Derivatives of NPC\(_1\)\(_2\)(NSO\(_X\)\(_3\)) and (NPC\(_1\)\(_2\))\(_2\)NSO\(_X\), Part XX [1]

Reactions of Some Inorganic Ring Systems with N,N'-Dimethylethylenediamine

Barteld de Ruiter, Goert Kuipers, Jan H. Bijlaart, and Johan C. van de Grampel*

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

Z. Naturforsch. 37b, 1425–1429 (1982); received June 18, 1982

Phosphorus-Sulfur-Nitrogen Heterocycles, Diazaphospholidines, NMR Spectra

Reactions of the ring systems (NPC\(_1\)\(_2\)\(_2\)), (NPC\(_1\)\(_2\))\(_2\)NSO\(_X\), and NPC\(_1\)\(_2\)NSO\(_X\)\(_2\)\(_2\) (X = Cl, Ph) with N,N'-dimethylethylenediamine lead to mono-, bis-, and tris(spiro cyclic) compounds as the only characterizable products. The \(^1\)H and \(^31\)P NMR parameters are reported and briefly discussed.

Generally, di- and tetrasubstituted secondary amino derivatives of hexachlorocyclophosphazene, (NPC\(_1\)\(_2\)\(_3\)), possess non-geminal structures [2]. The very few examples of geminal compounds have either been isolated in low yield or are derivatives of aziridine, an amine with a rather deviating behaviour [3, 4]. Recently, Goldschmidt has reported an indirect preparation pathway for geminal secondary amino derivatives [5].

An interesting other route to geminal compounds is substitution reactions of the ring system with a difunctional secondary amine, leading to spirocyclic compounds. The mono- and bis(spiro cyclic) N,N'-dimethylethylenediamino derivatives of (NPC\(_1\)\(_2\)\(_2\)) have already been described [6]. As we were particularly interested in the NMR characteristics of geminal derivatives of the ring systems (NPC\(_1\)\(_2\)\(_2\)), (NPC\(_1\)\(_2\))\(_2\)NSO\(_X\), and NPC\(_1\)\(_2\)NSO\(_X\)\(_2\) (see Fig. 1; X = Cl, Ph), we have conducted a number of reactions between these rings and N,N'-dimethylethylenediamine; for the spirocyclic compounds

![Diagram]

Reactions with (NPC\(_1\)\(_2\))\(_2\)NSO\(_X\) offer a significantly less simple picture. A 1:2 molar ratio reaction in ether affords the (air-sensitive) mono(spiro cyclic) NPC\(_1\)\(_2\)NP(NMeCH\(_2\))\(_2\)NSO\(_X\) and NPC\(_1\)\(_2\)NP(NMeCH\(_2\))\(_2\)NSO\(_X\). The compounds [NPC\(_1\)\(_2\)NP(NMeCH\(_2\))\(_2\)]\(_2\)NOPOh and [NPC\(_1\)\(_2\)NP(NMeCH\(_2\))\(_2\)]\(_2\)NSOPOh are obtained after reactions in ether (1:2 molar ratio) and acetonitrile (1:4), respectively.

Results and Discussion

* Preparation

Depending on the conditions used, reactions of (NPC\(_1\)\(_2\)\(_2\)) with N,N'-dimethylethylenediamine in ether afford the mono- and bis(spiro cyclic) compounds (NPC\(_1\)\(_2\)\(_2\))NP(NMeCH\(_2\))\(_2\) and NPC\(_1\)\(_2\)NP(NMeCH\(_2\))\(_2\)NSO\(_X\)\(_2\), containing the 1,3,2-diazaphospholidine (N\(_3\)P\(_2\)) ring [6]. The hitherto unknown tris(spiro cyclic) derivative [NP(NMeCH\(_2\))\(_2\)]\(_2\)NOPOh can be obtained by reaction of (NPC\(_1\)\(_2\)\(_2\)) with an excess of amine in boiling acetonitrile.

A similar straightforward reaction behaviour is observed for (NPC\(_1\)\(_2\))\(_2\)NSO; the compounds NPC\(_1\)\(_2\)NP(NMeCH\(_2\))\(_2\)NSOPOh and NPC\(_1\)\(_2\)NP(NMeCH\(_2\))\(_2\)NOPOh are obtained after reactions in ether (1:2 molar ratio) and acetonitrile (1:4), respectively.

Reprint requests to Dr. J. C. van de Grampel.

0340–5087/82/1100–1425/$01.00/0
structure. Presumably, the electron release of the four amino substituents in the hypothetical bis-
(spirocyclic) \([\text{NPCl}_2(\text{NSOCl})_2]_2\) leads to a cleavage of the sulfur-chlorine bond, thus initiating polymerization.

**trans-NPCl\(_2\)(NSOPh)\(_2\)** readily affords **trans-NP(NMeCH\(_2\))\(_2\)(NSOPh)\(_2\)**, which is accompanied by a second product (5% relative yield) with NMR parameters \(^{31}\text{P}: 16.5\text{ ppm}; \^3\text{J(PH)} 11.7\text{ Hz} \) very close to those of the main product (see Tables I and II). The side-product could neither be isolated nor identified.

Finally, **cis-NPCl\(_2\)(NSOCl)\(_2\)** affords the expected spirocyclic derivative **cis-NP(NMeCH\(_2\))\(_2\)(NSOCl)\(_2\)** after a reaction in ether. In acetonitrile, in which solvent the first chlorine substitution step of **cis-NPCl\(_2\)(NSOCl)\(_2\)** with secondary amines takes place at one of the sulfur centres \([7, 8]\), the reaction leads to a resinous mixture of products, in which traces of **cis-NP(NMeCH\(_2\))\(_2\)(NSOCl)\(_2\)** could be identified; no further oligomeric (e.g. bicyclic) products were observed.

**NMR spectra**

The \(^1\text{H}\) and \(^{31}\text{P}\) NMR data of the spirocyclic compounds are summarized in the Tables I and II, respectively. In the \(^1\text{H}\) NMR spectra two groups of signals can be distinguished; one (2.2–2.8 ppm) arises from the methyl-, the other one (3.1–3.4 ppm) from the methylene protons. The methyl signals are sharp, whereas the methylene groups may give rise to complicated resonance patterns \([9, 10]\) (see Fig. 2); this may be due to conformational effects within the \(\text{N}_2\text{PCl}_2\) ring(s). For compounds with two

---

**Table I.** \(^1\text{H}\)-NMR parameters of \(\text{N,N'}\)-dimethyl-
ethylenediamino derivatives of inorganic ring systems.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\delta(CH_3)) (ppm)</th>
<th>(\delta(CH_2))</th>
<th>(\delta(CH_3))</th>
<th>(\delta(CH_2))</th>
<th>(^3\text{J(PH)}) (Hz)</th>
<th>(^5\text{J(PH)}) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2)</td>
<td>2.55</td>
<td>11.6</td>
<td>3.10</td>
<td>10.8</td>
<td>1.2</td>
<td>11.8</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOPh})</td>
<td>2.58</td>
<td>11.9</td>
<td>3.13</td>
<td>10.8</td>
<td>1.2</td>
<td>11.8</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOCl})</td>
<td>2.46</td>
<td>11.6</td>
<td>3.16</td>
<td>10.8</td>
<td>1.2</td>
<td>12.0</td>
</tr>
</tbody>
</table>

---

**Table II.** \(^{31}\text{P}\)-NMR parameters of relevant compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\delta(\text{PCl}_2)) (ppm)</th>
<th>(\delta([\text{NP(NMeCH}_2\text{)}_2])) (ppm)</th>
<th>(^2\text{J(PP)}) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2)</td>
<td>22.1</td>
<td>19.9</td>
<td>41.8</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOPh})</td>
<td>26.7</td>
<td>18.3</td>
<td>51.6</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOCl})</td>
<td>26.3</td>
<td>18.4</td>
<td>65.9</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOPh})</td>
<td>22.1</td>
<td>19.9</td>
<td>41.8</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOCl})</td>
<td>26.7</td>
<td>18.3</td>
<td>51.6</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOPh})</td>
<td>26.3</td>
<td>18.4</td>
<td>65.9</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOCl})</td>
<td>22.1</td>
<td>19.9</td>
<td>41.8</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOPh})</td>
<td>26.7</td>
<td>18.3</td>
<td>51.6</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOCl})</td>
<td>26.3</td>
<td>18.4</td>
<td>65.9</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOPh})</td>
<td>22.1</td>
<td>19.9</td>
<td>41.8</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOCl})</td>
<td>26.7</td>
<td>18.3</td>
<td>51.6</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOPh})</td>
<td>26.3</td>
<td>18.4</td>
<td>65.9</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOCl})</td>
<td>22.1</td>
<td>19.9</td>
<td>41.8</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOPh})</td>
<td>26.7</td>
<td>18.3</td>
<td>51.6</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOCl})</td>
<td>26.3</td>
<td>18.4</td>
<td>65.9</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOPh})</td>
<td>22.1</td>
<td>19.9</td>
<td>41.8</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOCl})</td>
<td>26.7</td>
<td>18.3</td>
<td>51.6</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOPh})</td>
<td>26.3</td>
<td>18.4</td>
<td>65.9</td>
</tr>
<tr>
<td>(\text{NPCl}_2\text{NP(NMeCH}_2\text{)}_2\text{NSOCl})</td>
<td>22.1</td>
<td>19.9</td>
<td>41.8</td>
</tr>
</tbody>
</table>

---

\(^a\) Apparent coupling constant (where applicable);  
\(^b\) apparent coupling constant;  
\(^c\) data from \([6]\).

---
Fig. 2. ¹H-NMR spectra of a. [NP(NMeCH₂)₂]₃, b. NPCl₂NP(NMeCH₂)₂NSOPh, c. [NP(NMeCH₂)₂]₂NSOPh, and d. trans-NP(NMeCH₂)₂(NSOPh)₂.

or three chemically equivalent phosphorus atoms
the spectra show the second-order humps, already
familiar from other derivatives of the ring systems
[11, 12]. Typical spectra are shown in Fig. 2.

It is remarkable (cf. [7]), that the chemical shift
of the methyl protons is hardly affected by sub-
stitution of chlorine ligands of other phosphorus
centres, as illustrated by the shift values for the
three derivatives of (NPCl₂)₃. A considerable upfield
shift of the methyl signals is observed on replacing
sulfur-bonded chlorine atoms by phenyl groups.
By analogy with the dimethylamino derivatives [12]
we assign the high-field signals in the spirocyclic
derivatives of (NPCl₂)₂NSOPh to the methyl groups
cis with respect to the phenyl group. The methylene
signals show a relationship between chemical shift
and electron-withdrawing capacity of the other ring
units. The shielding effect of the different groupings
decreases in the order SOPh > P(NMeCH₂)₂ >
PCl₂ > SOCl.

The introduction of a spirocyclic centre affects
the ³¹P NMR shift of the directly involved phospho-
rus atom in a way strongly depending on the nature
of the central ring. It varies from an upfield shift
of 13.1 ppm for cis-NP(NMeCH₂)₂(NSOCl)₂ as com-
pared with cis-NPCl₂(NSOCl)₂ as well as npole
downfield shift (about 1 ppm) for the three derivatives
of (NPCl₂)₃. The chemical shifts can be roughly
compared with those of corresponding dimethyl-
amino derivatives (if available; see Table II).

As expected [13], the chemical shifts of the
phosphorus atoms, not directly involved in the
substitution process, are also considerably affected;
in general, a downfield shift of about 5 ppm for
every introduced spirocyclic centre is noticed for
both PCl₂ and P(NMeCH₂)₂ groupings.

Experimental

All reactions were carried out under dry nitrogen.
(NPCl₂)₃ was kindly provided by Otsuka Chemical
Co., Ltd., Osaka, Japan; cis-NPCl₂(NSOCl)₂,
trans-NPCl₂(NSOPh)₂, (NPCl₂)₂NSOCl, and
(NPCl₂)₂NSOPh were prepared as described else-
where. N,N'-Dimethylethylenediamine (Aldrich)
was distilled over KOH prior to use. Solvents were
dried by conventional methods. Elemental analyses
were carried out at the Microanalytical Department
of this University under supervision of Mr. A. F.
Hamminga. NMR spectra were taken by or under supervision of Mr.
C. Kruk at the Department of Organic Chemistry
of the University of Amsterdam with a Varian
XL-100 FT spectrometer, operating at 40.5 MHz;
85% H₃PO₄ was used as external reference. Field
frequency lock was achieved by using the ²H
resonance line of the solvent.

Preparation of {NP(NMeCH₂)₂}₃

A solution of 9.70 g (0.11 mol) of N,N'-dimethyl-
ethylenediamine in 200 ml of acetonitrile is added
in 15 min to a well-stirred solution of 3.48 g (0.01 mol) of (NPCl)₂ in 200 ml of the same solvent at room temperature. The mixture is boiled under reflux for 17 h. The solvent and excess of amine are thoroughly driven off in vacuo and the residue is extracted several times with boiling ether. Crystallization of the ether-soluble fractions from ether affords 26% of pure [NP(NMeCH₂)]₂, m.p. 245 °C (dec.).

**Analysis**

Calcd C 36.64 H 7.69 N 32.05.
Found C 36.70 H 7.61 N 32.25.

**Preparation of NPCl₂NP(NMeCH₂)₂NSOPh**

A solution of 0.53 g (6.0 mmol) of N,N'-dimethyl-ethylenediamine in 60 ml of ether is added in 30 min to a well-stirred solution of 1.11 g (3.0 mmol) of (NPCl)₂NSOPh in 60 ml of the same solvent, cooled at —30 °C. The mixture is allowed to warm up to room temperature and stirred for 17 h. The precipitated amine dihydrochloride is filtered off and washed thoroughly with boiling ether. Crystallization of the ether-soluble fractions from ether affords 26% of pure NPCl₂NP(NMeCH₂)₂NSOPh, m.p. 107.5–108.5 °C.

**Analysis**


**Preparation of trans-NP(NMeCH₂)₂(NSOCl)₂**

A solution of 0.93 g (3.0 mmol) of cis-NPCl₂NSOCl in 60 ml of ether is added in 30 min to a well-stirred solution of 1.18 g (3.0 mmol) of (NPCl)₂NSOCl in 60 ml of the same solvent at —30 °C. The mixture is allowed to warm to room temperature and stirred for 17 h. The precipitated amine dihydrochloride is filtered off and washed thoroughly with ether. Crystallization of the ether-soluble fractions from ether affords 26% of pure cis-NPCl₂NP(NMeCH₂)₂NSOCl, m.p. 190–191 °C.

**Analysis**

Found C 14.06 H 2.95 N 20.34 S 9.30 Cl 30.87.

**Preparation of cis-NP(NMeCH₂)₂(NSOCl)₂**

A solution of 0.93 g (3.0 mmol) of diamin in 60 ml of ether is added in 30 min to a well-stirred solution of 1.11 g (3.0 mmol) of (NPCl)₂NSOCl in 60 ml of the same solvent at —30 °C. The mixture is allowed to warm to room temperature and stirred for 17 h. The precipitated amine dihydrochloride is filtered off and washed thoroughly with ether. Crystallization of the ether-soluble fractions from ether affords 26% of pure cis-NPCl₂NP(NMeCH₂)₂NSOCl, m.p. 190–191 °C.

**Analysis**

Calcd C 41.88 H 6.29 N 24.43 S 15.72.
Found C 41.86 H 6.28 N 24.42 S 15.70.

**Preparation of cis-NPCl₂NP(NMeCH₂)₂(NSOCl)₂**

A solution of 1.06 g (12.0 mmol) of diamin in 60 ml of ether is added in 30 min to a well-stirred solution of 1.11 g (3.0 mmol) of (NPCl)₂NSOCl in 60 ml of the same solvent at —30 °C. The mixture is allowed to warm to room temperature and stirred for 17 h. The precipitated amine dihydrochloride is filtered off and washed thoroughly with ether. Crystallization of the ether-soluble fractions from ether affords 26% of pure cis-NPCl₂NP(NMeCH₂)₂NSOCl, m.p. 190–191 °C.

**Analysis**

Calcd C 46.92 H 4.88 N 15.66.
Found C 46.79 H 4.87 N 15.72.


