

Some Reactions of Hexachlorocyclo- diphosphazanes with Amines: *cis-trans* Isomerism in Aminocyclodiphosphazane

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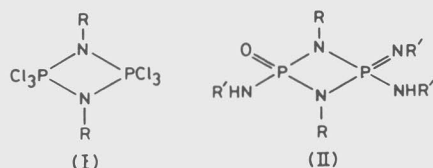
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Interaction of 1,3-diaryl-2,2,2,4,4,4-hexachlorocyclo-
diphosphazanes (Ia, b) with some amines in dry benzene furnishes the
expected amino derivatives (IIa-o). Geometrical isomers have been
isolated in the reaction of Ia with *m*-toluidine only. The structures of
the products have been elucidated on the basis of chemical and
physicochemical evidences.

The synthesis of chlorocyclodiphosphazanes has been
reported by Becke-Goehring *et al.*¹. Michaelis² also
synthesised hexachlorocyclodiphosphazanes of type
(I) by the interaction of phosphorus pentachloride with
certain amines.

The author was prompted to synthesise some
aminocyclodiphosphazane derivatives (IIa-o) in view
of the fact that some these compounds (IIb, d, e, g, f
and m) showed broad spectrum activity on different
organisms³ such as *B. subtilis*, *B. mycoides*, *B. cereus*,
E. coli and *S. typhosa*.



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|--|---|
| <p>R' = (a) C₆H₅
(c) C₆H₄CH₃ (m)
(e) C₆H₅CH₂
(g) C₆H₅NH
(i) C₆H₄OCH₃ (o)
(k) C₆H₄
(m) C₆H₄CH₃ (m)
(o) C₆H₅CH₂</p> | <p>(b) C₆H₄CH₃ (o)
(d) C₆H₄CH₃ (p)
(f) C₆H₅Br (o)
(h) C₅H₄N (2)
(j) C₄H₃O (2)
(l) C₆H₄CH₃ (o)
(n) C₆H₄CH₃ (p)</p> |
|--|---|

The starting materials 2,2,2,4,4,4-hexachlorocyclo-
diphosphazanes (Ia, b) were prepared by the method of
Chapmann and Kirsanov^{4,5}. The interaction of Ia, b
with some aryl amines, after filtering the insoluble

amine hydrochloride, gave the amino derivatives of
substituted cyclodiphosphazanes (IIa-o; cf. Table 1).
The structures of the products were established as 1,3-
diaryl-2,4-diaryl-amino-4-oxo-2-aryliminocyclodi-
phosphazanes (IIa-o) by elemental analyses and IR,
UV and PMR data.

The IR spectra of IIa-o exhibited a doublet band at
700-750 characteristic of the cyclic $\nu(\text{P}-\text{N})$ mode⁶, a
band at 1280-1300 characteristic of the exocyclic $\nu(\text{P}=\text{N})$
and a band at 1200-1220 cm⁻¹ characteristic of
 $\nu(\text{P}=\text{O})$.

In the present study, only one cyclodiphosphazane
compound was isolated from each reaction although
TLC indicated the probable presence of a second
isomer in the reaction between hexachlorocyclo-
diphosphazane (Ia) and *m*-toluidine. Separation of these
isomeric species, both analysing for C₃₅H₃₇N₅P₂O,
was effected by fractional crystallization. The two
isomers exhibited different IR characteristics. The *cis*-
isomer, m.p. 191°, exhibited hyperfine structure in its
IR spectrum in the region 470-650 cm⁻¹ and an
additional band at 1960 cm⁻¹. The *trans*-isomer, m.p.
150°, did not show any of these characteristics in its IR
spectrum.

The R_f values (TLC) of the two isomeric compounds
were also different. Thus, the compound, m.p. 191°,
was tentatively assigned the *cis*-structure since it was
more polar and tightly held by the adsorbent than the
trans-isomer, m.p. 150°. Shaw and Ibrahim⁷ have
reported the existence of geometrical isomerism in the
four-membered ring system.

The UV spectra of IIa-o displayed absorption bands
in the region 265-275 nm corresponding to $n-\pi^*$
transition characteristic of delocalization within the
four-membered ring structure⁸. The UV spectra and
molecular weight determinations indicated that these
compounds were dimeric⁸.

The structure of compound (IIl), as a representative
example, was further confirmed on the basis of its
60 MHz and 100 MHz PMR spectra. The PMR
spectrum exhibited four signals for methyl protons at
 δ 1.9, 2.2, 2.55 and 3.4 ppm in the intensity ratio of
2:1:1:1. The band at δ 3.4 ppm was assigned to the
CH₃ protons of the *o*-tolyl groups and the others for
the three CH₃ groups of the *o*-toluidino groups. The
aromatic protons appeared as two separate signals
indicating the existence of two types of aromatic
protons, i.e. aromatic protons in the *o*-tolyl part of the
molecule and those in the *o*-toluidino part of the
molecule.

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Table 1—Characterization Data of Aminocyclodiphosphazanes (IIa-o)

Compd	m.p. (°C)	Mol. wt found (calc.)	Solvent of crystalliz- ation	Found (Calc.) %			
				C	H	N	P
IIa	—	559.20 (563.11)	Benzene- ethanol	68.10 (68.25)	5.50 (5.54)	12.10 (12.44)	10.90 (11.00)
IIb	212	602.13 (605.58)	Toluene- ethanol	67.83 (69.41)	6.05 (6.15)	11.57 (11.65)	10.11 (10.23)
IIc (cis)	191	603.72 (605.58)	Do	68.65 (69.41)	6.00 (6.15)	11.60 (11.65)	10.15 (10.23)
IIc (trans)	150(d)	601.94 (605.58)	Chloroform	68.55 (69.41)	5.95 (6.15)	11.60 (11.65)	10.02 (10.23)
II d	> 150	604.11 (605.58)	Toluene- AcOH	68.35 (69.41)	5.97 (6.15)	11.55 (11.65)	10.20 (10.23)
IIe	250	601.87 (605.58)	Benzene- ethanol	67.47 (69.41)	5.85 (6.15)	11.62 (11.65)	10.09 (10.23)
II f	197(d)	— (800.20)	Toluene- ethanol	47.98 (48.03)	3.35 (3.52)	8.70 (8.75)	7.58 (7.74)
II g	240	606.56 (608.56)	Do	62.70 (63.15)	5.62 (5.63)	18.30 (18.41)	10.00 (10.18)
II h	220	561.68 (566.35)	AcOH- ethanol	59.77 (61.50)	4.87 (4.98)	19.64 (19.79)	10.80 (10.94)
II i	218	692.43 (695.61)	Do	58.60 (60.43)	5.04 (5.36)	16.10 (16.11)	8.85 (8.91)
II j	180(d)	570.00 (573.05)	Toluene- ethanol	60.55 (60.78)	4.52 (4.92)	12.00 (12.22)	10.70 (10.81)
II k	—	549.50 (563.00)	Chloroform	67.80 (68.20)	5.10 (5.50)	12.20 (12.40)	11.00 (11.00)
II l	205(d)	600.00 (605.00)	Ethanol	68.87 (69.42)	6.01 (6.12)	11.46 (11.57)	10.00 (10.24)
II m	210	598.00 (605.00)	Benzene- ethanol	69.22 (69.42)	6.01 (6.12)	11.40 (11.59)	10.20 (10.24)
II n	—	592.00 (605.00)	Do	69.23 (69.42)	5.84 (6.12)	11.35 (11.59)	9.95 (10.24)
II o	230(d)	590.00 (605.00)	Toluene- ethanol	68.89 (69.42)	6.00 (6.12)	11.19 (11.59)	10.10 (10.24)

References

- 1 Becke-Goehring M, Lichner L & Scharf B, *Z anorg chem*, **343** (1966) 154; *Chem Abstr*, **64** (1966) 15728 g.
- 2 Mechaelis A W, *Ann*, **326** (1903) 129; **401** (1915) 290.
- 3 Haroon B M & Arifien A E, Unpublished results.
- 4 Chapmann A C, Paddock N L & Searle H T, *J chem Soc*, (1961) 1825.
- 5 Zhumorova I N & Kirsanov A V, *Zh obshch khim*, **32** (1962) 2576; *Chem Abstr*, **58** (1963) 7848f.
- 6 Shaw R A, Keat R & Miller M C, *J chem Soc*, (1967) 1404.
- 7 Shaw R A, Ibrahim E H & Smith B C, *Tetrahedron Lett*, (1969) 3061.
- 8 Trippett S, *J chem Soc*, (1962) 4731.