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### Preparation, Spectroscopic and Structural Investigations of Spiro Derivatives of Hexachlorocyclotriphosphazatriene

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PREPARATION, SPECTROSCOPIC AND STRUCTURAL  
INVESTIGATIONS OF SPIRO DERIVATIVES OF HEXA-  
CHLOROCYCLOTRIPHOSPHAZATRIENE

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Abstract Mono-( $N_3P_3Cl_4Y_2$ ), bis-( $N_3P_3Cl_2Y_4$ ) and  
tris-spiro derivatives ( $N_3P_3Y_6$ ) have been prepared  
with ethylene, 1,3-propylene and 1,4-butylen gly-  
cols ( $Y_2$  = glycol residue). The  $^1H$  NMR spectra of  
mono- and tris-derivatives are relatively simple;  
those of the bis- very complex due to the intrinsic  
asymmetry of the methylene protons. This effect is  
made use of in studying the replacement pattern of  
 $N_3P_3Cl_4[O(CH_2)_3O]$  with primary and secondary amines.  
Homonuclear  $^1H$  decoupling simplifies the spectra and  
allows an unambiguous distinction to be made between  
the different isomeric possibilities of the bis  
amino derivatives  $N_3P_3Cl_2R_2[O(CH_2)_3O]$  where R =  
amino residue. Primary amines give geminal, second-  
ary amines nongeminal trans-derivatives. The trans-  
structure of the bis-pyrrolidino derivative has been  
confirmed by X-ray crystallography.

From the reactions of hexachlorocyclotriphosphazatriene,  $N_3P_3Cl_6$ , with the appropriate quantities of ethylene, 1,3-propylene and 1,4-butylen glycols mono- ( $N_3P_3Cl_4Y_2$ ), bis- ( $N_3P_3Cl_2Y_4$ ) and tris-spiro derivatives ( $N_3P_3Y_6$ ) ( $Y_2$  = glycol residue) have been isolated.

The  $^1H$  NMR spectra of the methylene protons of the glycol residues are relatively simple in the mono- ( $N_3P_3Cl_4Y_2$ ) e.g.  $Y_2 = O(CH_2)_3O$  (Figure 1a) and tris-derivatives ( $N_3P_3Y_6$ ) although long-range virtual coupling can be observed in some of the latter e.g.  $Y_2 = O(CH_2)_2O$  (Figure 1b).

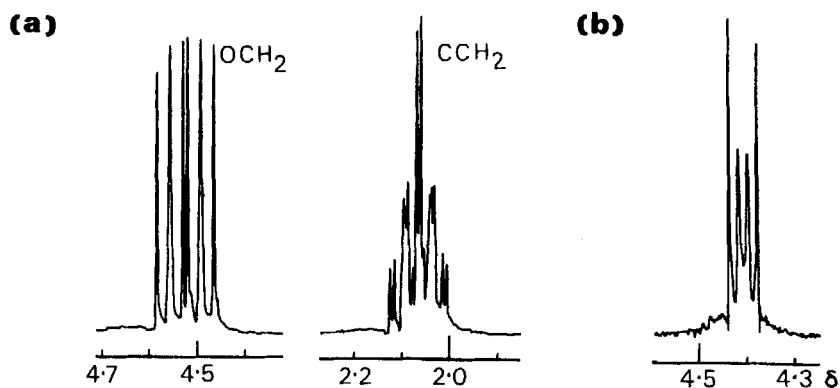


FIGURE 1  $^1H$  NMR spectra of (a)  $N_3P_3Cl_4[O(CH_2)_3O]$  and (b)  $N_3P_3[O(CH_2)_2O]_3$  at 200 MHz.

The methylene signals of the bis-derivatives ( $N_3P_3Cl_2Y_4$ ) are very much more complex due to the intrinsic asymmetry of the proton environments of the methylene groups, e.g. in  $N_3P_3Cl_2[O(CH_2)_3O]_2$  (Figure 2), where in addition to the other coupling effects, the  $OCH_2$  and  $CCH_2$  protons give rise to AB quartets.

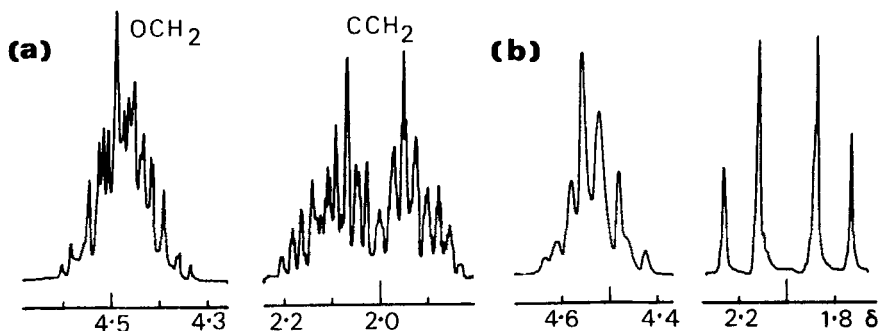


FIGURE 2 (a) <sup>1</sup>H and (b) <sup>1</sup>H homonuclear decoupled NMR spectra of N<sub>3</sub>P<sub>3</sub>Cl<sub>2</sub>[O(CH<sub>2</sub>)<sub>3</sub>O]<sub>2</sub> at 200 MHz.

This intrinsic asymmetry effect is made use of in a study of the replacement pattern of the remaining chlorine atoms in the mono-spiro derivative, N<sub>3</sub>P<sub>3</sub>Cl<sub>4</sub>Y<sub>2</sub> [Y<sub>2</sub> = O(CH<sub>2</sub>)<sub>3</sub>O], by primary and secondary amines. <sup>31</sup>P NMR spectroscopy is very useful to distinguish between geminal and nongeminal derivatives of the type N<sub>3</sub>P<sub>3</sub>Cl<sub>2</sub>R<sub>2</sub>Y<sub>2</sub> (R = amino group); the geminal bis-amino derivatives give ABX, the nongeminal bis-compounds give AB<sub>2</sub> spectra. However, these spectra throw no light on the cis/trans isomerism of the nongeminal derivatives.

The <sup>1</sup>H NMR spectra of the propylene dioxy residue can however clarify the cis/trans problem, the signals from the trans-isomer being expected to be much more complex than those of the cis-isomer, as in the former intrinsic asymmetry occurs. Homonuclear decoupling of the OCH<sub>2</sub> and CCH<sub>2</sub> protons from each other substantially simplifies the spectra. The anticipated findings for the propylenedioxy groups (homonuclear decoupled) are given in the Table. Only the OCH<sub>2</sub> protons experience marked heteronuclear coupling to phosphorus.

TABLE Anticipated number of lines in the homonuclear decoupled proton NMR spectra of propylene dioxy derivatives.

Compound	Number of Lines	
	OCH <sub>2</sub>	CCH <sub>2</sub>
N <sub>3</sub> P <sub>3</sub> Cl <sub>4</sub> Y <sub>2</sub>	2	1
N <sub>3</sub> P <sub>3</sub> Cl <sub>3</sub> RY <sub>2</sub>	10	4
gem-N <sub>3</sub> P <sub>3</sub> Cl <sub>2</sub> R <sub>2</sub> Y <sub>2</sub>	8	4
<u>cis</u> nongem-N <sub>3</sub> P <sub>3</sub> Cl <sub>2</sub> R <sub>2</sub> Y <sub>2</sub>	4	1
<u>trans</u> nongem-N <sub>3</sub> P <sub>3</sub> Cl <sub>2</sub> R <sub>2</sub> Y <sub>2</sub>	8	1

The <sup>1</sup>H NMR data of the compounds we have prepared point clearly to geminal structures for R = primary, and to trans-nongeminal structures for R = secondary amino groups. To confirm this a single crystal X-ray analysis of N<sub>3</sub>P<sub>3</sub>Cl<sub>2</sub>pyr<sub>2</sub>[O(CH<sub>2</sub>)<sub>3</sub>O] (pyr = pyrrolidino) was carried out (Figure 3).

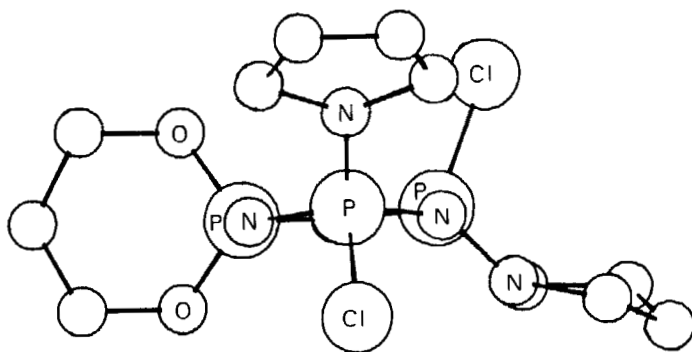


FIGURE 3 Molecular structure diagram of N<sub>3</sub>P<sub>3</sub>Cl<sub>2</sub>pyr<sub>2</sub>[O(CH<sub>2</sub>)<sub>3</sub>O]

The crystallographic results confirm the deductions made from <sup>1</sup>H NMR spectroscopy and increase confidence in their predictive value.