Correspondence

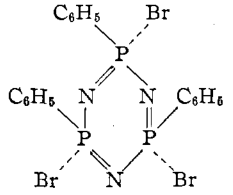
Identification of *cis*- and *trans*-Tribromotriphenyltriphosphonitriles

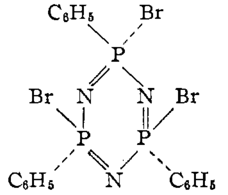
Sir:

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.

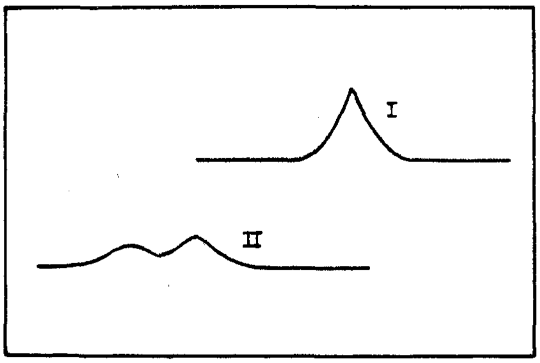


Fig. 1.—Tracings of phosphorus-31 nuclear magnetic resonance spectra of $N_3P_3(C_6H_5)_3Br_3$: I, 194–195° fraction; II, 152–153° fraction.

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

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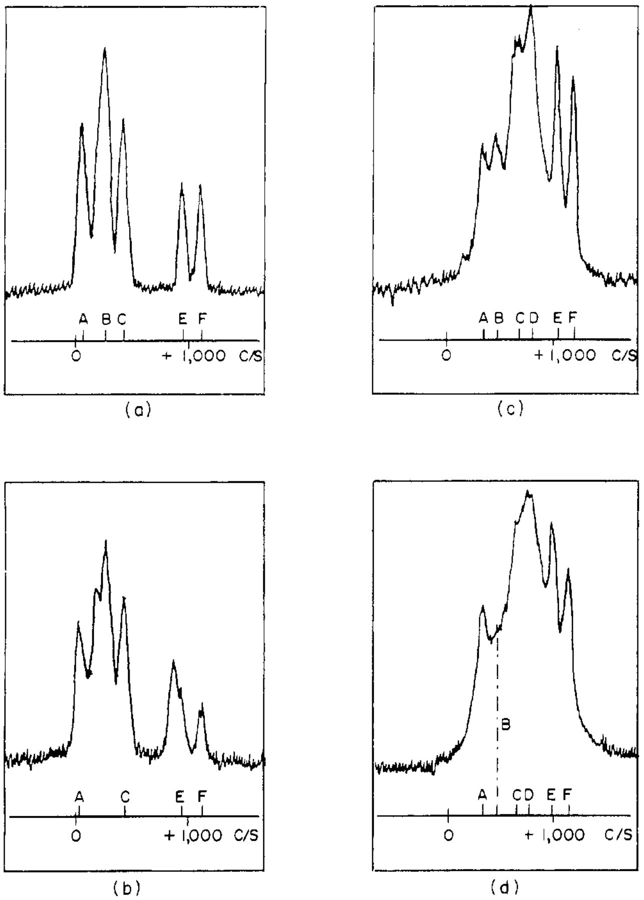

Fig. 1.—^{11}B n.m.r. spectra at 19.3 Mc./sec. of: (a) decaborane (I), (b) 2-bromodecaborane (II), (c) bis-(diethyl sulfide)-decaborane (III), (d) bis-(diethyl sulfide)-2-bromodecaborane (IV). The origin of the frequency scale is the $B(OCH_3)_3$ capillary line position. Increasing number corresponds to increasing field (1930 c.p.s. = 100 p.p.m.)

bromodecaborane (IV, m.p. 101°) were synthesized by treating diethyl sulfide with decaborane (I) and 2-bromodecaborane (II), respectively. The ^{11}B n.m.r. spectra of these four compounds, taken at 19.3 Mc./sec., are shown in Fig. 1; the solvent used for I and II was benzene while deuteriochloroform was used for III and IV. A reference spectrum of III in benzene was found to be identical with that determined in deuteriochloroform. The terminal protons of each compound were excited at 60.0 Mc./sec. to decouple successively the various boron nuclei. The area measurements show an intensity ratio of 2:6:2 for the AB:CD:EF regions of spectra c and d.

The decaborane spectrum has been interpreted[3] and the high field doublet was assigned to the two equivalent boron atoms 2 and 4. Spectrum b, previously interpreted,[5] identifies 2-bromodecaborane. The spectral differences of compounds III and IV indicate that the low field doublet of spectrum c is due to borons 2 and 4. In spectrum d, the singlet A is due to the substituted 2 boron and is superimposed on the first part of the doublet of the 4 boron. Inductive arguments based on these spectra may be given to show that the higher field doublet arises from borons 1 and 3. Lines E and F of spectrum c are surprisingly sharp. The same observation[6] in the spectrum of the $B_{12}H_{12}^{-2}$ may be attributed to the high degree of symmetry of its icosahedral structure.[7] In accord with the structure of $B_{10}H_{12}$-(ligand)$_2$ compounds as originally assigned,[1a] we would expect a higher degree of symmetry for borons 1 and 3 than for borons 6 and 9. The similarity of the bonding hybrids[8] between $B_{12}H_{12}^{-2}$ and the 1-B and 3-B borons suggests the same conclusion that the E and F lines of spectrum c correspond to borons 1 and 3. A similar treatment of 1,2,3,4-tetradeuteriodecaborane would add further proof that this assignment is correct.

Acknowledgment.—We thank Mr. G. D. Vickers for obtaining the ^{11}B n.m.r. spectra and acknowledge the partial support of this work by the Office of Naval Research.

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The Covalent Radius of Xenon

Sir:

The evaluation of electronegativities in terms of the "relative compactness" of atoms depends on estimates of "covalent" radii of the "inert" elements.[1] The recent determination of the bond length in xenon tetrafluoride[2] gives the first opportunity to test the validity of these estimates. The "covalent" radius of xenon was earlier determined[1] by a graphical extrapolation of crystal ionic radii, following Pauling, who, however, used "univalent crystal radii" and obtained somewhat different values.[3] The value of 2.09 Å. thus estimated fits exactly the empirical equation relating the "covalent" radii of all the "inert" elements, which was used in determining the radon radius.[4] It is of interest to apply this value to calculate the bond length in XeF_4, for comparison with the observed value.

The electronegativity, measured as the relative compactness of the atoms of the elements, is determined as the ratio of the average electronic density of an atom to that of a hypothetical isoelectronic inert atom.[1] For any of the "rare gas" family this ratio is, of course, 1.00. Since these elements have until recently been considered chemically inert, this value has seemed to have no real significance as an electronegativity.

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