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Phosphorus-31 Nuclear Magnetic Resonance Data for Some Compounds Containing Alicyclic or Heterocyclic Substituents

Richard J. Cremlyn*

School of Natural Sciences, Hatfield Polytechnic, Hatfield, Herts., United Kingdom

Michael Woods

Department of Chemistry, Birkbeck College (University of London), London WC1E 7HX, United Kingdom

The ^{31}P ^1H NMR spectra of 77 four-coordinate phosphorus compounds containing *cis*- or *trans*-4-*tert*-butylcyclohexyl, 1-menthyl, *exo*- or *endo*-norbornyl, bornyl, 1- or 2-adamantyl, morpholinyl, pyrrolidinyl, or piperazinyl ring systems have been determined. The NMR data are arranged according to the nature of the atoms adjacent to phosphorus and are discussed briefly. The spectra of compounds containing a P–O–P linkage confirm that they exist as diastereoisomers.

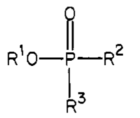
Numerous organophosphorus compounds are well-established pesticides (*1*). Recently, the synthesis and the reactivity of alicyclic and heterocyclic phosphorochloridates have been studied in some detail with a view to establishing their suitability as potential pesticides (*2*, *5–8*). In this paper, we present phosphorus-31 NMR data for derivatives of these types of compounds.

It is generally agreed that atoms adjacent to phosphorus are a dominant factor in influencing the magnitude of phosphorus-31 chemical shifts (*9*). In particular, an increase in the electronegativity of atoms bonded directly to phosphorus usually results in an upfield shift. Data for some phosphoryl compounds containing P–N and/or P–O bonds are given in Tables I, III, and V and illustrate the above statements. As the number of oxygen atoms in the molecules increases, the chemical shift becomes more negative; i.e., the phosphorus nucleus is more shielded.

There is a remarkable uniformity in many of the shifts recorded for these phosphoryl compounds, and it is clear that the bulky alicyclic or heterocyclic substituents (see Figure 1) make little relative contribution to the chemical shift. In contrast, the presence of a strong electron-withdrawing substituent (e.g., PhNHCONH) results in an appreciable shift to higher field. The ^{31}P NMR spectra of the phosphazenyl derivatives **4**, **7**, **15**, and **43** consist of two doublets with ^2J(P–N–P) in the range 22–31 Hz.

Table II summarizes data for some related thiophosphoryl derivatives; the chemical shifts are in the range normally as-

Table I. Phosphorus NMR Data for Phosphoryl Compounds


$R^1O-P(=O)(R^2)-R^3$

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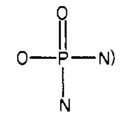
$O-P(=O)(N)-N$)

no.	R^1	R^2	R^3	δ_P[a]	ref[b]
1	A[c]	PhNH-NH	PhNH-NH	11.7	*6*
2	A	PhNH	$HOCH_2CH_2NH$	8.4	*6*
3	A	PhNH	PhNHCONH	−1.9	*6*
4	A	PhNH	$Ph_3P{=}N$	10.9,[d] −0.9 ^2J(P-P) = 30 Hz	*6*
5	A	PhNH	NH_2	7.6	*6*
6	A	$C_6H_{11}NH$	H_2N-NH	8.8	*6*
7	A	$C_6H_{11}NH$	$Ph_3P{=}N$	9.3,[d] 6.7 ^2J(P-P) = 22 Hz	*6*
8	A	PhNHCONH-NH	PhNHCSNH-NH	10.9	*6*
9	A	OC_4H_8N (morpholino)	OC_4H_8N	12.0	*6*
10	B	PhNH-NH	PhNH-NH	10.8	*6*
11	C	PhNH-NH	PhNH-NH	10.7	*6*
12	C	PhNH-NH	$HOCH_2CH_2NH$	8.4	*6*
13	C	OC_4H_8N (morpholino)	OC_4H_8N	11.6	*6*
14	D	PhNH-NH	PhNH-NH	10.8	*7*
15	D	PhNH	$Ph_3P{=}N$	10.6,[d] −1.2 ^2J(P-P) = 31 Hz	*7*
16	E	PhNH-NH	PhNH-NH	11.4	*7*
17	F	PhNH-NH	PhNH-NH	11.9	*8*
18	I	PhNH	$Ph_3P{=}N$	9.7,[d] −1.4 ^2J(P-P) = 32 Hz	*5*
19	J	H_2N-NH	Ph	8.6	*5*
20	J	$Me_2C{=}NNH$	Ph	4.2	*5*
21	J	MeNHCONHNH	$4\text{-}ClC_6H_4$	2.0	*5*
22	J	PhNHCONHNH	$4\text{-}ClC_6H_4$	7.5	*5*
23	J	PhNHNH	$4\text{-}ClC_6H_4$	1.4	*5*

[a] All compounds in this and subsequent tables were measured in deuteriochloroform solutions. [b] References in this and subsequent tables give details of the preparation of the compounds. [c] See Figure 1 for substituents A–J. [d] $Ph_3P{=}N-$.

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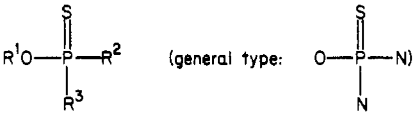
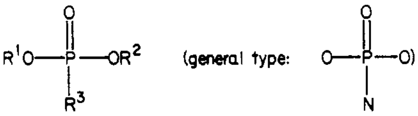
Table II. Phosphorus NMR Data for Thiophosphoryl Compounds[a]

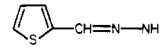
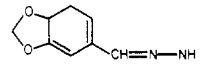
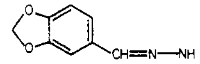


no.	R^1	R^2	R^3	δ_P	ref
24	A	PnNH-NH	PnNH-NH	70.8	*2*
25	A	PhNHCONHNH	PhNHCONHNH	69.2	*6*
26	A	$C_6H_{11}NH$	$C_6H_{11}NH$	66.6	*2*
27	A	C_4H_8NO (morpholino)	C_4H_8NO	74.0	*6*
28	A	$4\text{-}NO_2C_6H_4C(Me){=}N{-}NH$	$4\text{-}NO_2C_6H_4C(Me){=}N{-}NH$	60.9	*6*
29	B	PhNH-NH	PhNH-NH	67.9	*6*
30	C	PhNH-NH	PhNH-NH	71.3, 68.2	*6*
31	C	OC_4H_8N (morpholino)	OC_4H_8N	74.0	*6*
32	D	PhNH-NH	PhNH-NH	70.6	*7*
33	F	PhNH-NH	PhNH-NH	72.5	*8*

[a] See footnotes to Table I.

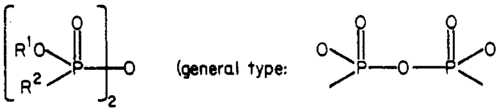
Table III. Phosphorus NMR Data for Phosphoryl Compounds[d]



no.	R^1	R^2	R^3	δ_P	ref
34	A	A	PhNH-NH	4.0	*6*
35	A	A	H_2N-NH	6.2	*6*
36	A	A	$C_6H_{11}NH$	6.2	*6*
37	A	A	$HOCH_2CH_2NH$	7.4	*6*
38	A	A	Glu=N–NH[a]	6.1	*6*
39	A	A	PhNHCONH-NH	2.3	*6*
40	A	A	PhNHCSNH-NH	1.6	*6*
41	A	A	$4\text{-}NO_2C_6H_4C(Me){=}N{-}NH$	–0.6	*2*
42	A	A	$4\text{-}PhOC_6H_4SO_2NH\text{-}NH_2$	3.8	*2*
43	A	A	$Ph_3P{=}N$	10.8,[b] 1.4 ^2J(P-P) = 28 Hz	*6*
44	A	PhNH	H	–12.5	*6*
45	A	PhNH	PhN^+H_3[c]	–1.4	*6*
46	A	B	PhNH-NH	3.9	*6*
47	A	Ph	PhNH-NH	0.1	*6*
48	A	Ph	H_2N-NH	2.7	*6*
49	A	Ph	PhNHCONH-NH	–0.8	*6*
50	A	C	PhNH-NH	4.0, 3.6	*6*
51	B	B	PhNH-NH	4.7	*6*
52	C	Ph	PhNH-NH	–0.5	*6*
53	D	Ph	PhNH-NH	0.4	*6*
54	E	Ph	PhNH-NH	–0.4	*7*
55	G	Ph	$C_6H_{11}NH$	–7.5	*2*
56	I	Ph	PhNH-NH	–5.5	*5*
57	I	Ph	$Me_2C{=}N{-}NH$	–2.5	*5*
58	I	Ph		–9.6	*5*
59	I	Ph		–3.7	*5*
60	J	$4\text{-}ClC_6H_4$	$H_2N{=}NH$	–6.3	*5*
61	J	OPh	$Me_2C{=}N{-}NH$	–6.2	*5*
62	J	$4\text{-}ClC_6H_4$		–7.3	*5*

[a] Glucose hydrazone, $HOH_2C(CHOH)_4CH{=}N{-}NH$. [b] $Ph_3P{=}N$. [c] Anilinium salt. [d] See Figure I for substituents A-J.

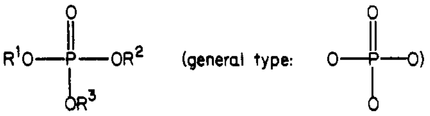
Table IV. Phosphorus NMR Data for Pyrophosphates[a]



no.	R^1	R^2	δ_P	ref
63	A	PhNH	–9.9, –10.3	*6*
64	A	$C_6H_{11}NH$	–3.2, –3.5	*6*
65	C	PhNH	–8.8, –10.2	*6*
66	D	OPh	–7.2, –8.0	*7*
67	I	PhNH	–10.2, –10.5	*5*
68	I	$C_6H_{11}NH$	–3.1, –3.6	*5*
69	Ph	K	–9.8, –10.2	*5*
70	$4\text{-}ClC_6H_4$	K	–9.7, –10.3	*5*
71	J	PhNH	–10.2, –10.5	*5*

[a] See Figure 1 for substituents A-J.

Table V. Phosphorus NMR Data for Phosphoryl Compounds



no.	R^1	R^2	R^3	δ_P	ref
72	A	H	H	–0.7	*6*
73	A	A	H	–0.8	*6*
74	B	H	H	0.6	*6*
75	E	PhN^+H_3	PhN^+H_3	–2.1	*7*
76	D	PhN^+H_3	PhN^+H_3	–2.9	*7*
77	I	Ph	PhN^+H_3	–6.5	*2*

sociated with P=S compounds (*9*). Data for pyrophosphates and pyrophosphoramides are given in Table IV. These derivatives contain two asymmetric phosphorus atoms and can exist as two stereoisomers, viz., racemic and meso forms. This feature is conformed by their ^{31}P NMR spectra as two signals are observed. An assignment of these signals to individual stereoisomers has not been attempted.

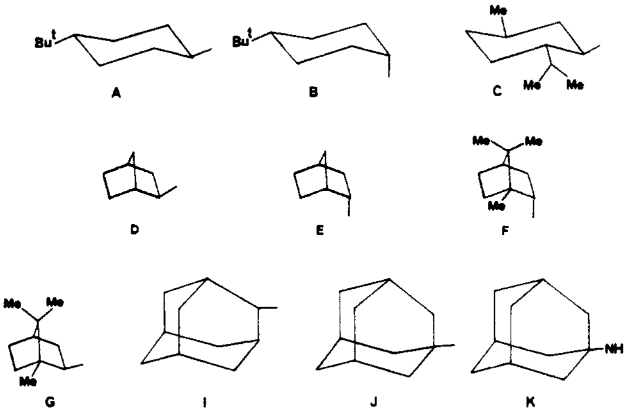


Figure 1. (A) *trans*-4-*tert*-Butylcyclohexyl; (B) *cis*-4-*tert*-butylcyclohexyl; (C) 1-menthyl; (D) *exo*-norbornyl; (E) *endo*-norbornyl; (F) bornyl; (G) isobornyl; (I) 2-adamantyl; (J) 1-adamantyl; (K) 1-adamantylamino.

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Experimental Section

cis- and *trans*-4-*tert*-butylcyclohexyl- and 1-menthylphosphorochloridates and -phosphorochloridothioates were prepared by phosphorylation of *cis*- and *trans*-4-*tert*-butylcyclohexanol and 1-menthol with phosphorus oxychloride or thiophosphoryl chloride in the presence of a tertiary base (*3*, *4*). The preparation of *exo*- and *endo*-norbornyl- (*7*) and bornyl- (*8*) phosphorochloridates and -phosphorochloridothioates has been described in detail elsewhere. Chloridates from 1- and 2-adamantols, 1-adamantylamine (*5*), pyrrolidine, morpholine, and piperazine (*2*) were obtained by a literature method. The various derivatives listed in Tables I–V, viz., amidates, azides, hydrazides, hydrazones, were obtained by treatment of the chloridates with amines, sodium azide, and hydrazine, as previously described (*2*, *5*, *7*, *8*).

Phosphorus NMR spectra were obtained from a Bruker HFX-90 spectrometer operating at 36.43 MHz. Chemical shifts are expressed on the δ scale with upfield shifts negative; the external standard is 85% phosphoric acid.

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Synthesis of Triphenyltin Halide–Diorganocyanamide Complexes

Eugene J. Kupchik* and Homayoun Naima

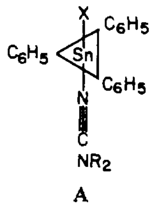
Department of Chemistry, St. John's University, Jamaica, New York 11439

Four new triphenyltin halide–diorganocyanamide complexes were synthesized by allowing triphenyltin chloride and triphenyltin iodide to react separately with dibenzylcyanamide and benzyltritylcyanamide. Their Mössbauer spectra indicate that they have a trigonal bipyramidal structure.

The synthesis of complexes of triphenyltin bromide with dibenzylcyanamide and benzyltritylcyanamide has previously been described (*1*). We now wish to describe some other triphenyltin halide–diorganocyanamide complexes.

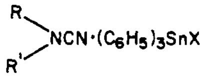
Four new triphenyltin halide–diorganocyanamide complexes were synthesized by allowing triphenyltin chloride and triphenyltin iodide to react separately with dibenzylcyanamide and benzyltritylcyanamide in refluxing acetonitrile. The new complexes were identified by elemental analysis (Table I) and by their infrared spectra (Table II).

The Mössbauer parameters of the new complexes as well as those of the previously synthesized triphenyltin bromide complexes are given in Table II. Poller and Ruddick (*2*) have concluded that large quadrupole interactions of 4.0–2.6 mm s^{-1} for triphenyltin compounds are associated with trigonal bipyramidal structures. Ensling et al. (*3*) have calculated that triphenyltin compounds in which the three phenyl groups occupy the equatorial positions of a trigonal bipyramid should exhibit a quadrupole splitting value of 3.1 mm s^{-1}. Thus, the data in Table II indicate that the complexes probably have structure A. Evidence that the nitrile nitrogen rather than the amino nitrogen is bonded to the tin has previously been given (*1*).



A

Table I. Triphenyltin Halide–Diorganocyanamide Complexes[a]


$RR'NCN\cdot(C_6H_5)_3SnX$

compd	R	R′	X	reaction time,[b] h	yield,[c] %	mp,[d] °C
I	$C_6H_5CH_2$	$C_6H_5CH_2$	Cl	20	95	85–87
II	$C_6H_5CH_2$	$C_6H_5CH_2$	I	72	92	83–85
III	$C_6H_5CH_2$	$(C_6H_5)_3C$	Cl	18	44	143–144
IV	$C_6H_5CH_2$	$(C_6H_5)_3C$	I	144	38	141–142

[a] Elemental analyses (C, H, N, X, and Sn) in agreement with theoretical values were obtained and submitted for review. [b] The triphenyltin halide and diorganocyanamide (1/1 mole ratio) were refluxed in acetonitrile for the indicated reaction time. [c] Based on material that melts within 5 °C of the analytical sample. [d] Refers to the analytical sample.

Experimental Section

Melting points were determined with a Mel-Temp capillary melting-point apparatus and are uncorrected. The infrared data (4000–400 cm^{-1}) were obtained by using KBr pellets with a Perkin-Elmer Infracord, Beckman IR 8 infrared spectrophotometer and a Perkin-Elmer Model 21 double-beam infrared spectrophotometer which was fitted with a cesium bromide prism and purged with nitrogen. The far-infrared data (400–140 cm^{-1}) were obtained with a Perkin-Elmer FIS-3 far-infrared spectrophotometer (CsI pellets). The Mössbauer spectral data were obtained at 77 K relative to $BaSnO_3$ by Austin Science Associates, Inc., Austin, TX. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

***Preparation of Triphenyltin Chloride–Dibenzylcyanamide Complex* (*I*).** A mixture of triphenyltin chloride (1.11 g, 0.002 88 mol), dibenzylcyanamide (*12*) (0.64 g, 0.0029 mol), and acetonitrile (10 mL) was refluxed for 20 h. Evaporation of the clear solution left 1.658 g (95%) of I, mp 85–87 °C. A single recrystallization from petroleum ether (bp 30–60 °C) gave

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