bands of PMT. An alternative possibility for the 281-cm^{-1} band is the metal–ligand asymmetric stretch. The 198-cm^{-1} band probably corresponds to the metal–ligand deformation mode.

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The Configuration of Bis(N-dimethylamino)tetrachlorotriphosphonitrile

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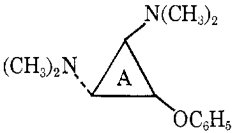
Three forms of the compound $P_3N_3Cl_4[N(CH_3)_2]_2$ have been reported, melting at 103,[1] 82,[2] and 62°.[2] The first of these, I, is formed predominantly and we reported previously[3] that it was a nongeminal *cis* isomer. This conclusion was drawn from the reaction sequence

$$\text{I} \xrightarrow[AlCl_3]{C_6H_6} \underset{\text{II}}{P_3N_3(Cl)_2(C_6H_5)_2[N(CH_3)_2]_2} \xrightarrow{(CH_3)_2NH(g)} \underset{\text{III}}{P_3N_3(C_6H_5)_2[N(CH_3)_2]_4}$$

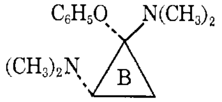
and the knowledge, from proton magnetic resonance measurements, that, in III, two $[N(CH_3)_2]$ groups are attached to the same phosphorus and the other two to separate phosphorus atoms and are *cis* to each other. In II, the spectra showed that the $[N(CH_3)_2]$ groups are each on a phosphorus atom to which a phenyl group is also attached. It was also based on the assumption that no isomerization takes place during the reactions. Since our report, two papers[2,4] have appeared in which evidence was given that I is the *trans* isomer. Further, there have appeared reports of isomerization of aminophosphonitriles in the presence of $AlCl_3$[5] or of amine hydrochlorides.[6] We, therefore, reinvestigated the structure of I and found other evidence that it is, indeed, the *trans* rather than the *cis* isomer.

This was obtained by proton nmr measurements for $P_3N_3Cl_3[N(CH_3)_2]_2(OC_6H_5)$, IV, mp 55°, which was prepared in 95% yield by the action of KOC_6H_5 on I (1:1 mole ratio) in refluxing benzene.

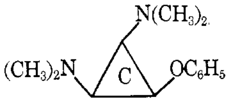
There are six possible configurations for IV as shown below. The apices of the triangles represent the phosphorus atoms in the ring. Given below each structure are the anticipated pmr spectral characteristics. The apparent[3] coupling constant, J'_{PH}, values are in cps.



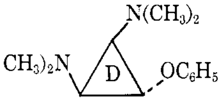
2 doublets
$J'_{PH} = 17.5$ for each



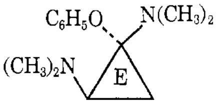
2 doublets
$J'_{PH} = 17.5, 12.5$



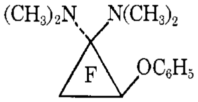
1 doublet
$J'_{PH} = 17.5$



1 doublet
$J'_{PH} = 17.5$



2 doublets
$J'_{PH} = 17.5, 12.5$



2 doublets
$J'_{PH} = 11.6$ for each

Proton nmr spectra were obtained for compound IV on a Varian A-60 nmr spectrometer system operating at 60 Mc/sec with tetramethylsilane employed as an internal reference. Samples were prepared as 20% solutions (w/v) in $CDCl_3$. The spectrum showed two distinct doublets, each having a $J'_{PH} = 17.5$ cps. This is uniquely characteristic of structure A.

It now appears that Friedel-Crafts phenylation of I to give II is accompanied by isomerization of the $N(CH_3)_2$ groups to the *cis* configuration, the effective agent being $AlCl_3$. Although isomerization probably was not complete, the yield of II, 38%, indicates that the *cis* isomer was more amenable to isolation under the conditions used.

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The 20°K Spectrum of Sodium Thiochromite

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There has been much interest in recent years in the spectra of transition metal compounds in which the ligand field is essentially octahedral but possesses a small trigonal distortion.[1-3] Attempts have been made to determine the source of band intensity and the

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