. T. Stroutchkov, *Zh. Strukt. Khim.* **16**, 104 (1975).
10. J. Martin and J. B. Robert, *Acta Crystallogr. Sect. B* **35**, 1623 (1979).
11. F. A. L. Anet and J. Krane, *Tetrahedron Lett.* 5029 (1973).
12. J. Martin and J. B. Robert, *Org. Magn. Reson.* **9**, 637 (1977).
13. C. Thomas, *Interpretation of the Infra-Red Spectra of Organophosphorus Compounds*, Heyden, London (1974).
14. K. W. Bagnall and M. W. Waderley, *J. Chem. Soc. Dalton Trans.* 889 (1974).
15. M. Kainosho, T. Morofushi and A. Nakamura, *Bull. Chem. Soc. Jpn* **42**, 845 (1969).
16. J. P. Majoral and J. Navech, *Spectrochim. Acta Part A* **28**, 2247 (1972).
17. J. A. Mosbo and J. G. Verkade, *J. Org. Chem.* **42**, 1549 (1977).
18. R. O. Hutchins, B. E. Maryanoff, M. J. Castillo, K. D. Hargrave and A. T. McPhail, *J. Am. Chem. Soc.* **101**, 1600 (1979).
19. W. Kung, R. E. Marsh and M. Kainosho, *J. Am. Chem. Soc.* **99**, 5471 (1977).
20. A. C. Guimares, J. B. Robert, C. Taieb and J. Tabony, *Org. Magn. Reson.* **11**, 411 (1978).
21. A. Grand, J. Martin and J. B. Robert, *Acta Crystallogr. Sect. B* **32**, 1244 (1976).
22. A. Grand, Thèse d'Etat, Grenoble (1979).
23. S. C. Peake, M. Fild, R. Schmutzler, R. K. Harris, J. M. Nichols and R. G. Frees, *J. Chem. Soc. Perkin Trans. 2* 380 (1972).
24. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark and J. R. Van Wazer, *Topics in Phosphorus Chemistry*, Vol. 5, *^{31}P NMR*, John Wiley, New York (1967).
25. G. M. Blackburn, J. S. Cohen and I. Weatherrall, *Tetrahedron* **27**, 2903 (1971).
26. L. R. Smith and J. L. Mills, *J. Am. Chem. Soc.* **98**, 3852 (1976).
27. J. L. Mills, in *Homoatomic Rings, Chains and Macromolecules of Main-Group Elements*, ed. by A. L. Theinfold, Elsevier, New York (1977).
28. D. Purdela, *J. Magn. Reson.* **5**, 23 (1971).
29. D. G. Gorenstein, *J. Am. Chem. Soc.* **97**, 898 (1975).
30. J. Martin, unpublished results.
31. D. E. C. Corbridge, *The Structural Chemistry of Phosphorus*, Chapt. 14. Elsevier Scientific Publishing Company, Amsterdam (1974).
32. R. W. Warrent, C. N. Caughlan, J. H. Hargis, K. C. Yee and W. G. Berntrude, *J. Org. Chem.* **43**, 4266 (1978).
33. J. D. Lee and G. W. Goodacre, *Acta Crystallogr. Sect. B* **27**, 1055 (1971).
34. J. D. Lee and G. W. Goodacre, *Acta Crystallogr. Sect. B* **27**, 1841 (1971).
35. J. Kumamoto, J. R. Cox and F. H. Westheimer, *J. Am. Chem. Soc.* **78**, 4858 (1956).
36. F. Ribas Prado, C. Giessner-Prettre, B. Pullman and J. P. Daudey, *J. Am. Chem. Soc.* **101**, 1737 (1979).
37. B. E. Mann, *J. Chem. Soc. Perkin Trans. 2* 30 (1972).
38. C. A. Tolman, *Chem. Rev.* 313 (1977).
39. H. R. Hays and D. J. Peterson, in *Organic Phosphorus Compounds*, Vol. 3, ed. by G. M. Kosolapoff and L. Maier, Wiley Interscience, New York (1972).
40. L. Maier, in *Organic Phosphorus Compounds*, Vol. 4, ed. by G. M. Kosolapoff and L. Maier, Wiley Interscience, New York (1972).
41. W. McFarlane, *Proc. R. Soc. A* **306**, 185 (1968).
42. G. A. Gray, S. E. Cremer and K. L. Marsi, *J. Am. Chem. Soc.* **98**, 2109 (1976).
43. J. B. Stothers, *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, Academic Press, New York (1972).
44. H. Goldwhite, personal communication.
45. J. B. Lambert and W. L. Olliver Jr, *Tetrahedron* **27** 4245 (1971).
46. K. Moedritzer, L. Maier and L. C. D. Groenweghe, *J. Chem. Eng. Data* **7**, 307 (1962).
47. T. Terao, S. Matsui and K. Akasaka, *J. Am. Chem. Soc.* **99**, 6136 (1977).
48. J. P. Albrand, D. Gagnaire, J. Martin and J. B. Robert, *Org. Magn. Reson.* **5**, 33 (1973).
49. J. Martin, J. B. Robert and C. Taieb, *J. Phys. Chem.* **80**, 2417 (1976). 1981

Received 24 April 1980; accepted 26 June 1980