Organic Magnetic Resonance, 1974, Vol. 6, pp. 494 to 496.

Long Range ^{31}P—^{1}H Couplings in Phosphorylated Iminothiazolines and Iminooxazolines

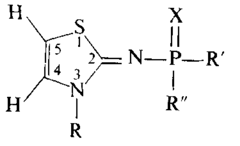
C. K. Tseng and A. Mihailovski
Stauffer Chemical Company, Western Research Center, Richmond, California 94804, USA

(Received 20 March 1974; accepted 9 May 1974)

Abstract—Long range ^{31}P—^{1}H coupling constants of 21 phosphorylated iminothiazolines and two phosphorylated iminooxazolines have been studied. The size of the ^{31}P—^{1}H coupling in the H—C—N—C=N—P framework is larger than that in the H—C—S—C=N—P framework which is in turn larger than the H—C—O—C=N—P framework. The value of the ^{31}P—^{1}H coupling through the H—C—N—C=N—P framework decreases in the order of P > PS > PO, whereas a reverse trend is observed for the H—C—S—C=N—P framework. A planar zig-zag configuration has been proposed for the long range ^{31}P—^{1}H couplings.

LONG range ^{31}P—^{1}H coupling through five bonds has been observed in many types of phosphorus compounds.[1–10] The magnitude of the coupling depends on two factors: (i) the electron density and hybridization of the phosphorus atom and (ii) the availability of the π electrons to facilitate the interaction between the hydrogen spin and the phosphorus spin.

We have prepared various phosphorylated iminothiazolines of **1**. The protons at the 4 and 5 positions exhibit long range ^{31}P—^{1}H coupling through the H—C—N—C=N—P and H—C—S—C=N—P frameworks. The presence of the sulfur and the nitrogen atoms at the 1 and 3 positions provides an interesting comparison between these two atoms in facilitating the interaction between the proton and phosphorus spins. By changing the substituents at the phosphorus atom, we can observe the change of the value of the ^{31}P—^{1}H coupling due to the change of the hybridization of the phosphorus atom.



(1)

EXPERIMENTAL

The proton NMR spectra were taken on a Varian HA-60-IL spectrometer fitted with a standard variable temperature probe. The proton chemical shifts are expressed in the δ-scale using tetramethylsilane as a reference standard. The coupling constants were measured directly from the 50 Hz scale of the spectrometer. The values were the average of four measurements.

The phosphorylated iminothiazolines and iminooxazolines were synthesized by either of two general procedures. The heterocyclic base was directly phosphorylated with the appropriate halophosphorus reagents, or, for compounds with both alkoxy and alkylthio groups on phosphorus, by rearrangement of the thiono to the thiolo phosphoramide with alkyl iodide. Unequivocal structural assignments were based on a combination of infrared, proton NMR and elementary analysis.

The phosphorylated guanidine was synthesized by the first method described but with tetramethylguanidine in place of a heterocyclic imine. The following are given as examples of the procedures employed.

2-(O,O-Dimethylthiophosphorylimino)-3-methyl-4-thiazoline. A solution of 21·7 g of 2-imino-3-methyl-4-thiazoline hydrogen iodide[11] in 130 ml of benzene and 28·8 g of 25% sodium hydroxide solution were stirred with 14·4 g of *O,O*-dimethyl chlorothiophosphate for 2 h at 30 °C. The benzene layer was dried over anhydrous $MgSO_4$ and evaporated to give a viscous oil which solidified on cooling. Recrystallization from petroleum ether/benzene gave 15·4 g of the title compound, m.p. 53·5 to 55·5 °C (72% yield). IR(KBr): 1570 (C=N), 1050 and 1020 cm^{-1} (P—O—C). NMR(in $CDCl_3$): δ 3·46 (s, 3 H, methyl), 3·68 (d, 6 H, methyl), 6·40 (d of d, 1 H, vinyl), 6·80 (d of d, 1 H, vinyl).

Anal. Calc. for $C_6H_{11}N_2O_2PS_2$: C, 30·25; H, 4·64; N, 11·76; S, 26·92. Found: C, 30·50; H, 4·73; N, 11·75; S, 26·77.

2-(O-Ethyl-S-methylthiophosphorylimino)-3-methyl-4-thiazoline. A solution of 11·6 g of 2-(*O,O*-diethylthiophosphorylimino)-3-methyl-4-thiazoline and 18·6 g of methyl iodide in 30 ml of benzene and 40 ml of *n*-hexane was refluxed for 2·5 h. The solvent was evaporated and the residual oil was dissolved in 100 ml of benzene. This solution was filtered and the solvent evaporated to give 10·3 g of the title compound as a pale-yellow liquid (89% yield). IR(film): 1550 (C=N), 1220 (P=O), 1040, 780 cm^{-1} (P—O—C). NMR(in $CDCl_3$): δ 1·39 (t, 3 H, methyl), 2·24 (d, 3 H, methyl), 3·48 (s, 3 H, methyl), 4·18 (d of q, 2 H, methylene), 6·38 (d of d, 1 H, vinyl), and 6·81 (d of d, 1 H, vinyl).

Anal. Calc. for $C_7H_{13}N_2O_2PS_2$: C, 33·32; H, 5·19; N, 11·11; S, 25·42. Found: C, 33·77; H, 5·36; N, 10·65; S, 25·47.

2-(O,O-Dimethylthiophosphorylimino)-3,4-dimethyl-4-oxazoline. This compound was prepared in 25% yield from 12·9 g of 2-imino-3, 4-dimethyl-4-oxazoline hydrogen iodide, 12 g of triethylamine and 8·6 g of *O,O*-dimethyl chlorothiophosphate, using 120 ml acetone as solvent. IR(film): 1660 (C=N), 1040 cm^{-1} (P—O—C). NMR($CDCl_3$): δ 2·06 (d, 3 H, methyl), 3·22 (s, 3 H, methyl), 3·70 (d, 6 H, methyl), 6·89 (d of q, 1 H, vinyl).

Anal. Calc. for $C_7H_{13}N_2O_3PS$: C, 35·59; H, 5·55; N, 11·86. Found: C, 35·75; H, 5·69; N, 11·73.

O,O-Dimethylthiophosphoryltetramethylguanidine. To 15 g of 1,1,-3,3-tetramethylguanidine in 100 ml of benzene and 27·6 g of 25% aqueous sodium hydroxide were added 27·6 g of *O,O*-dimethyl chlorothiophosphate dissolved in 20 ml benzene at 30 °C. After the mixture was stirred for 2·5 h at room temperature, the aqueous phase was separated and extracted with benzene. Evaporation of the combined benzene solutions gave 30 g of a colorless liquid in 73% yield. IR(film): 1550 (C=N), 1040, and 1060 cm^{-1} (P—O—C). NMR(in $CDCl_3$): δ 2·98 (d, 12 H, methyl), and 3·70 (d, 6 H, methyl).

RESULTS AND DISCUSSION

The proton NMR parameters of 2-(*O,O*-dimethylthiophosphorylimino)-3-methyl-4-thiazoline ($R = CH_3$, $R' = R'' = CH_3O$, and $X = S$) in various solvents are listed in Table 1. The coupling constants show no change with solvents. The five-bond ^{31}P—^{1}H couplings have been confirmed by the ^{1}H{^{31}P} heteronuclear decoupling method. No significant ^{31}P—^{1}H coupling was observed for the methyl protons at the 3 position. The half-height width of these methyl protons is 0·68 Hz, whereas that of the methoxy protons is 0·64 Hz. Of the two ring protons, the higher field absorption (6·40 ppm) was assigned to H-5 and the lower field absorption (6·80 ppm) to H-4. These assignments were based on the

Printed in Northern Ireland.

Table 1. Proton NMR parameters of 2-(*O*,*O*-dimethylthiophosphorylimino)-3-methyl-4-thiazoline

	CCl$_4$	CDCl$_3$	C$_6$D$_6$	CD$_3$COCD$_3$	CD$_3$CN
δCH$_3$O	3·62	3·68	3·60	3·62	3·63
δCH$_3$N	3·46	3·46	2·67	3·48	3·42
δH-5	6·34	6·40	5·57	6·61	6·49
δH-4	6·80	6·80	5·73	7·13	6·95
^3J(4H—5H)	4·80	4·87	4·83	4·79	4·82
^5J(4H—P)	2·28	2·27	2·21	2·26	2·30
^5J(5H—P)	1·32	1·37	1·42	1·38	1·34
^3J(H—P)	13·73	13·52	13·79	13·50	13·54

fact that nitrogen is more electronegative than sulfur. The assignments were further substantiated by the chemical shifts of H-4 (6·78 ppm) in 2-(*O*,*O*-dimethylthiophosphorylimino)-3-methyl-5-chloro-4-thiazoline and H-5 (6·05 ppm) in 2-(*O*,*O*-dimethylthiophosphorylimino)-3,4-dimethyl-4-thiazoline.

The substituents at the 3 position show little effect on the long range ^{31}P—^{1}H couplings, except when R is hydrogen as shown in Table 2 when significant changes in the *J*(4H—P), *J*(5H—P) and *J*(4H—5H) were observed. This seems to indicate that the contribution of **2** is important when R is hydrogen. The double bond character of the C$_4$—C$_5$ bond in **1** is larger than that in **2** due to conjugation in **2**.[12] Therefore the value of the *J*(4H—5H) will be expected to decrease when R is hydrogen.

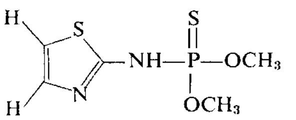
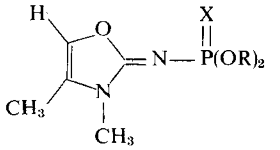

(2)

Table 3 lists the absolute values of the *J*(4H—P), *J*(5H—P) and *J*(4H—5H) of various phosphorus containing iminothiazolines by varying R′, R″ and X. The absolute value of *J*(5H—P) is smaller than that of *J*(4H—P). The long range ^{31}P—^{1}H couplings through the H—C—O—C=N—P framework in 2-(*O*,*O*-diethylphosphorylimino)-3,4-dimethyl-4-oxazoline (**3a**) and 2-(*O*,*O*-dimethylthiophosphorylimino)-3,4-dimethyl-4-oxazoline (**3b**) are 0·47 and 0·63 Hz, respectively. These results suggest that the nitrogen atom provides better interaction between the phosphorus spin and the proton spin than the sulfur atom, which is in turn better than the oxygen atom.


(**3a**) X = O; R = C$_2$H$_5$
(**3b**) X = S; R = CH$_3$

The hybridization of the phosphorus bonding orbital has a significant effect on the long range ^{31}P—^{1}H couplings.[13] The absolute value of *J*(4H—P) decreases in the order of P > PS > PO, whereas that of *J*(5H—P) increases in the order of P < PS ≃ PO. An alternative explanation would be that *J*(4H—P) and *J*(5H—P) have opposite signs. In this case, both *J*(4H—P) and *J*(5H—P) will have the same relation to phosphorus substitution. The signs of the long range ^{31}P—^{1}H couplings in this work await determination.

The five-bond ^{31}P—^{1}H couplings in tri-3-furylphosphine derivatives[9,10] were reported to be in the order of P < PO ≃ PS and tri-2-pyridylphosphine derivatives[4,5] of P < PO < PS. Only one example was reported in the literature where the order was reversed. Moritz, Saxby and Sternhell found *O*-styryldiphenylphosphine to have five-bond ^{31}P—^{1}H coupling of 1.10 Hz, whereas its methyl iodide derivative gave no coupling.[3] The reported values of five-bond ^{31}P—^{1}H couplings in trivalent phosphorus compounds were generally small and were in the range of 0·74 ~ 1·18 Hz.[3–5,9,10] These values are comparable to those observed *J*(5H—P) (0·46 ~ 0·86 Hz) shown in Table 3 where X is a lone pair of electrons. However, the values of *J*(4H—P) of the same series are in the range of 3·50 ~ 4·89 Hz. To our knowledge, they are the first examples of unusually large five-bond ^{31}P—^{1}H couplings in trivalent phosphines.

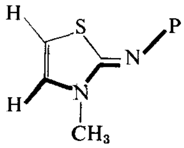
Table 2. Coupling constants of 3-substituted phosphoryliminothiazolines

R	R′	R″	X	*J*(4H—P)	*J*(5H—P)	*J*(4H—H-5)
CH$_3$	SCH$_3$	OCH$_3$	O	1·98	1·39	4·82
C$_2$H$_5$	SCH$_3$	OCH$_3$	O	1·95	1·37	4·92
CH$_2$C$_6$H$_5$	SCH$_3$	OCH$_3$	O	1·98	1·37	4·92
CH$_2$CH=CH$_2$	SCH$_3$	OCH$_3$	O	1·93	1·35	4·94
CH$_3$	OCH$_3$	OCH$_3$	S	2·27	1·37	4·87
CH$_2$C≡CH	OCH$_3$	OCH$_3$	S	2·25	1·33	4·95
CH$_2$C$_6$H$_5$	OCH$_3$	OCH$_3$	S	2·27	1·33	4·90
CH$_2$CH=CH$_2$	OCH$_3$	OCH$_3$	S	2·27	1·35	4·91
H	OCH$_3$	OCH$_3$	S	1·70	1·40	4·56

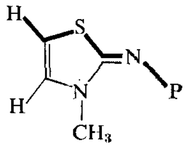
Table 3. Coupling constants of various phosphorus containing iminothiazolines

R	X	R′	R″	*J*(4H—P)	*J*(5H—P)	*J*(4H—5H)
CH$_3$		C$_6$H$_5$	C$_6$H$_5$	4·89	0·65	4·89
CH$_3$		SC$_2$H$_5$	C$_2$H$_5$	3·99	0·70	4·96
CH$_3$		SC$_2$H$_5$	SC$_2$H$_5$	3·50	0·86	4·91
CH$_3$		OC$_2$H$_5$	OC$_2$H$_5$	3·82	0·46	4·90
CH$_3$	S	C$_2$H$_5$	C$_2$H$_5$	2·18	1·70	4·88
CH$_3$	S	C$_2$H$_5$	OC$_2$H$_5$	2·19	1·55	4·87
CH$_3$	S	OCH$_3$	OCH$_3$	2·27	1·37	4·87
CH$_3$	S	OC$_2$H$_5$	OC$_2$H$_5$	2·30	1·41	4·86
CH$_3$	O	C$_2$H$_5$	SCH$_3$	1·82	1·62	4·87
CH$_3$	O	OCH$_3$	SCH$_3$	1·98	1·39	4·82
CH$_3$	O	OC$_2$H$_5$	SCH$_3$	1·97	1·41	4·91
CH$_3$	O	OC$_2$H$_5$	OC$_2$H$_5$	1·75	1·25	4·91

It is believed that the long range ^{31}P—^{1}H coupling is associated with the extended planar zig-zag configuration.[14] J(4H—P) and J(5H—P) in the H—C—N—C=N—P and H—C—S—C=N—P frameworks can be explained as stereospecific interactions along planar zig-zag paths indicated by the heavy lines in **4** and **5**.

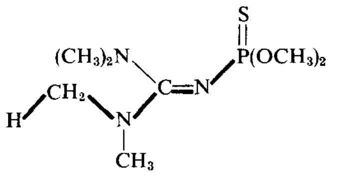


(4)



(5)

The methyl protons at the 3 position do not have the right steresopecific configuration and thus exhibit no long range ^{31}P—^{1}H coupling. The observation of the long range ^{31}P—^{1}H coupling of 0·90 Hz in *O*,*O*-dimethylthiophosphoryltetramethylguanidine (**6**) is further evidence of the importance of the planar zig-zag configuration.



(6)

Since phosphoryliminothiazolines have a C=N—P moiety, there is a possibility of **4** being a favored representation over **5**, or vice versa. Variable temperature studies ranging from 60 to −90 °C show little change in the proton NMR spectra, which suggests that the inversion of the nitrogen atom in the C=N—P system is too fast to be detected over the temperature ranges studied. The same conclusion was reached on phosphoryliminooxazolidines.[15]

REFERENCES

1. K. Khaleeluddin and J. M. W. Scott, *Chem. Commun.* 511 (1966).
2. F. Kaplan and C. O. Schulz, *Chem. Commun.* 376 (1967).
3. A. G. Moritz, J. D. Saxby and S. Sternhell, *Australian J. Chem.* **21**, 2565 (1968).
4. H. J. Jakobsen, *J. Mol. Spectry.* **34**, 245 (1970).
5. C. E. Griffin and W. A. Thomas, *J. Chem. Soc.* (*B*) 477 (1970).
6. W. McFarlane, *Org. Magn. Resonance* **1**, 3 (1969).
7. T. H. Siddall III and W. E. Stewart, *Spectrochim. Acta* **24A**, 81 (1968).
8. M. P. Simonnin and C. Charrier, *Org. Magn. Resonance* **1**, 27 (1969).
9. F. Taddei and P. Vivarelli, *Org. Magn. Resonance* **2**, 319 (1970).
10. P. Dembech, G. Seconi, P. Vivarelli, L. Schenetti and F. Taddei, *Org. Magn. Resonance* **4**, 185 (1972).
11. W. Wilson and R. Woodger, *J. Chem. Soc.* 2943 (1955).
12. R. H. Cox and A. A. Bothner-By, *J. Phys. Chem.* **73**, 2465 (1969).
13. S. L. Manatt, G. L. Juvinall, R. I. Wagner and D. D. Elleman, *J. Amer. Chem. Soc.* **88**, 2689 (1966).
14. S. Sternhell, *Quart. Rev.* (*London*) **23**, 236 (1969).
15. C. K. Tseng, W. J. Smith and E. J. Gaughan, *Spectry. Letters* **3**, 317 (1970).