TABLE IV
EQUILIBRIUM CONSTANTS FOR THE COMBINATION OF EAEP AND dien WITH SIX METAL IONS

	−log K		
Cation	dien	EAEP	dien-EAEP
H^+ pK_1	4.34	3.50	
pK_2	9.13	6.59	
pK_3	9.94	9.51	
Cu(II)	15.9	13.4	2.5
Ni(II)	10.7	9.4	1.3
Co(II)	8.1	7.0	1.1
Zn(II)	8.9	6.7	2.2
Cd(II)	8.4	6.2	2.2

aromatic polyamines in general, the relatively low basicity of the heterocyclic nitrogen atoms generally results in a decrease of metal chelate stability compared to that of the analogous aliphatic polyamines. A few interesting exceptions to this generalization are cited in the above discussion. Although comparisons with completely heterocyclic polyamines are not possible because of a paucity of stability data for metal chelates of these substances, it seems that the compounds prepared in the present investigation have chelating tendencies intermediate between the completely aliphatic and completely aromatic polyamines. Although their chelating tendencies are somewhat lower, the α-pyridyl-substituted polyamines are more effective than are the aliphatic polyamines in binding metal ions in neutral and in acidic solutions because the aromatic compounds have much lower affinities toward hydrogen ions.

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Phosphorus Complexes of Group III Acids. IV. B^{11}, F^{19}, H^1, and P^{31} Nuclear Magnetic Resonance Studies of Boron Complexes of Polycyclic Phosphites[1]

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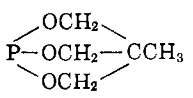
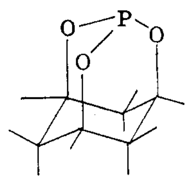
The B^{11}, F^{19}, H^1, and P^{31} nuclear magnetic resonance spectra of adducts of the polycyclic phosphites $C_5H_9O_3P$ and $C_6H_9O_3P$ with BH_3, $B(CH_3)_3$, and BF_3 have been obtained and compared with the spectra of the corresponding phosphates. The spectra of a carbon analog of $C_6H_9O_3P$, the polycyclic orthoformate of *cis*-cyclohexane-1,3,5-triol, BH_3 and $B(CH_3)_3$ adducts of trimethyl phosphite, and the BH_3 adduct of $(CH_3)_3P$ were also examined. Assignment of proton resonances in the adamantane-like compounds was effected by spin decoupling methods. Correlations of proton chemical shifts with Lewis acidity of the boron moiety were obtained for the protons of the polycyclic bases. Possible contributions to chemical shifts in these polycyclic molecules are discussed.

Recently a number of 1:1 adducts of the two polycyclic phosphites 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, $C_5H_9O_3P$, and 1-phospha-2,8,9-trioxaadamantane, $C_6H_9O_3P$, with several boron Lewis acids have been synthesized and characterized.[2,3] The rigidity of the polycyclic structures of $C_5H_9O_3P$ and $C_6H_9O_3P$ tends to minimize rehybridization of the atomic orbitals in the molecules upon coordination to various acceptor systems. The possibility that minimal conformational changes from one adduct to another in the base moiety would perhaps lend some simplifying aspects to n.m.r. spectral interpretation as well as to speculations on the relative acid strengths of the borane groups, boron trimethyl, and boron trifluoride led us to study the n.m.r. spectra of the B^{11}, F^{19}, H^1, and P^{31} nuclei in these adducts.



$C_5H_9O_3P$



$C_6H_9O_3P$

The acid strengths of the boron moieties of the adducts of the phosphite bases are $BH_3 > B(CH_3)_3 \cong BF_3$. The BH_3 adducts of $C_5H_9O_3P$ and $C_6H_9O_3P$ are undissociable high-melting solids whereas the $B(CH_3)_3$ adducts are easily dissociable solids.[2,3] Due to the reaction of BF_3 with phosphites to produce cleavage products in the presence of moderate BF_3 pressures, dissociation studies of these systems could not be carried out. However, the ease with which BF_3 could be pumped away from the solid polycyclic phosphite complexes indicates an acid strength comparable to that of boron trimethyl. Substantiation for the order of acid strengths given is obtained from a consideration of thermodynamic data obtained for BH_3, $B(CH_3)_3$, and BF_3 adducts of $(CH_3)_3P$. The $B(CH_3)_3$ and BF_3 moieties of the $(CH_3)_3P$ adducts are of about the same acid strength as is shown by the relative heats of dissociation (ΔH) of the adducts, which are 16.47 and 18.9 kcal./mole, respectively.[4] That the

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(1) Presented in part at the 4th Omnibus Conference on Experimental Aspects of Nuclear Magnetic Resonance Spectroscopy, Mellon Institute, Pittsburgh, Pa., March, 1963.

(2) C. W. Heitsch and J. G. Verkade, *Inorg. Chem.*, **1**, 392 (1962).

(3) J. G. Verkade and C. W. Heitsch, *ibid.*, **2**, 512 (1963).

(4) F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958).

TABLE I

CHEMICAL SHIFTS (P.P.M.)[a]

Compound	B^{11}	P^{31}	$H^1(BH_3)$	$H^1(BCH_3)$	F^{19}	J_{BP}, c.p.s.	J_{BH}, c.p.s
$C_6H_9O_3PBH_3$	60.5	−117	−0.23			97.6	97.6
$C_6H_9O_3PB(CH_3)_3$	32.3	−128		0.25		Not obsd.	
$C_6H_9O_3PBF_3$	20.0	−138			146	Not obsd.	
$C_6H_9O_3P$		−137[b]					
$C_5H_9O_3PBH_3$	62.1	−97	−0.31			96.0	96.0
$C_5H_9O_3PB(CH_3)_3$	10.2	−91		0.03		Not obsd.	
$C_5H_9O_3PBF_3$	20.2	−93			143	Not obsd.	
$C_5H_9O_3P$		−92[b]					
$(CH_3O)_3PBH_3$	63.8	−118	−0.33			97.2	97.2
$(CH_3O)_3PB(CH_3)_3$	31.2	−106		0.17		Not obsd.	
$(CH_3O)_3P$		−140					
$(CH_3)_3PBH_3$						63.5	95.6
$(CH_3)_2HPBH_3$						50[c]	90[c]

[a] Standards used were: $B(OCH_3)_3$, external and internal for B^{11}; 85% aqueous H_3PO_4, external for P^{31}; $Si(CH_3)_4$, internal for H^1; $FCCl_3$, internal for F^{19}. [b] See ref. 5. [c] J. N. Shoolery, *Discussions Faraday Soc.*, **19**, 215 (1955).

TABLE II

PROTON CHEMICAL SHIFTS (P.P.M. *vs.* $Si(CH_3)_4$[a]) AND DIPOLE MOMENTS

Compound	H_{ax}	H_{eq}	$\frac{H_{ax} + H_{eq}}{2}$	$H_{ax} - H_{eq}$	H_{CH}	H_{CH_3}	H_{CH_2}	J_{HH}, c.p.s.	J_{HCOP}, c.p.s.	μ, D.
$C_6H_9O_3PO$	−1.90	−2.56	−2.23	0.66	−5.00			14	20[c]	7.46[e]
$C_6H_9O_3PBH_3$	−2.05	−2.85	−2.45	0.80	−4.88			14	12.5	8.82[h]
$C_6H_9O_3PB(CH_3)_3$	−1.98	−2.87	−2.43	0.89	−4.38			14	6.7	. . .[d]
$C_6H_9O_3PBF_3$	−1.97	−2.87	−2.42	0.90	−4.33			14	Not obsd.	. . .[d]
$C_6H_9O_3P$	−1.93	−2.90	−2.41	0.97	−4.24			14	6.3 (6.0[c])	4.51[f]
$C_6H_9O_3As$	−1.95	−2.94	−2.45	0.99	−4.23			14		2.66[g]
$C_7H_{10}O_3$	−1.79	−2.55	−2.37	0.76	−4.23[b]			12.5		3.34[g]
$C_5H_9O_3PO$						−0.80	−4.48		7.0[c]	7.10[f]
$C_5H_9O_3PBH_3$						−0.80	−4.30		4.2	8.60[h]
$C_5H_9O_3PB(CH_3)_3$						−0.70	−3.98		2.2	. . .[d]
$C_5H_9O_3PBF_3$						−0.70	−3.95		2.0	. . .[d]
$C_5H_9O_3P$						−0.68	−3.93		1.8[c]	4.15[f]
$C_5H_9O_3As$						−0.62	−4.00			2.36[f]

[a] Spectra determined in CD_3CN at arbitrary concentrations. [b] This chemical shift refers to the three equivalent C–H hydrogens in the molecule. The chemical shift of the remaining hydrogen on the orthoformyl carbon is −5.50 p.p.m. [c] See ref. 5. [d] The $B(CH_3)_3$ and BF_3 adducts dissociate (see above). [e] Since the compound is insoluble in 1,4-dioxane, in which all the other moments were measured, this value was estimated by adding the difference in moments for $C_5H_9O_3P$ and $C_5H_9O_3PO$ to 4.51 D., the moment for $C_6H_9O_3P$. [f] T. L. Brown, J. G. Verkade, and T. S. Piper, *J. Phys. Chem.*, **65**, 2051 (1961). [g] Details to be published, J. G. Verkade and T. J. Huttemann. [h] See ref. 2 and 3.

BH_3 adduct of $(CH_3)_3P$ is much more stable to dissociation is reflected by the fact that $(CH_3)_3P$ displaces $(CH_3)_3N$ from $(CH_3)_3NBH_3$ for which the heat of dissociation has been estimated as 31.3 kcal./mole.[4] The adduct $(CH_3)_3PBH_3$ does not dissociate.[4] Although $C_5H_9O_3P$ and $C_6H_9O_3P$ are similar in structure, their base strengths are somewhat different. This is demonstrated by measured heats of dissociation of their $B(CH_3)_3$ adducts, which are 14.4 and 15.9 kcal./mole, respectively.[2,3] This order of base strengths is consistent with the higher dipole moment observed for $C_6H_9O_3P$ (4.51 D.) compared to $C_5H_9O_3P$ (4.15 D.).[3]

Table I contains n.m.r. data for the various nuclei associated with the acid moiety of the adducts as well as for the P^{31} nucleus of the various bases. Due to apparent cleavage of trimethyl phosphite by BF_3, no stable adduct was obtained. Upfield shifts with respect to the reference standard involved are designated by positive signs. The absence of consistent trends in the B^{11} and P^{31} chemical shifts and the present lack of a theoretical basis on which to rationalize shifts of these heavier nuclei precludes interpretation of these data. It is striking that the values of J_{BP} and J_{BH} are the same to a high degree of accuracy for the borane complexes of the two polycyclic phosphites as well as trimethyl phosphite. In contrast, however, the borane complexes of both trimethylphosphine and dimethylphosphine do not exhibit these coincidences. These systems will be further investigated using heteronuclear decoupling techniques. The weaker complexes of both polycyclic phosphites containing the $B(CH_3)_3$ and BF_3 groupings afforded no observable B–P coupling, possibly due to rapid ligand exchange.

The greater base strength of $C_6H_9O_3P$ seems to be associated with the more consistent Lewis acid proton shifts. It can be seen from Table I that comparison of adducts of BH_3 and $B(CH_3)_3$ reveals a consistent downfield shift for $C_5H_9O_3P$ derivatives with respect to $C_6H_9O_3P$ complexes. This observation is consistent with the interpretation that the stronger base should result in higher electron density at the protons on the Lewis acid. The relative shift in the boron trimethyl protons from the $C_6H_9O_3P$ adduct to that of the

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(5) J. G. Verkade and R. W. King, *Inorg. Chem.*, **1**, 948 (1962).

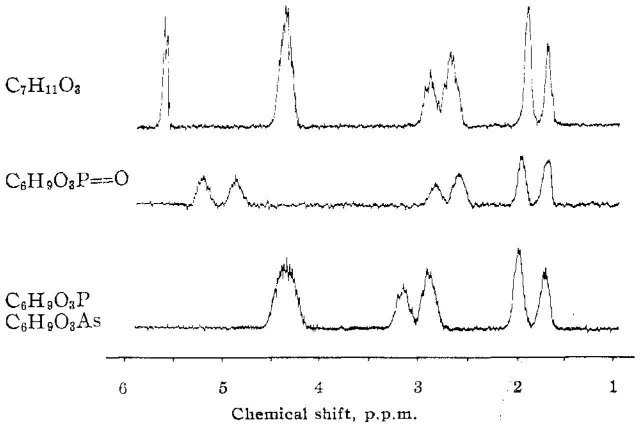

Fig. 1.—H^1 resonance spectra of adamantane-like molecules in $CDCl_3$ solution. All peaks downfield with respect to TMS.

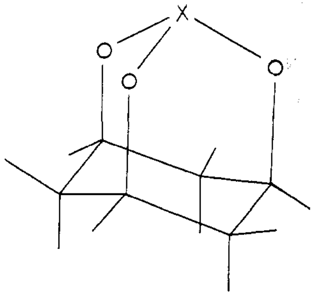

Fig. 2.—X = As in $C_6H_9O_3As$; X = P in $C_6H_9O_3P$; X = P=O in $C_6H_9O_3P{=}O$; X = C—H in $C_7H_{10}O_3$.

$C_5H_9O_3P$ adduct is rather remarkable. Whether or not the above electron density argument can be used in the case of the F^{19} shifts is more open to question.

Table II contains resonance data for the protons bound to the base. The arsenic analogs of $C_6H_9O_3P$ and $C_5H_9O_3P$ and the tricyclic orthoformate of *cis*-cyclohexane-1,3,5-triol ($C_7H_{10}O_3$) are included for comparison. All proton shifts in this table are downfield with respect to the standard. While the oxygen atom is not usually thought of as a Lewis acid, the formal similarity between the oxygen atom and the isoelectronic borane group has been cited frequently. Hence the phosphates have also been included here for comparison. It is quite apparent that the P=O bond is stronger than any known $P \rightarrow B$ bond. Thus we assume the order of decreasing acid strength with respect to polycyclic phosphites $O > BH_3 > B(CH_3)_3 \cong BF_3$. If the relative acidities of the boron acids increase up the columns as shown in Table II, it is noteworthy that the values for J_{HCOP} increase as well. Coupling in $C_6H_9O_3P$ and its adducts where the P–O–C–H bond system is planar is consistently about three times as great as in the corresponding $C_5H_9O_3P$ compounds where the P–O–C–H system is *gauche*.[5] This implies a dihedral angle dependence of coupling similar to that calculated for H–C–C–H systems[6] using σ-bond contributions only. The observed variations in coupling are consistent with an increase in s character of the P–O bonds with increasing Lewis acidity of the ligand. The

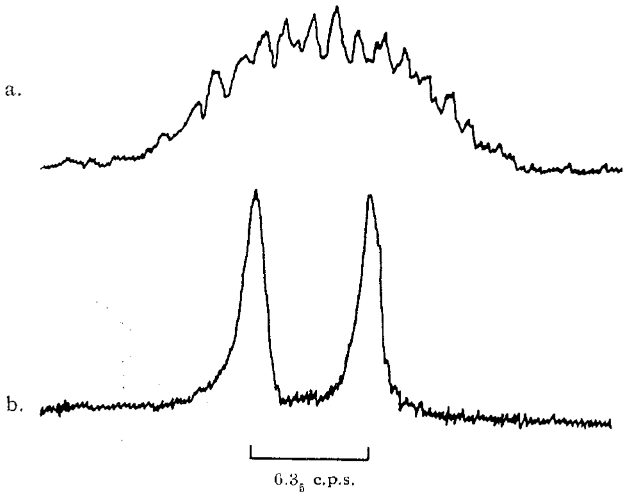

Fig. 3.—Spin decoupling in $C_6H_9O_3P$: a, methine proton; b, methine proton with strong irradiation of both methylene protons, showing coupling to phosphorus.

assignments of chemical shifts of the methyl and methylene protons in $C_5H_9O_3P$ and its adducts were directly evident from the integration of the spectra and the relative shift values. This was also true for the methinyl protons in $C_6H_9O_3P$ and its adducts.

By analogy with other substituted cyclohexanes and acetylated sugars,[7] the axial methylene protons should appear at higher field than the equatorial; this tentative assignment was confirmed by multiple resonance experiments.

The ring proton spectra shown in Fig. 1 of the four adamantane-like compounds depicted in Fig. 2 are similar, with much unresolved fine splitting, from which it is not possible directly to extract any except *gem* proton–proton couplings.

From line widths, however, there appears to be in all cases greater coupling from the methine to the low-field rather than the high-field methylene protons. This was confirmed in the orthoformate by irradiating each methylene proton in turn with a radiofrequency field of 1.7 mgauss while scanning the other with a much lower power. The lower field multiplet then collapsed to a rough triplet, spacing 2.7 c.p.s., and that at higher field to a singlet of width <1 c.p.s. Qualitatively similar results were obtained with $C_6H_9O_3P$. Irradiation of the high- and low-field methylene protons of $C_6H_9O_3P$ in turn reduced the width of the methine proton peak from 12 to 10 and 8.5 c.p.s., respectively. Simultaneous irradiation of both methylene protons with 2.0 mgauss radiofrequency fields simplified the methine resonance to an equal-intensity doublet, due to H–C–O–P coupling, shown in Fig. 3. The coupling constant of 6.35 c.p.s. agrees with that obtained from the P^{31} spectrum.[5]

The results for $C_6H_9O_3PO$ were similar but were complicated by a long-range P–CH_2 coupling of about 2 c.p.s. Irradiation of the lower CH_2 proton multiplet (1.1 mgauss) caused collapse of the higher proton peaks

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(6) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(7) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw Hill Book Company, Inc., New York, N. Y., 1959, Chapter 14.

to a doublet of spacing 2 c.p.s. Similar irradiation of the higher-field CH_2 doublet produced from that at lower field a quartet of spacing approximately 2.5 c.p.s. due to splitting by both the phosphorus and the adjacent ring methine protons. Greater coupling from the methine to the low-field than to the high-field methylene proton was confirmed by irradiating the methylene protons in turn with a radiofrequency field of 2.3 mgauss, whereupon the line width (5.5 c.p.s.) of each component of the CH doublet was reduced to 2 and 4.5 c.p.s., respectively.

In an unconstrained cyclohexane ring an equatorial hydrogen should be exactly *gauche* with respect to the hydrogens of the adjacent methylene group and equally coupled to each. Examination of models shows that in the orthoformate the axial carbon–oxygen bonds are bent inward due to the angle at the oxygen atom being greater than the tetrahedral angle,[8] thus decreasing the dihedral angle formed by and increasing the predicted coupling of the methine and equatorial methylene protons.[6] This is in accord with the above assignment. The analogous spectra of the adamantane-type phosphorus esters suggest a similar distortion in structure for these molecules.

The adamantane-like molecules can be considered to contain a chair-form cyclohexane ring with a partial negative charge distribution on the XO_3 ($X = P$, As, CH) moiety situated above the ring. As a consequence, a corresponding positive charge must be distributed on the cyclohexane ring with the probable result that a larger portion of the positive charge resides on the methinyl carbons by transfer through the C–O bonds than on the methylene carbons. In the absence of solvent, the effect of the positive charges is to shift H_{ax} and H_{eq} slightly downfield to an equal extent while H_{CH} is shifted relatively further downfield.

The existence of an effective point dipole somewhere along the threefold axis of the adamantane-like systems would serve to differentiate hydrogens whose C–H bonds formed different angles with respect to the axis of the dipole.[9] Such a dipole would cause H_{ax} to shift downfield with respect to H_{eq} since the electric field due to the dipole is almost parallel to the C–H_{ax} bond axis and hence affects H_{ax} to a greater degree than H_{eq}, whose C–H bond axis is nearly perpendicular to the field. The methinyl hydrogen may be shifted downfield somewhat by the molecular dipole, however the effect of the relatively large positive charge on the neighboring carbon is undoubtedly dominant. The basic order of the chemical shifts in terms of relative fields in these systems in the absence of a solvent is predicted to be $H_{eq} < H_{ax} < H_{CH}$, contrary to our interpretation of the decoupling data.

Chemical shifts due to solvent interactions are qualitatively predictable on the basis of a model discussed by Buckingham.[9] The solvent molecules are expected to be oriented around the solute molecule with the negative ends of their dipoles directed toward the cyclohexane portion of the system. Similarly the positive ends of their dipoles will be directed toward the XO_3 moiety of the solute molecule. Hence the reaction field produced by the solvent molecules around such a solute acts in concert with any molecular dipole effect which may be operative to differentiate further the axial and equatorial protons such that H_{ax} should become more deshielded and H_{eq} more shielded.

Although the molecular dipole effect and solvation contradict our assignment of the relative positions of H_{ax} and H_{eq}, consideration of the effect of increasing the dielectric constant of the solvent upon the chemical shifts of these protons supports our conclusion. The solvent molecules around the solute produce a "reaction field" which increases with the dielectric constant of the solvent and is in the opposite sense to that of the solute dipole, as seen from a point remote from the solute molecule.[9] However, the C–H bonds lying between the molecular and solvent dipoles will experience a greater potential gradient. Although relatively small, the effect of increasing the dielectric constant of the solvent on the proton resonances of the adamantane-like systems is predicted to cause downfield shifts of H_{CH} and H_{ax}, and a small upfield shift of H_{eq} due to interactions of the solvent electric fields along the respective C–H bond directions. These predictions for $C_6H_9O_3P$, $C_7H_{10}O_3$, and $C_6H_9O_3As$ are substantiated by the data presented in Table III. It is likely that the almost insignificant solvent effect upon H_{eq} is due to the negligible component of the reaction field along the C–H_{eq} bond.

That the observed solvent shifts are not due to orientation of induced magnetic dipoles along with the solvent electric dipoles is shown by the similarity of chemical shifts in dimethyl sulfoxide and deuterioacetonitrile. In the latter solvent the axis of greatest magnetic susceptibility lies along the axis of the electric dipole,[10] whereas, assuming the S=O and C=O groups to behave similarly, in the former they will be at right angles. Any appreciable anisotropic contribution should result in very different shifts in the two solvents.

It is interesting that the solvent shifts are similar in the phosphite, arsenite, and orthoformate of cyclohexanetriol. This implies that the latter compound possesses a dipole in the same sense as that of the phosphite and arsenite, which is of appreciable magnitude. The apical proton of the orthoformate, contrary to expectation from the arguments used for the axial protons, moves markedly downfield with increasing solvent polarity; however, this proton is somewhat acidic and may take part in weak hydrogen bonding with the more polar solvents. The anomalously large shift in deuteriochloroform supports this. Such anomalous deshielding occurs for the majority of protons listed in Table III and appears to be nearly uniform in its action since the mean chemical shift of the adamantane-

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[8] L. E. Sutton, Scientific Editor, "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

[9] A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

[10] Reference 7, p. 179.

TABLE III

PROTON CHEMICAL SHIFTS (−P.P.M. *vs.* $Si(CH_3)_4$) AT INFINITE DILUTION IN SOLVENTS OF DECREASING DIELECTRIC CONSTANT

Compound	Solvent	H_{ax}	H_{eq}	$\frac{H_{ax} + H_{eq}}{2}$	$H_{eq} - H_{ax}$	$H_{methinyl}$	H_{CH}	H_{CH_3}	$H_{orthoformyl}$
$C_6H_9O_3P$	DMSO[a]	1.95	2.90	2.42	0.95	4.28			
	CD_3CN	1.93	2.90	2.41	0.97	4.24			
	$(CH_3)_2CO$	...[b]	2.92			4.30			
	CH_2Cl_2	1.90	2.98	2.44	1.08	4.30			
	$CDCl_3$	1.89	3.04	2.47	1.15	4.34			
	CCl_4	1.82	2.99	2.40	1.17	4.20			
	C_6H_{12}	1.84	2.95	2.40	1.11	4.15			
$C_6H_9O_3As$	DMSO[a]	1.94	...[b]			4.26			
	CD_3CN	1.95	2.94	2.45	0.99	4.23			
	$(CH_3)_2CO$	...[b]	2.93			4.27			
	CH_2Cl_2	1.89	3.05	2.47	1.16	4.28			
	$CDCl_3$	1.88	3.10	2.49	1.12	4.36			
	CCl_4	1.79	3.02	2.41	1.23	4.24			
	C_6H_{12}	...[b]	2.99			4.14			
$C_7H_{10}O_3$	DMSO[a]	1.80	...[b]			4.25			5.55
	CD_3CN	1.79	2.55	2.17	0.76	4.23			5.50
	$(CH_3)_2CO$	...[b]	2.59			4.27			5.48
	CH_2Cl_2	1.73	2.66	2.20	0.93	4.28			5.55
	$CDCl_3$	1.78	2.77	2.26	0.99	4.36			5.64
	CCl_4	1.65	2.65	2.15	1.00	4.24			5.38
	C_6H_{12}	...[b]	...[b]			4.14			5.40
$C_5H_9O_3P$	DMSO[a]						3.92	0.65	
	CD_3CN						3.93	0.68	
	$(CH_3)_2CO$						3.96	0.76	
	CH_2Cl_2						3.92	0.71	
	$CDCl_3$						3.93	0.72	
	CCl_4						3.86	0.72	
	C_6H_{12}						3.78	0.60	
$C_5H_9O_3As$	DMSO[a]						3.46	0.65	
	CD_3CN						4.00	0.62	
	$(CH_3)_2CO$						4.01	0.65	
	CH_2Cl_2						4.10	0.62	
	$CDCl_3$						4.04	0.65	
	CCl_4						3.95	0.63	
	C_6H_{12}						3.92	0.56	

[a] Dimethyl sulfoxide. [b] Proton peaks of solvent interfere.

type methylene protons is affected while their shift difference is normal. Such behavior has previously been observed in deuteriochloroform solutions.[11]

In the bicyclooctane derivatives $C_5H_9O_3P$ and $C_5H_9O_3As$ the solvent shifts of the methyl group are small and erratic, but it is remote from the molecular dipole and its resonance may be determined by other, smaller effects. The methylene protons are situated with respect to the phosphorus–oxygen system analogously to the methine protons of the adamantane-like esters and, as expected, undergo deshielding with an increasing polarity of the solvent. Solvent shifts with the more polar adducts could not be studied due to their insolubility in solvents of low dielectric constant.

If our assignment of the n.m.r. spectra of these compounds is correct, electric fields due to a molecular dipole and solvent reaction fields at the methylene protons in the adamantane-like systems do not account for the chemical differentiation of H_{ax} and H_{eq}. Further support for this contention stems from the constancy of the H_{ax} and H_{eq} chemical shifts of $C_6H_9O_3P$ and $C_6H_9O_3As$ in spite of the marked difference in their dipole moments. Differential shielding of methylene hydrogens in a variety of cyclohexane compounds has been explained in terms of diamagnetic anisotropies of nearby C–C and C–O bonds.[12] Anisotropy effects were estimated using the point-dipole approximation of McConnell,[13] assuming the magnetic dipole in all cases to lie at the midpoint of the bond, with dimensions taken from a Dreiding model of the orthoformate. Deviations from adamantane symmetry in the orthoformate are small; the geometrical factors in the expressions for the effects of the C–O and C–C bonds are opposite and nearly equal. If the anisotropies of these bonds were equal, neglecting a small contribution from the C–H bonds, there would be no differential shielding; however, if the transverse magnetic susceptibility of both C–O and C–C bonds exceeds the longitudinal[14] and by a smaller amount for the C–O bond, the equatorial methylene proton would be preferentially deshielded by the dominant effect of the C–C transverse magnetic susceptibility, as is observed. The lack of reliable anisotropy data makes the magnitude of this effect uncertain. The differences in chemical shift between

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(11) Reference 7, p. 405. See also R. Kaiser, *Can. J. Chem.*, **41**, 430 (1963).

(12) L. M. Jackman, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 115.

(13) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

(14) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **80**, 1728 (1958).

H_{ax} and H_{eq} in Tables II and III are greater by about 0.3 p.p.m. than those observed in a variety of cyclohexane systems in spite of the argument[13] that the C–O and C–C bond anisotropies tend to cancel in their effect on these protons. It is possible that a relatively large long-range magnetic anisotropy effect is operative in the X–O bonds (X = P, As, C–H). It seems unlikely that ring-current effects are appreciable since these might be expected to be larger in the hetero rings (which have more available p-electrons), causing shielding of H_{eq}, in disagreement with observation. It is tentatively concluded, however, that although all the adamantane-like molecules seem to exhibit a rather large effective diamagnetic anisotropy which is greater along the threefold molecular axis than transverse to it, its source is presently difficult to explain.

As the Lewis acidity of the boron moiety is increased in the complexes of $C_6H_9O_3P$ (Table II), H_{ax} moves downfield whereas H_{eq} shows a very slight upfield shift. From the near constancy of the mean positions of H_{ax} and H_{eq}, it may be inferred that the charge density on the methylene carbon is little affected by changes occurring on complexing. The effect of withdrawing electron density from the phosphorus atoms is associated with decreasing the chemical difference in H_{eq} and H_{ax}, which tends to indicate a decrease in the diamagnetic anisotropy with an increase of polarity of the molecules. A large downfield shift of the methine proton occurs with increasing acidity of the boron group, but here anisotropy effects are probably insignificant compared to those of charge density. Such would also be the case in the adducts of $C_5H_9O_3P$.

Although the proton shielding trends in the boron adducts of $C_6H_9O_3P$ and $C_5H_9O_3P$ are consistent, the H_{ax} shielding value for $C_6H_9O_3PO$ is anomalously high with respect to the same proton in $C_6H_9O_3PBH_3$. Hence caution must be exercised in attempting to correlate chemical shifts with Lewis acidities of dissimilar species where the type of bonding to phosphorus may be very different.

Spectra were obtained on Varian instruments operating at 14,100 gauss with appropriate radiofrequency units and probes and were calibrated by side-band interpolation. The polycyclic phosphites,[2,15] phosphates,[16,17] and phosphite adducts[2,3,18] were prepared by methods described previously. The arsenite of the adamantane structure was synthesized according to the preparation described for the arsenite of the bicyclo[2.2.2]octane structure.[16] The orthoformate of *cis*-cyclohexane-1,3,5-triol was synthesized according to the method of Stetter.[19] The preparation of $(CH_3)_3PBH_3$ was accomplished by direct combination of B_2H_6 and $(CH_3)_3P$.[20]

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[15] K. D. Berlin, C. Hildebrand, J. G. Verkade, and O. C. Dermer, *Chem. Ind.* (London), 291 (1963).

[16] J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, **25**, 663 (1960).

[17] H. Stetter and K. Steinacker, *Ber.*, **85**, 451 (1952).

[18] C. W. Heitsch and J. G. Verkade, *Inorg. Chem.*, **1**, 863 (1962).

[19] H. Stetter, *Chem. Ber.*, **86**, 791 (1953).

[20] A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
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Trimethylazido Compounds of Group IVA Elements[1]

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Azidotrimethyl derivatives of silicon, germanium, tin, and lead have been prepared, and a comparative study of their physical properties has been carried out. Infrared and electronic spectra have been interpreted in terms of dative π-bonding in the silicon and germanium compounds. In the organosilicon conversion series,[2] the azide group occupies the same position as isocyanate.

Recent publications have described the synthesis and characterization of group IVA triphenylmetal azides.[3,4] This paper reports a comparative study of the trimethylmetal azides, $(CH_3)_3MN_3$, of these elements. The synthesis of azidotrimethylsilane has been reported independently by four different groups over the past 2 years.[5–8] Azidotrimethylstannane has also been prepared by Luijten and co-workers,[9,10] but the other two members of the series, azidotrimethylger-

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[1] Presented in part before the Inorganic Division, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.

[2] C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, pp. 173–174.

[3] J. S. Thayer and R. West, *Inorg. Chem.*, **3**, 406 (1964).

[4] W. T. Reichle, *ibid.*, **3**, 402 (1964).

[5] R. West and J. S. Thayer, *J. Am. Chem. Soc.*, **84**, 1763 (1962).

[6] L. Birkofer, A. Ritter, and P. Richter, *Chem. Ber.*, **96**, 2750 (1963).

[7] W. Sundermeyer, *ibid.*, **96**, 1293 (1963).

[8] J. W. Connolly and G. Urry, *Inorg. Chem.*, **1**, 718 (1962).

[9] J. G. A. Luijten, M. J. Janssen, and G. J. M. Van Der Kerk, *Rec. Trav. Chim.*, **81**, 202 (1962).

[10] G. J. M. Van Der Kerk, J. G. A. Luijten, and M. J. Janssen, *Chimia*, **16**, 10 (1962).