Correspondence

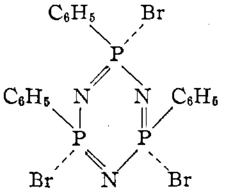
Identification of *cis*- and *trans*-Tribromotriphenyltriphosphonitriles

Sir:

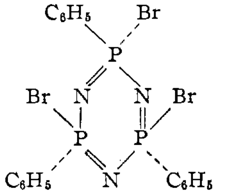
By carrying out the reaction of phenylphosphorus(III) dibromide with bromine and ammonium bromide[1] in *sym*-tetrabromoethane and fractionally crystallizing the product from *n*-heptane, it has been possible to obtain two forms of pure tribromotriphenyltriphosphonitrile, which melt at 152–153° and 194–195°, respectively. Microanalytical, infrared, and molecular weight data indicate no essential differences between the two and thus suggest that they must be isomers.[1]

Anal. Calcd. for $N_3P_3(C_6H_5)_3Br_3$: C, 35.67; H, 2.49; N, 6.93; P, 15.33; Br, 39.57; mol. wt., 606. Found (152–153° fraction): C, 35.92; H, 2.58; N, 6.94; P, 15.25; Br, 39.31; mol. wt., 621. Found (194–195° fraction): C, 35.74; H, 2.53; N, 6.87; P, 15.30; Br, 39.59; mol. wt., 622.

This suggestion is confirmed by the nuclear magnetic resonance data for phosphorus-31 reproduced in Fig. 1. These data, obtained for benzene solutions at 24.3 Mc. and referred to 85% aqueous H_3PO_4, clearly identify the higher melting compound as the *cis*-isomer (I) and the lower melting compound as the *trans*-isomer (II). The single resonance peak at −16.4 p.p.m. for the former indicates that all three phosphorus atoms are in the same environment, as expected for a *cis* configuration. The two resonance peaks at −20.1 and −18.0 p.p.m., and in a ratio of 1:2, for the latter indicate two phosphorus atoms in one environment (larger peak) and one atom (smaller peak) in a different environment, as expected for a *trans* configuration. The peaks are broadened by unresolved P–P and P–H spin coupling.



I (*cis*)



II (*trans*)

This represents the first clear-cut identification of geometrical isomers among the phosphonitrilic compounds in terms of the nuclear magnetic resonance of phosphorus.

Acknowledgment.—The authors are particularly indebted to Drs. M. M. Crutchfield and C. F. Callis of the Monsanto Chemical Company, St. Louis, Mo., for measurement and interpretation of the nuclear magnetic resonance spectra. This investigation was supported by the Materials Laboratory of Wright Air Development Command, Wright-Patterson Air Force Base, Ohio, under Contract AF-33(616)-5486. Reproduction of this communication in whole or in part is permitted for any purpose of the United States Government.

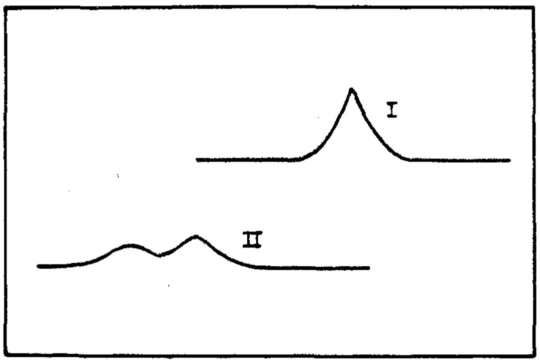


Fig. 1.—Tracings of phosphorus-31 nuclear magnetic resonance spectra of $N_3P_3(C_6H_5)_3Br_3$: I, 194–195° fraction; II, 152–153° fraction.

Noyes Chemical Laboratory
University of Illinois
Urbana, Illinois
T. Moeller
P. Nannelli

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[1] T. Moeller and P. Nannelli, *Inorg. Chem.*, **1**, 721 (1962).

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^{11}B Nuclear Magnetic Resonance Spectra of $B_{10}H_{12}(ligand)_2$ Compounds

Sir:

We wish to report the interpretation of the ^{11}B n.m.r. spectra of $B_{10}H_{12}(ligand)_2$ compounds which is in agreement with their established structure.[1,2]

It has been suggested previously[2] that the ^{11}B n.m.r. spectra of such compounds should be similar to that of decaborane[3] with an appropriate shift of the doublet to higher field due to the electrons supplied by the ligands. Our results indicate, however, that the spectra of decaborane and the $B_{10}H_{12}(ligand)_2$ compounds (derivatives of $B_{10}H_{14}^{-2}$)[1] are not similar and that the assumption previously made was not justified.

If a bromine atom is substituted for a terminal proton attached to a specific boron atom, a change in the spectrum will be observed as a collapse of the doublet to a single line accompanied by a shift to lower field. The substituted boron atom then is identified. Bis-(diethyl sulfide)-decaborane (III)[4] and bis-(diethyl sulfide)-2-

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[1] (a) J. van der Maas Reddy and W. N. Lipscomb, *J. Am. Chem. Soc.*, **81**, 754 (1959); (b) D. E. Sands and A. Zalkin, *Acta Cryst.*, **15**, 410 (1962).

[2] R. J. Pace, J. Williams, and R. L. Williams, *J. Chem. Soc.*, 2196 (1961).

[3] R. E. Williams and I. Shapiro, *J. Chem. Phys.*, **29**, 667 (1958).

[4] B. M. Graybill and M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 2673 (1961).