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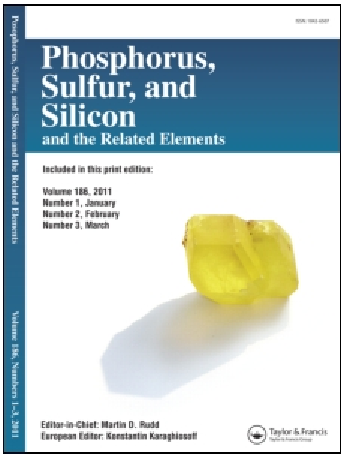

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DERIVATIVES OF NPCI$_2$(NSOCI)$_2$ AND (NPCI$_2$)$_2$ NSOCI, PART XXII.[1] CARBON-13 NMR INVESTIGATIONS ON DIMETHYLAMINO AND *N,N'*-DIMETHYLETHYLENEDIAMINO DERIVATIVES OF NPCI$_2$(NSOX)$_2$ AND (NPCI$_2$)$_2$ NSOX (X = Cl, Ph)

B. de Ruiter[a]; J. C. Van de Grampel[a]
[a] Laboratorium voor Anorganische Chemie, Rijksuniversiteit Groningen, AG Groningen, The Netherlands

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DERIVATIVES OF $NPCl_2(NSOCl)_2$ AND $(NPCl_2)_2NSOCl$, PART XXII.[1] CARBON-13 NMR INVESTIGATIONS ON DIMETHYLAMINO AND *N,N'*-DIMETHYLETHYLENEDIAMINO DERIVATIVES OF $NPCl_2(NSOX)_2$ AND $(NPCl_2)_2NSOX$ (X = Cl, Ph).

B. de RUITER and J. C. van de GRAMPEL*

Laboratorium voor Anorganische Chemie, Rijksuniversiteit Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

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^{13}C NMR data of selected dimethylamino and *N,N'*-dimethylethylenediamino derivatives of the ring systems $NPCl_2(NSOX)_2$ and $(NPCl_2)_2NSOX$ (X = Cl,Ph) show that the chemical shifts of the amino carbon atoms are relatively insensitive to the number and disposition of the ligands. The coupling constant $^2J(PC)$ is more sensitive; in dimethylamino derivatives it is significantly smaller in $PClNMe_2$ groupings than in $P(NMe_2)_2$ ones. This is probably connected with the difference in conformation of the dimethylamino ligand in these groupings in the solid state. In spirocyclic *N,N'*-dimethylethylenediamino derivatives the methylene groups show much larger $|^2J(PC)|$-values than the methyl groups. This difference is again ascribed to conformational effects.

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INTRODUCTION

During the last few years a rapidly growing amount of literature data has become available concerning ^{13}C NMR spectra of amino derivatives of compounds with pentavalent phosphorus (e.g. phosphine oxides and cyclodiphosphazanes[2–7]).

Recently we reported the synthesis of a number of dimethylamino and *N,N'*-dimethylethylenediamino derivatives of the ring systems $NPCl_2(NSOX)_2$ and $(NPCl_2)_2NSOX$ (Figure 1, X = Cl, Ph).[8–12] As an extension to our earlier reported ^{13}C NMR investigations of the dimethylamino derivatives of the S-phenylated rings[11] we have now conducted ^{13}C NMR measurements of some dimethylamino deriva-

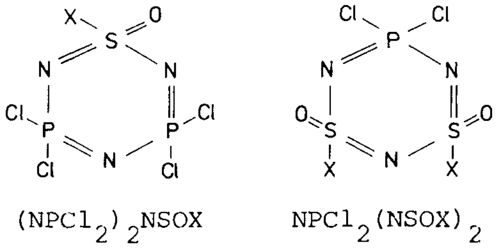

FIGURE 1 General structures of $1\lambda^6,2,4,6,3\lambda^5,5\lambda^5$-thiatriazadiphosphorine-1-oxides and $1\lambda^6,3\lambda^6,2,4,6,5\lambda^5$-dithiatriazaphosphorine-1,3-dioxides.

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* Author to whom all correspondence should be addressed.

tives of the S-chlorinated rings and of all *N,N'*-dimethylethylenediamino derivatives previously reported. In the present paper we describe the results of these measurements.

RESULTS AND DISCUSSION

Dimethylamino Derivatives

A list of ^{13}C NMR data of dimethylamino derivatives of $NPCl_2(NSOCl)_2$ and $(NPCl_2)_2NSOCl$ is given in Table 1. The proton-noise decoupled spectra of derivatives with one phosphorus nucleus are easily interpretable. ^{13}C atoms in sulfur-bonded groups cause a singlet (in some cases a long-range coupling with ^{31}P is observed), whereas those in phosphorus-bonded groups give rise to a doublet due to a two-bond coupling with the ^{31}P nucleus (1.9–4.9 Hz). On the analogy of literature data concerning dimethylamino derivatives of P(V) compounds[3,5] $^2J(PC)$ is assumed to be positive. Most of the spectra of compounds containing two phosphorus nuclei show second-order effects. Derivatives possessing two chemically equivalent phosphorus nuclei show the X part(s) of one or two AA'X spin systems (deceptively simple triplets), which are well-documented in the literature.[13] The doubling of the signals for phosphorus-bonded dimethylamino groups in $[NP(NMe_2)_2]_2NSONMe_2$ is due to a chemical inequivalence (groups *cis* and *trans* with respect to the sulfur-bonded dimethylamino group).

From Table 1 it appears that all signals for P-bonded groups lie around 35 ppm, and that no conspicuous relationship between ^{13}C chemical shift and molecular structure can be discerned. $^2J(PC)$ is more sensitive to alterations in the molecule; in $PClNMe_2$ groupings its value tends to decrease with increasing degree of chlorine substitution at the other ring units. However, if the chlorine ligand in geminal position is replaced $^2J(PC)$ shows a relatively sharp increase (which has also been noticed for derivatives of the S-phenylated systems[11]).

TABLE 1

^{13}C NMR data of dimethylamino derivatives

compound	δ(PNC) (ppm)	$^2J(PC)$ (Hz)	δ(SNC) (ppm)	$^4J(PC)^a$ (Hz)
cis-$NPCl_2NSOClNSONMe_2$			37.4	0.3
trans-$NPCl_2NSOClNSONMe_2$			37.8	—
$(1\alpha,3\alpha,5\alpha)$-$NPClNMe_2(NSOCl)_2$	35.7	3.7		
$(1\alpha,3\alpha,5\beta)$-$NPClNMe_2(NSOCl)_2$	36.3	2.4		
$(1\alpha,3\alpha,5\beta)$-$NPClNMe_2NSOClNSONMe_2$	35.8	2.4	37.4	0.4
$(1\alpha,3\alpha,5\beta)$-$NPClNMe_2(NSONMe_2)_2$	35.3	1.9	37.7	—
trans-$NP(NMe_2)_2(NSONMe_2)_2$	35.4	4.9	37.3	—
cis-$NPCl_2NPClNMe_2NSOCl$	35.4	3.6^b		
trans-$NPCl_2NPClNMe_2NSOCl$	35.7	2.9^b		
$(1\alpha,3\alpha,5\alpha)$-$(NPClNMe_2)_2NSOCl$	35.5	3.1^b		
$(1\alpha,3\alpha,5\alpha)$-$(NPClNMe_2)_2NSONMe_2$	35.5	2.4^b	37.7	—
$[NP(NMe_2)_2]_2NSONMe_2$	35.1 34.9	3.8^b 3.8^b	36.9	—

[a] When observed.
[b] $|{}^2J(PC) + {}^4J(PC)|$.

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It is well-known that in P(III)-N compounds ${}^{2}J(\mathrm{PC})$ is extremely sensitive to conformational effects,[14] but the behavior of ${}^{2}J(\mathrm{PC})$ in P(V)-N compounds is much less well understood. It is, however, likely that the molecular conformation in these compounds also contributes considerably to the value of ${}^{2}J(\mathrm{PC})$. It should be noticed in this context that in solid chlorodimethylaminocyclophosphazenes the conformation of the dimethylamino group with respect to the ring plane in $PClNMe_2$ units is different from that in $P(NMe_2)_2$ units. The angle between the plane $N_{exo}C_2$ (dimethylamino) and the plane $PN_{exo}Cl$ in $PClNMe_2$ units is always near 90°, while the angle between the planes $N_{exo}C_2$ and $P(N_{exo})_2$ in $P(NMe_2)_2$ units is about 45°;[15–17] it can be assumed that this is also true for dimethylamino derivatives of the mixed P,N,S ring systems. The difference in ${}^{2}J(\mathrm{PC})$ within $PClNMe_2$ groupings on the one, and $P(NMe_2)_2$ groupings on the other hand may well be attributable to conformational effects of this type.

N,N′-Dimethylethylenediamino Derivatives

Reactions of $NPCl_2(NSOX)_2$ and $(NPCl_2)_2NSOX$ (X = Cl,Ph) with *N,N′*-dimethylethylenediamine lead to spirocyclic derivatives containing one or two 1,3-dimethyl-1,3,2-diazaphospholidine (N_2PC_2) rings.[12] Only a limited number of ^{13}C NMR data on these five-membered ring systems with pentavalent phosphorus are known;[4,6] the few data show a rather large variation for all parameters, in particular those concerning the methylene carbon atoms.

The ^{13}C NMR parameters of the *N,N′*-dimethylethylenediamino derivatives of the ring systems are listed in Table 2. In all compounds, with the exception of *trans*-$NP(NMeCH_2)_2(NSOPh)_2$, both the methyl and the methylene group(s) show two signals. Similar to the situation for the dimethylamino carbon atoms in $[NP(NMe_2)_2]_2NSONMe_2$ (Table 1), this is due to a chemical inequivalence, arising from the two different ligands at the sulfur center(s).

In the spirocyclic compounds both types of carbon atoms are more shielded than in 1,3-dimethyl-1,3,2-diazaphospholidines with trivalent phosphorus, of which more data are known.[18,19] The magnitude of $\lvert {}^{2}J(\mathrm{PC}) \rvert$ (methyl groups) is comparable with

TABLE 2

^{13}C NMR data of *N,N′*-dimethylethylenediamino derivatives

	CH₃			CH₂		
compound	δ(C) (ppm)	$\lvert {}^{2}J(\mathrm{PC}) \rvert$ (Hz)	$\lvert {}^{4}J(\mathrm{PC}) \rvert$[a] (Hz)	δ(C) (ppm)	$\lvert {}^{2}J(\mathrm{PC})$ (Hz)	$\lvert {}^{4}J(\mathrm{PC}) \rvert$[a] (Hz)
cis-$NP(NMeCH_2)_2(NSOCl)_2$	30.0	5.0		46.8	16.2	
	30.9	5.3		47.0	15.1	
trans-$NP(NMeCH_2)_2(NSOPh)_2$	30.4	4.7		46.5	13.9	
$NPCl_2NP(NMeCH_2)_2NSOCl$	30.3	4.9	—	46.8	14.9	0.7
	31.1	4.9	0.5	47.1	14.5	0.5
$NPCl_2NP(NMeCH_2)_2NSOPh$	30.3	5.3	—	46.6	13.8	—
	30.5	4.9	0.6	46.8	13.6	—
$[NP(NMeCH_2)_2]_2NSOPh$	30.2	4.3[b]		46.0	13.2[b]	
	30.6	3.9[b]		46.3	12.9[b]	

[a] When observed.

[b] $\lvert {}^{2}J(\mathrm{PC}) + {}^{4}J(\mathrm{PC}) \rvert$.

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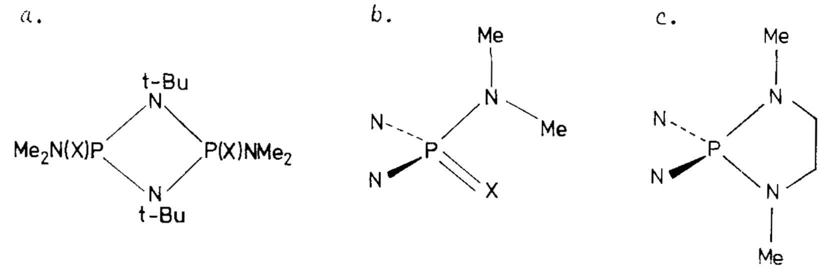


FIGURE 2

that of ${}^2J$(PC) in corresponding dimethylamino derivatives (Table 1 and Ref. 11), and is much smaller than ${}^2J$(PC) in P(III) compounds (general value about 24 Hz). In contradistinction, the value of $|{}^2J(\text{PC})|$ (methylene groups) is much larger than in the dimethylamino derivatives, and even significantly larger than in P(III) compounds (about 10 Hz). The remarkable difference in $|{}^2J(\text{PC})|$ between methyl and methylene carbons is probably again due to conformational effects; the data known for other 1,3-dimethyl-1,3,2-diazaphosph(V)olidines show the same phenomenon.[4,6] Interestingly, a similar behavior is observed in dimethylamino derivatives of selected cyclodiphosph(V)azanes (see Figure 2a);[5] at sufficiently low temperatures the ^{13}C NMR signals of these four-membered ring derivatives are doubled due to restricted rotation about the exocyclic P—N bonds. In the "frozen" conformation the dimethylamino nitrogen lone pair is supposed to lie in the direction orthogonal to the $PN_{exo}X$ plane (see Figure 2b), leading to a distinct structural similarity between this system and the spirocyclic compounds treated in this paper (see Figure 2c). At temperatures below coalescence the two different methyl carbon atoms show a striking difference in ${}^2J$(PC) values (<1 and 10–13 Hz, respectively), when X = S or Se. It is tempting to connect these values with those of Table 2 where also two significantly different series of values of $|{}^2J(\text{PC})|$ are listed. The methyl groups in the spiro compounds are then related to that methyl group in the cyclodiphosphazane derivatives which shows the smaller coupling constant; thus, from the structural relationship discussed above, this methyl group will be the one *trans* with respect to the chalcogen atom (as already suggested by the authors[5]).

Phenyl Derivatives

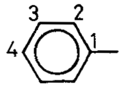
The ^{13}C NMR parameters of the phenyl groups, present in three *N,N'*-dimethylethylenediamino derivatives, have also been determined. The data are given in Table 3.

TABLE 3

^{13}C NMR parameters of the phenyl groups in some spirocyclic compounds

compound	δ(C-1)[a] (ppm)	${}^3J$(PC) (Hz)	δ(C-2)[a] (ppm)	δ(C-3)[a] (ppm)	δ(C-4)[a] (ppm)
trans-$NP(NMeCH_2)_2(NSOPh)_2$	145.0	2.7	125.0	128.4	131.8
$NPCl_2NP(NMeCH_2)_2NSOPh$	145.2	4.9	124.5	128.4	131.6
$[NP(NMeCH_2)_2]_2NSOPh$	146.9	4.6	124.0	127.3	129.8

a



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They correspond very well with those of dimethylamino derivatives with the same degree of chlorine substitution,[11] and seem independent on the mutual position of the amino ligands (geminal or non-geminal).

EXPERIMENTAL

The synthesis of the compounds has been described previously.[8-10,12]

^{13}C NMR spectra of saturated $CDCl_3$ solutions (in 5 mm tubes) were recorded at 25.2 MHz with a Varian XL-100 spectrometer, operating in the Fourier transform mode. The central resonance line of the solvent was used as reference peak (76.9 ppm downfield from TMS). Proton-noise decoupled spectra were taken under the following conditions: sweep width 5000 Hz, acquisition time 0.8 s, pulse width 75 or 27 μs. $^2J(PC)$ was determined from expanded spectra (sweep width 150–600 Hz; acquisition time 26.60–6.67 s). Field frequency lock was achieved by using the ^2H resonance line of the solvent.

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