TABLE IV

CHANGE OF ABSORBANCE OF 4 × 10^{-4} *M* Cr(VI) in 0.1 *M* NaCl + 0.9 *M* $HClO_4$ WITH TEMPERATURE

T, °C.	A_{350}
10.2	0.521
18.0	0.517
22.0	0.511
25.8	0.510

Discussion

Table V compares various equilibria involving $HCrO_4^-$. The formation constants for chromic acid obtained in this study may be compared with the value of 1.2 obtained at ionic strength = 1.0 by King and Tong,[2] who measured the effect of changing hydrogen ion concentration on the dimerization of $HCrO_4^-$. The present authors feel that the value certainly lies between the values 4.5 and 6.5 on the basis of more direct means of measurement. It should also be noted that King and Tong[2] found it necessary to postulate the existence of $HCr_2O_7^-$ in order to fit their data, although they could find no change in absorbance due to its formation. If a value of about 5.0 for the dissociation constant of H_2CrO_4 is applied to the data of King and Tong the postulate that $Cr_2O_7^{2-}$ is protonated is no longer required.

TABLE V

THERMODYNAMICS OF $HCrO_4^-$ REACTIONS

	Ionic strength	*K*, l./mole	ΔF_{25}, kcal./mole	ΔH_{25}, kcal.	ΔS_{25}, cal./deg.
$HCrO_4^- + H^+ \rightarrow H_2CrO_4$	1.0	0.2[a] 0.83[b]	0.9 ± 0.2	−2.1	2.5
$HCrO_4^- + H^+ + Cl^- \rightarrow CrO_3Cl^- + H_2O$	1.0	17[a]	−1.7 ± 0.2	. . .	. . .
$HCrO_4^- + HSO_4^- \rightarrow CrSO_7^{2-} + H_2O$	3.0	4.1[a]	−0.85 ± 0.10	0.0	2.7
$HCrO_4^- + H_3PO_4 \rightarrow H_2CrPO_7^- + H_2O$	0.25	9.4[b]	−1.95	. . .	. . .
$HCrO_4^- + H_2PO_4^- \rightarrow HCrPO_7^{2-} + H_2O$	0.25	2.9[b]	−0.6	. . .	. . .
$HCrO_4^- + HCrO_4^- \rightarrow Cr_2O_7^{2-} + H_2O$	1.0	98[c]	−21.	. . .	. . .

[a] This work. [b] Ref. 3. [c] Ref. 2.

The results of the study of the formation of CrO_3Cl^- may be compared with those of Cohen and Westheimer,[7] who did the same study in 86.5% acetic acid. They found the same spectra of $HCrO_4^-$ and CrO_3Cl^- as those reported here and a formation constant (K_b) of 1.11 × 10^5. Acetic acid is a weakly ionizing medium and as such favors formation of CrO_3Cl^- much more than an aqueous medium.

Cohen and Westheimer[7] noted a similarity in the change in spectrum for Cr(VI) effected by substituting phosphate and chloride ions for hydroxide in the acid chromate ion. Substitution of sulfate can now be said to have about the same effect. It is notable that the ultraviolet absorption spectra of $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions are nearly identical. Addition of protons to $HCrO_4^-$ to form chromic acid has quite a different effect on the spectrum from that of substitution for OH^- groups. The charge-transfer spectrum of CrO_4^{2-} exhibits small shifts in wave lengths for band maxima and considerable decrease in probability for electronic transitions upon the addition of one or two protons.

Acknowledgment.—The authors wish to thank the Office of Ordnance Research, United States Army, for the use of the Beckman Model DU spectrophotometer.

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[7] M. Cohen and F. H. Westheimer, *J. Am. Chem. Soc.*, **74**, 4389 (1952).

Notes

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Configurations of Isomeric Phenyl-N-dimethylaminotetraphosphonitriles. The Use of H^1 Nuclear Magnetic Resonance and Double Resonance Techniques

BY JANET H. SMALLEY, F. E. DICKSON, AND I. I. BEZMAN

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In two recent papers[1,2] it was demonstrated that proton magnetic resonance spectra can be used to determine both positional and *cis–trans* configurations of a series of dimethylaminotriphosphonitriles. This paper extends the procedure to an analysis of the configurations of three phenyl-N-dimethylaminotetraphosphonitriles, $P_4N_4(C_6H_5)_4[N(CH_3)_2]_4$, and, by implication, substantially resolves the configurations of three phenylchlorotetraphosphonitriles, $P_4N_4(C_6H_5)_4Cl_4$, from which they were made. Specific configurations have not been reported previously for any of these compounds.

Cyclic tri- and tetraphosphonitriles of the formula $[NP(A)B]_3$ and $[NP(A)B]_4$ have the groups A and B attached to the phosphorus atoms. The bond angles are such that one group is above and the other is below the hypothetical plane of the ring and indicate the existence of geometric isomers. In the case of the trimer, two isomers can exist; for the tetramer, four

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[1] I. I. Bezman and C. T. Ford, *Chem. Ind.* (London), 163 (1963).

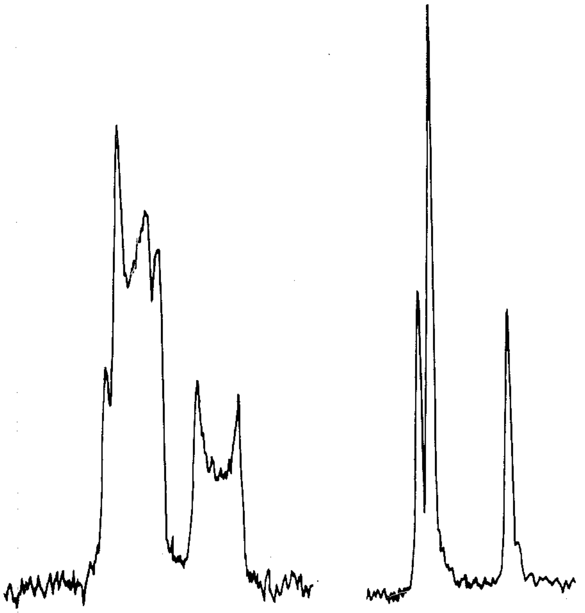
[2] C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, **3**, 177 (1964).

isomers are possible. Several such isomers have been reported in which A is a phenyl group and B is either chlorine or bromine. The syntheses have involved the reaction of phenylphosphorus tetrahalide and the corresponding ammonium halide in a solvent such as *sym*-tetrahaloethane.

Using this procedure,[3] Humiec and Bezman obtained an isomer of $P_3N_3(C_6H_5)_3Cl_3$ melting at 161–163°. Shaw and Stratton[4,5] isolated the other isomer of the trimer, melting at 188°, and also three tetrameric isomers, melting at 148, 202, and 248°. Nannelli and Moeller[6] obtained two isomers of $P_3N_3(C_6H_5)_3Br_3$, melting at 152–153 and 194–195°. The phosphorus-31 nuclear magnetic resonance spectrum of the 194–195° isomer showed one resonance peak while that of the 152–153° isomer had two. It was concluded that the former was the *cis* isomer and the latter was the *trans* isomer.

We have recently allowed $C_6H_5PCl_4$ and NH_4Cl to react in *sym*-tetrachloroethane and, by careful work-up of the products in a manner similar to that of Shaw and Stratton,[4] we also obtained three isomeric phenylchlorotetraphosphonitriles, compounds A, B, and C, melting at 248–258, 202, and 148°, respectively. The melting point range of compound A persisted despite many efforts to narrow it by recrystallization from various solvent systems. Its infrared spectrum was identical with that of the 248° isomer reported by Shaw[5] and Stratton. The infrared spectra of compounds B and C were likewise identical with those of Shaw and Stratton's 202 and 148° isomers. It should be noted that compounds A, B, and C were isolated from a single reaction mixture. An over-all yield of 30% tetramers was obtained, and the relative yields of compounds A, B, and C were 19:1:3.5, respectively.

Compounds A, B, and C were easily and quantitatively converted to the corresponding phenyl-N-dimethylaminotetraphosphonitriles by treatment with aqueous dimethylamine solution. Three distinct compounds of the formula $P_4N_4(C_6H_5)_4[N(CH_3)_2]_4$ were obtained, compounds AA, BB, and CC, melting at 178–180, 154–155.5, and 139–141° and made from reference compounds A, B, and C, respectively. In a review article,[7] two phenyl-N-dimethylaminotetraphosphonitriles are tabulated as melting at 178–180 and 154° and are attributed to unpublished work of Shaw and Stratton. These are probably the same as our compounds AA and BB. Compound CC has not been reported previously. *Anal.* Calcd. for $P_4N_4(C_6H_5)_4[N(CH_3)_2]_4$: C, 57.83; H, 6.67; N, 16.87; P, 18.64; Cl, 0.00. Found for compound AA: N, 16.60; Cl, 0.00. Found for compound BB: N, 16.67; Cl, 0.00. Found for compound CC: C, 57.58; H, 6.47; N, 16.61; P, 18.56; Cl, 0.00. The infrared spectra of the compounds showed typical ring absorptions in the tetramer region.



Compound CC Normal Proton NMR Spectrum

Compound CC Decoupled Spectrum P^{31} Irradiating Frequency 24.28 mc/sec

Figure 1.

Proton magnetic resonance spectra were obtained for compounds AA, BB, and CC as ~20% solutions in $CDCl_3$ and referenced to tetramethylsilane as an internal standard. The measurements were made with a Varian A-60 n.m.r. spectrometer equipped with an N.M.R. Specialties Model HD-60A heteronuclear spin decoupler. Spin decoupling experiments, which involve the application of a second strong oscillatory field near the resonance frequency of the heteronucleus while observing the transitions of the protons, were performed in order to establish that the observed doublet systems did indeed represent single protonic environments and that the additional broadening was due entirely to long-range coupling to phosphorus atoms further removed.[8] It is believed that these decoupling experiments are the first ever to be performed on a Varian A-60 n.m.r. spectrometer system.

The spectrum of compound CC (Fig. 1) showed three sets of doublets occurring at 130.0, 150.0, and 155.2 c.p.s. from tetramethylsilane. The coupling constant (J'_{PH}) in each case was 10.5 c.p.s. and is characteristic of phosphorus–methyl proton coupling in this type of compound.[2] On irradiation of the phosphorus at 24.28 Mc./sec., the three doublets collapsed to three distinct singlets. The three sets of doublets and the corresponding singlets in the decoupled spectrum indicate three distinct chemical environments existing in the molecule for $-N(CH_3)_2$ groups. Of the four possible *cis–trans* isomers of $P_4N_4(C_6H_5)_4[N(CH_3)_2]_4$, only one represents three environments for the $-N(CH_3)_2$ groups. This isomer is that in which three $-N(CH_3)_2$ groups are *cis* (above the hypothetical plane of the ring) and one is *trans*. The environments are determined by the immediate neighbors of the $-N(CH_3)_2$ group on

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[4] R. A. Shaw and C. Stratton, *J. Chem. Soc.*, 5004 (1962).

[5] Dr. Shaw kindly furnished us with the spectra of his compounds.

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TABLE I

H^1 NUCLEAR MAGNETIC RESONANCE DATA FOR $P_4N_4(C_6H_5)_4[N(CH_3)_2]_4$

Parent compd.	$P_4N_4(C_6H_5)_4Cl_4$ m.p., °C.	N-Dimethylamino deriv. compd.	$P_4N_4(C_6H_5)_4[N(CH_3)_2]_4$ m.p., °C.	No. of doublets	J, c.p.s.	J'_{PH}, c.p.s.	Shift in C_6H_6 soln., c.p.s.
A	248–258	AA	178–180	1	142.9	10.5	+1.6
B	202	BB	154–155.5	1	159.2	10.5	+0.9
C	148	CC	139–141	3	130.0	10.2	+1.7
					150.0	10.5	+0.5
					155.2	10.5	+0.8

the same side of the ring and attached to the nearest neighboring phosphorus atoms.[2] The three environments for compound CC can be described as follows: (1) One $-N(CH_3)_2$ group flanked on either side by $-N(CH_3)_2$ groups; chemical shift 130.0 c.p.s. (2) Two $-N(CH_3)_2$ groups flanked on either side by one C_6H_5 group and a $-N(CH_3)_2$ group; chemical shift 150.0 c.p.s. (3) One $-N(CH_3)_2$ group (*trans* to the above) flanked on either side by two C_6H_5 groups; chemical shift 155.2 c.p.s. The three above-described environments are analogous to the environments found in the previously reported[1] compound, $P_3N_3(C_6H_5)_2[N(CH_3)_2]_4$, for which the chemical shifts for similar environments were found to be 133.2, 150.9, and 157.2 c.p.s., respectively.

The spectrum of compound BB displayed one doublet at 159.5 c.p.s., and a sharp singlet was observed in the decoupled spectrum, indicating all the $-N(CH_3)_2$ groups to be in the same deshielded environment. Comparison with the chemical shifts for compound CC indicated that the $-N(CH_3)_2$ groups in compound BB are flanked by two phenyl groups. The only symmetrical isomer which exhibits this environment is that in which the $-N(CH_3)_2$ groups are alternately *cis* and *trans*.

The spectrum of compound AA also showed one doublet, at 142.9 c.p.s., which, upon double irradiation of the phosphorus, collapsed to a singlet, indicating that all the $-N(CH_3)_2$ groups were again in the same environment. The shift, however, is not consistent with any of those characteristic of compound CC. It is considerably lower (~10 c.p.s.) than that of the $-N(CH_3)_2$ groups flanked by phenyls or by a combination of phenyl and $-N(CH_3)_2$, and it is higher (~10 c.p.s.) than that for an $-N(CH_3)_2$ group flanked by $-N(CH_3)_2$ groups. A further experiment was performed in an attempt to clarify this anomalous chemical shift.

It has been well established[9] that neighboring phenyl groups and aromatic solvents can cause a marked effect on the chemical shift of aliphatic protons, due to the diamagnetic anisotropy of the phenyl ring. In the previously described environments, those $-N(CH_3)_2$ groups assumed to be neighbored by phenyls were found to appear at much lower fields (~25–30 c.p.s. lower) than the corresponding $-N(CH_3)_2$ flanked only by other $-N(CH_3)_2$ groups. It was logical to assume, therefore, that if benzene were added to each $CDCl_3$ solution, the resulting spectra should reveal a relatively large shift for $-N(CH_3)_2$ groups flanked only by $-N(CH_3)_2$ groups and much smaller shifts for $-N(CH_3)_2$ groups which are flanked by phenyls or a combination of both (since the major phenyl deshielding effect is already inherent in the molecule).

Table I summarizes the results of the above-described experiment and also includes the other data. The doublet ascribed to the $-N(CH_3)_2$ group flanked only by two other $-N(CH_3)_2$ groups in compound CC shifted 1.7 c.p.s. in benzene solution while the other two doublets were affected to a much lesser degree (~0.6 c.p.s.). The doublet of compound BB shifted 0.9 c.p.s., while that of compound AA shifted 1.6 c.p.s. Although the latter shift is in accord with the 1.7 c.p.s. shift noted in compound CC for the $-N(CH_3)_2$ group flanked only by other $-N(CH_3)_2$ groups and is an indication that all the $-N(CH_3)_2$ groups in compound AA are in a *cis* configuration, the relatively small numerical values of all shift changes brought about by benzene casts some uncertainty on this deduction and does not rule out completely the possibility of a *trans* configuration in which two adjacent $-N(CH_3)_2$ groups are on one side of the ring and the other two are on the other side. However, we believe the benzene data have some significance in indicating the *cis* configuration to be the more probable structure. Thus, if an arrow is used to indicate the side of the PN ring on which a $-N(CH_3)_2$ group is located, the data presented above indicate that compound AA is probably ↑↑↑↑ but may be ↑↑↓↓; compounds BB and CC have the configurations ↑↓↑↓ and ↑↑↑↓, respectively.

Finally, with the assumption that conversion of the chlorophosphonitriles, compounds A, B, and C, to the corresponding $-N(CH_3)_2$ derivatives takes place with no geometric rearrangement, the data also establish the configurations of the former. The fact that AA, BB, and CC were obtained in quantitative yield substantiates the validity of this assumption. A recent publication[10] describes several cases of *cis–trans* isomerization of aminochlorotriphosphonitriles by treatment of an isomer with the corresponding amine hydrochloride. In all cases, mixtures of the starting isomer and its corresponding *cis* or *trans* counterpart were formed.

Further work is now in progress through which we hope to establish unequivocally the structure of compound AA.

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A New Method for the Preparation of B_6H_{10}

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The study of the chemistry of B_6H_{10} has been largely hampered by a lack of a suitable method of preparation, which we now report from reaction of $B_9H_{14}^-$ ion[1,2] with polyphosphoric acid.[3] The yield is only 2.5% based upon $B_9H_{14}^-$, and 14 mole % of the volatile hydrides. Nevertheless, $B_9H_{14}^-$ can be made available in large quantities, the volatile materials are easily separated by use of standard vacuum line techniques, and the reaction is very easily carried out.

The starting material, $(C_2H_5)_3NHB_9H_{14}$, prepared by reaction[2] of $B_{10}H_{14}$ with KOH, was allowed to react at room temperature with polyphosphoric acid in an evacuated flask. The volatile boranes, B_2H_6 (40 mole % yield), B_4H_{10} (37%), B_5H_{11} and B_5H_9 (10%), B_6H_{10} (14%), and traces of B_8H_{12} and $B_{10}H_{14}$, were caught in a series of traps at $-196°$ and then separated in a small number of fractional condensations. Only B_8H_{12} remained with the B_6H_{10}, but it decomposed quantitatively[4] when the B_6H_{10} was warmed to 0° for vapor pressure measurements. Separation of the B_6H_{10}–B_8H_{12} mixture below $-20°$ may also yield reasonable amounts of B_8H_{12} for further study. All hydrides were identified by mass spectrometric methods,[5] and, in addition, the B_6H_{10} was shown to have a vapor pressure of 7.2 mm. at 0°.

We believe that this method of preparation is more convenient, in spite of the low yield, than boride hydrolysis,[6,7] discharge methods,[8,9] or base-catalyzed conversion[10,11] from other hydrides.

Experimental

The $(C_2H_5)_3NHB_9H_{14}$ was prepared according to the procedure of Benjamin, Stafiej, and Takacs.[2] Solid $(C_2H_5)_3NHB_9H_{14}$ (1 g., 4.7 mmoles) was then added slowly *in vacuo* to polyphosphoric acid. This mixture was continuously evacuated and stirred with the use of an Asco Laboratory gland stirrer (Arthur F. Smith Co.) which was lubricated with No. 90 Kel-F grease. Volatile products were trapped in three successive U-tubes cooled to $-196°$ with liquid nitrogen. After 3 days the effervescence had stopped, and the gas pressure measured with a McLeod gauge had been constant for 1 day. The $B_{10}H_{14}$ was then separated from more volatile hydrides by passage of the mixture through a U-tube cooled to $-23°$. Three quick passes through a $-63°$ trap then retained B_6H_{10} and B_8H_{12}, but allowed the B_2H_6, B_4H_{10}, B_5H_{11}, and B_5H_9 to pass through. After the B_6H_{10}–B_8H_{12} mixture was raised to 0° for measurement of its vapor pressure, a considerable pressure of H_2 remained upon recooling to $-196°$. Since the remaining liquid was pure B_6H_{10}, we concluded that the B_8H_{12} had decomposed. The presence of B_8H_{12} before the sample was warmed to 0° was proved by the observation of its characteristic pattern[4] in the mass spectrum, including, in particular, the maximum peak at 93 and the parent peak at 100 mass units. After the sample had been warmed to 0° this pattern disappeared, leaving only the B_6H_{10} peaks in the mass spectrum. About 0.12 mole of B_6H_{10} remained. Yields of B_2H_6 (0.33 mmole), B_4H_{10} (0.31 mmole), and B_5H_{11} and B_5H_9 (0.08 mmole) were also determined after separation by fractional condensation. The vapor pressure of B_6H_{10} at 0° (7.2 mm.) is in agreement with the value given by Stock,[6] and the mass spectrum was found to be exactly like the published spectrum.[5]

Acknowledgment.—We acknowledge support of this research by the Office of Naval Research, the U. S. Army Research Office (Durham), and the Advanced Research Projects Agency.

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CONTRIBUTION FROM THE BUREAU OF MINES,
PITTSBURGH COAL RESEARCH CENTER,
U. S. DEPARTMENT OF THE INTERIOR,
PITTSBURGH, PENNSYLVANIA

The Nature of the Nickel Boride Formed by the Action of Sodium Borohydride on Nickel Salts

BY L. J. E. HOFER, J. F. SHULTZ, R. D. PANSON, AND R. B. ANDERSON

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Investigations indicate that finely divided nickel boride is useful in catalysts[1,2] and fuel cell electrodes.[3] The action of solutions of sodium or potassium borohydride on solutions of nickel salts has been described as resulting in nickel boride, Ni_2B.[4,5] Though nickel boride formed by the action of sodium borohydride on nickel salts has received considerable attention as a catalyst, no structure study of this nickel boride has

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