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
UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

Trimethylazido Compounds of Group IVA Elements[1]

BY JOHN S. THAYER AND ROBERT WEST

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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).

mane and azidotrimethylplumbane, appear to be new. These compounds have enabled us to study the electronic spectrum of the azide group bonded to metals. The results, discussed below, have been interpreted in terms of π-bonding involving metal d-orbitals.

Synthesis.—The two general synthetic methods used for triphenylmetal azides[3] are also applicable, with minor modifications, to the trimethyl series. The silicon compound was obtained by refluxing chlorotrimethylsilane in tetrahydrofuran over NaN_3 and $AlCl_3$.

$$(CH_3)_3SiCl + NaN_3 \xrightarrow[THF]{AlCl_3} (CH_3)_3SiN_3 + NaCl \quad (1)$$

Aluminum azide, formed *in situ*, is apparently the actual azidizing agent.

The germanium, tin, and lead derivatives were prepared by a modification of the simple and convenient synthesis devised by Luijten, *et al.*[9] The trimethylmetal halide is treated with an aqueous acidic sodium azide solution.

$$(CH_3)_3MX + HN_3 \longrightarrow (CH_3)_3MN_3 + H^+ + X^- \quad (2)$$

$(CH_3)_3GeN_3$ may be prepared in an ether–water system, but excess HN_3 is required for good yields. $(CH_3)_3SnN_3$ and $(CH_3)_3PbN_3$ were obtained from the respective chlorides and excess HN_3 in water by extraction with ether. Complete extraction is difficult to obtain, and yields were only fair. The silicon and germanium compounds were purified by fractional distillation under nitrogen, whereas the tin and lead derivatives were recrystallized from benzene.

Results and Discussion

Physical Properties.—$(CH_3)_3SiN_3$ and $(CH_3)_3GeN_3$ are both colorless, volatile liquids, insoluble in water but miscible with all organic solvents. Both have higher boiling points than the corresponding chlorides or bromides, and unlike most organic azides are quite stable toward thermal decomposition.

$(CH_3)_3SnN_3$ and $(CH_3)_3PbN_3$ bear some resemblance to each other, but very little to the silicon and germanium analogs. Both form short, colorless, needlelike crystals, highly soluble in water and alcohols, considerably less soluble in ether, slightly soluble in benzene or carbon tetrachloride, and insoluble in hexane. $(CH_3)_3SnN_3$ melts without noticeable decomposition at 120°, but $(CH_3)_3PbN_3$ decomposes without melting above 200°.

The lability of these compounds toward hydrolysis follows the same trend observed for the triphenylmetal azides.[3,4] $(CH_3)_3SiN_3$ reacts rapidly with water under all conditions. $(CH_3)_3GeN_3$ is much more inert, being unreactive toward pure water and hydrolyzing only slowly in aqueous organic media. Hydrolysis is reversible, the degree of hydrolysis increasing as pH increases. The tin and lead compounds dissolve readily in water but give only traces of azide ion, detected by the color of the Fe^{+3} complex, even after long standing. They can be recovered unchanged by repeated extraction with ether.

The Place of Azide in the Organosilicon Conversion Series.—Eaborn[2,11] has developed a conversion series summarizing the reaction of organosilicon halides or pseudo-halides with silver salts. As the series is written below, any compound may be converted into one on its right, but not one on its left, by heating with the appropriate silver salt.

$$Si\text{–}I \longrightarrow Si_2S \longrightarrow Si\text{–}CN \sim Si\text{–}Cl \longrightarrow Si\text{–}NCS \longrightarrow Si\text{–}NCO \longrightarrow Si_2O \sim SiF$$

Chlorotrimethylsilane was found to react completely with dry silver azide to give $(CH_3)_3SiN_3$, but hexamethyldisiloxane was inert to this reagent. Conversely, $(CH_3)_3SiN_3$ is converted quantitatively to the siloxane by silver oxide, but is inert to silver chloride. $(CH_3)_3SiNCO$, prepared from the chloride and silver cyanate, yielded an equilibrium mixture of $(CH_3)_3SiN_3$ and starting material when treated with silver azide. A similar mixture was obtained when $(CH_3)_3SiN_3$ was treated with silver cyanate. Quantitative studies were not carried out on these mixtures, but the azide–isocyanate proportions were roughly equal. This places the azide group in the same position as isocyanate in the conversion series. The free energy change of the azide–isocyanate reaction appears to be very small, and the equilibrium position may perhaps depend on the nature of the other groups bonded to silicon.

$(CH_3)_3SiN_3$ has a labile azide group and has been used to prepare other silicon azides, with $AlCl_3$ as a catalyst.[8] The active azidizing agent is probably a mixed chloroaluminum azide formed in the reaction

$$(CH_3)_3SiN_3 + AlCl_3 \longrightarrow (CH_3)_3SiCl + AlCl_2N_3 \quad \text{etc.} \quad (3)$$

Infrared Spectra and Structure.—Table I lists maxima for the most important infrared absorption bands of these azides in the region from 500 to 4000 cm.$^{-1}$. Very weak bands have been omitted. Bands representing methyl group vibrations are nearly invariant for all methyl compounds of the same group IV element; this fact was used in making the frequency assignments in Table I, which follow those of Lippincott and Tobin[12] for group IV tetramethyl compounds.

The azide group gives rise to three infrared active bands.[13] Of these, the NNN asymmetric stretch (ν_3) is easily assigned, since it is the strongest band in the entire spectrum and the only one in the triple bond region near 2100 cm.$^{-1}$. Two bands not attributable to methyl vibrations are found near 1300 cm.$^{-1}$ in each compound. The stronger of these is assigned to the NNN symmetric stretch (ν_1), and the weaker band to an overtone of the NNN bending mode (ν_2). ν_2 itself appears near 675 cm.$^{-1}$ as a band of medium intensity. Compared to corresponding bands for the triphenylmetal azides[3] ν_3 shifts to lower frequency,

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[11] C. Eaborn, *J. Chem. Soc.*, 3077 (1950).

[12] E. R. Lippincott and M. C. Tobin, *J. Am. Chem. Soc.*, **75**, 4141 (1953).

[13] P. Gray and T. C. Waddington, *Trans. Faraday Soc.*, **53**, 901 (1957).

TABLE I

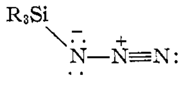
INFRARED SPECTRAL BANDS OF AZIDOTRIMETHYL COMPOUNDS

Assignment	I	II	III	IV
CH_3 asymm. stretch	3000 s[a]	2970 s	2998 m	2999 m
CH_3 symm. stretch	2912 s	2905 s	2925 m	2920 s
NNN asymm. stretch, ν_3	2131 v	2103 v	2045 v (2088 v)[b]	2034 v
CH_3 asymm. deformation	1430 m 1405	1451 m 1408	1465 s	1450 s
2 ν_2 (NNN)	1373 m	1363 m	1339 m	1333 m
NNN symm. stretch, ν_1	1332 m-s	1286 s	1286 s	1279 s
CH_3 symm. deformation	1259 s	1244 s	1213 m 1195	1143 m
?	1019 m	1013 m	1013 w	1013 w
M–N_3 asymm. stretch (?)	880 m	796 sh	. . .	. . .
CH_3 asymm. rocking	849 s	829 v	771 s	781 s
CH_3 symm. rocking	755 s	750 s	. . .	. . .
CH_3–M asymm. stretch	693 s	618 s	535 s	497 s 486
NNN bending, ν_2	685 m	675 m	665 m	655 w-m
CH_3–M symm. stretch	655 w	560 w	505 vw	. . .

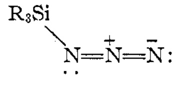
[a] v, very strong; s, strong; m, medium; w, weak; sh, shoulder; asymm., asymmetric; symm., symmetric. [b] Run in $CHCl_3$ solution.

while ν_1 and ν_2 shift to higher frequencies. These changes may reflect the greater electron-releasing character of the methyl group as compared to phenyl.

The azide stretching bands for $(CH_3)_3SiN_3$ appear at unusually high frequencies, an enhancement previously noted in other silyl azides.[3,7,14] Of the two principal



A



B

canonical structures A and B, dative π-bonding between N and Si would be favored by form A, increasing its relative contribution to the resonance hybrid and raising the frequency of the azide stretching bands.[3]

A portion of the microwave spectrum of $(CH_3)_3SiN_3$ was investigated by Dr. C. D. Cornwell. The spectrum observed at −78° consisted of approximately fifty lines over the region 19,400–20,700 Mc./sec. A detailed analysis was not attempted, but the complex spectrum appears to be that of a nonlinear molecule (asymmetric top). Recently silyl azide has also been shown to be nonlinear,[14] although the isostructural compound silyl isocyanate has a linear structure.[15]

Strong infrared bands characteristic of metal–nitrogen stretching modes were not observed. An otherwise unassigned band at 880 cm.$^{-1}$ is tentatively attributed to the silicon–nitrogen asymmetric stretching mode in $(CH_3)_3SiN_3$. This band appears at 727 cm.$^{-1}$ in $Si(NCO)_4$[16] and in the 900–1000 cm.$^{-1}$ region in silizanes.[17] In the spectrum of $(CH_3)_3GeN_3$, a shoulder at 796 cm.$^{-1}$ may represent Ge–N stretching. This absorption also lies at higher frequency than the Ge–N band in $Ge(NCO)_4$, which appears at 672 cm.$^{-1}$.[16] No bands attributable to metal–nitrogen stretching could be detected in $(CH_3)_3SnN_3$ or $(CH_3)_3PbN_3$ in the region studied.

Unlike all other azides that we have studied, $(CH_3)_3SnN_3$ shows a marked high-frequency shift for ν_3 when the spectrum is run in CH_2Cl_2 or $CHCl_3$ solution rather than as a Nujol mull. Such a shift suggests structural change upon dissolution. The low frequency of ν_3 in solid $(CH_3)_3SnN_3$ may result from azide bridging to an adjacent tin atom, giving rise to the pentacoordinate structure[10] now recognized for many solid trimethyltin compounds.[18–22] Other evidence suggesting a pentacoordinate structure for solid $(CH_3)_3SnN_3$ includes the relatively high melting point (120–121°, *cf.* $(CH_3)_3SnCl$, m.p. 37°) and the very low solubility in nonpolar solvents compared to tetracoordinate compounds such as $(CH_3)_3SnCl$.

Ultraviolet Spectra and Bonding.—Closson and Gray have recently interpreted the electronic spectra of organic azides in terms of molecular orbital theory.[23] Their assignment and notation is used in the following discussion. An energy level diagram for alkyl azides, according to Closson and Gray, is given in Fig. 1a.

Organic azides show two bands in the accessible portion of the ultraviolet at approximately 34,800 cm.$^{-1}$ (ϵ 24) and 46,000 cm.$^{-1}$ (ϵ ~500). According to Closson and Gray these are due to $\pi_y \rightarrow \pi_x^*$ (Δ_1) and $sp_x \rightarrow \pi_y^*$ (Δ_2) transitions, respectively.[23] Both transitions involve charge transfer from electron pairs largely localized on the nitrogen atom α to carbon into antibonding π-orbitals associated with the two more distant nitrogens. Electronegative substituents are expected to lower the energy of the orbitals on N_1 through an inductive effect, increasing the energies of both transitions, while electron-releasing substituents, such as silicon and germanium, should have the opposite effect.

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[14] E. A. V. Ebsworth, D. R. Jenkins, M. S. Mays, and T. M. Sugden, *Proc. Chem. Soc.*, 21 (1963).

[15] E. A. V. Ebsworth and M. S. Mays, *J. Chem. Soc.*, 4844 (1962).

[16] F. A. Miller and G. L. Carlson, *Spectrochim. Acta*, **17**, 977 (1961).

[17] A. L. Smith, *ibid.*, **16**, 87 (1960).

[18] H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, **2**, 740 (1963).

[19] R. Okawara, B. J. Hathaway, and D. E. Webster, *Proc. Chem. Soc.*, 13 (1963).

[20] I. R. Beattie, G. P. McQuillan, and R. Hulme, *Chem. Ind.* (London), 1424 (1962).

[21] I. R. Beattie and T. Gilson, *J. Chem. Soc.*, 2585 (1961).

[22] H. C. Clark, R. J. O'Brien, and J. Trotter, *Proc. Chem. Soc.*, 85 (1963).

[23] W. D. Closson and H. B. Gray, *J. Am. Chem. Soc.*, **85**, 290 (1963).

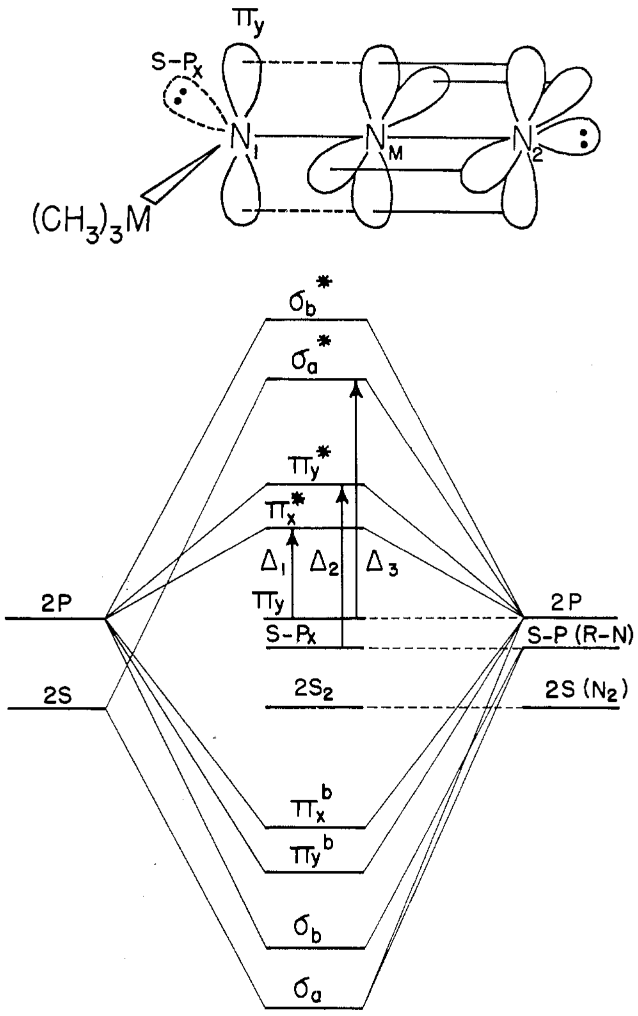


Fig. 1a.—Energy levels for alkyl azides, RN_3. Orbitals for N_1 and N_2 at right, for N_M at left.

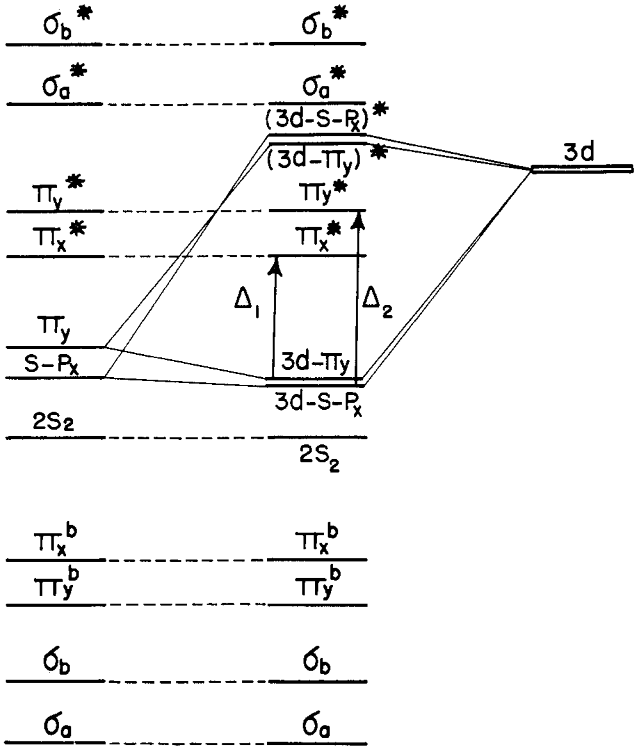
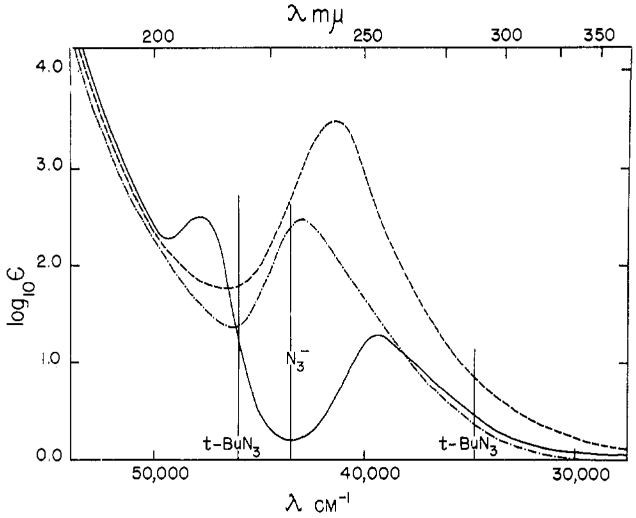


Fig. 1b. —Energy levels for $(CH_3)_3SiN_3$.

Fig. 2.—Ultraviolet absorption spectra: ———, $(CH_3)_3SiN_3$; —·—·—, $(CH_3)_3SnN_3$; – – – –, $(CH_3)_3PbN_3$.



$(CH_3)_3SiN_3$ and $(CH_3)_3GeN_3$ each show two ultraviolet bands (Fig. 2, Table II); their positions and intensities indicate that these correspond to the two transitions in alkyl azides. The $sp_x \rightarrow \pi_y^*$ band is not markedly changed, but the $\pi_y \rightarrow \pi_x^*$ band shifts to higher frequency, probably due to dative π-bonding. As shown in Fig. 1b, such an interaction would lower the energy of π_y, and to a lesser extent of sp_x, but would not affect the antibonding π-orbitals appreciably. Dative π-bonding would therefore oppose the inductive effect and increase transition energies. Similar effects of d-orbitals on energy levels have been noted in α-silyl ketones.[24]

TABLE II

ULTRAVIOLET ABSORPTION BANDS OF AZIDES

Compound	Solvent	ν, cm.$^{-1}$	ϵ	ν, cm.$^{-1}$	ϵ
$(CH_3)_3CN_3$[23]	Isooctane	34,700	23	46,400	500
$(CH_3)_3CN_3$[23]	CH_3OH	34,700	23	46,400	500
$(CH_3)_3SiN_3$	Isooctane	39,200	19	47,100	260
$(CH_3)_3SiN_3$	$(C_2H_5)_2O$	40,000	17	47,800	207
$(CH_3)_3SiN_3$	CH_3CN	39,600	23	47,200	225
$(CH_3)_3GeN_3$	Isooctane	39,200	23	47,200	252
$(CH_3)_3GeN_3$	$(C_2H_5)_2O$	39,500	21	47,400	244
$(CH_3)_3SnN_3$	$(C_2H_5)_2O$	43,500	313	...	...
$(CH_3)_3SnN_3$	CH_3CN	43,300	300	...	...
$(CH_3)_3SnN_3$	i-C_3H_7OH	43,000	325	...	...
$(CH_3)_3SnN_3$	CH_3OH	43,300	300	...	...
$(CH_3)_3PbN_3$	$(C_2H_5)_2O$	41,200	2700	...	...
$(CH_3)_3PbN_3$	CH_3CN	41,200	2700	...	...
$(CH_3)_3PbN_3$	i-C_3H_7OH	42,100	2880	...	...
$(CH_3)_3PbN_3$	CH_3OH	41,700	3530	...	...
NaN_3[23]	H_2O	43,500	430	...	...

$(CH_3)_3SnN_3$ and $(CH_3)_3PbN_3$ show only one strong ultraviolet band, probably due to the $sp_x \rightarrow \pi_y^*$ transition (Fig. 2, Table II). Our tentative interpretation is that there is little dative π-bonding, and the inductive effect predominates, causing a bathochromic shift of the $sp_x \rightarrow \pi_y$ absorption which swallows up the

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[24] D. F. Harnish and R. West, *Inorg. Chem.*, **2**, 1082 (1963).

weaker $\pi_x \rightarrow \pi_y{}^*$ band. As the M–N_3 bond becomes more ionic, the spectrum should become more like that of azide ion. Indeed, the spectrum of $(CH_3)_3SnN_3$ closely resembles that of azide ion in water. The spectrum of $(CH_3)_3PbN_3$ is similar, except that, for reasons not yet known, the intensity of the principal absorption band is far greater than that for $(CH_3)_3SnN_3$ or N_3^-.

Experimental

Reagents.—Mallinckrodt anhydrous ether was taken directly from unopened cans. Eastman Kodak tetrahydrofuran was distilled from lithium aluminum hydride and used immediately. Other solvents were spectral grade quality and used from previously unopened bottles. Chlorotrimethylsilane (Dow Corning) was used without further purification. The bromotrimethylgermane was a sample kindly prepared and purified by Mr. Roger Wood. Purified trimethyltin chloride and trimethyllead chloride were gifts of the M. and T. Chemicals Co. and the Ethyl Corporation, respectively. Reagent grade inorganic materials were used without further purification.

Azidotrimethylsilane (I).—A 2-l., three-necked flask was fitted with a stirrer and a reflux condenser. Anhydrous aluminum chloride (10 g., 0.075 mole) and sodium azide (71 g., 1.09 moles) were dissolved in 750 ml. of anhydrous tetrahydrofuran and refluxed for 1 hr. Trimethylchlorosilane (125 ml., 1.2 moles) in 150 ml. of tetrahydrofuran was added, and the entire mixture was refluxed for 67 hr. Volatile materials were then removed under vacuum and fractionally distilled under nitrogen; 150 ml. (125 g.) of a fraction boiling between 73 and 86° was collected and run through a gas chromatograph, using a methyl silicone oil column at 45°. Fractions identified were: $[(CH_3)_3Si]_2O$, 51%; $(CH_3)_3SiN_3$, 30%; tetrahydrofuran, 12%; unreacted $(CH_3)_3SiCl$, 2%. I was trapped out in Dry Ice and sent for analysis. The net conversion to I is 27%.

Anal. Calcd. for $C_3H_9N_3Si$: C, 31.28; H, 7.87; N, 36.46. Found: C, 31.41; H, 7.83; N, 36.34.

Azidotrimethylgermane (II).—A solution of sodium azide (3.0 g., 46 mmoles) in 100 ml. of 0.1 *N* HCl was shaken with a solution of bromotrimethylgermane (7.7 g., 38 mmoles) in 75 ml. of anhydrous ether for 30 min. The ethereal layer was removed and fractionally distilled. A clear, colorless liquid, boiling at 132–135°, was collected and redistilled to yield 3.0 g. (48.3%) of II (b.p. 135–136°).

Anal. Calcd. for $C_3H_9N_3Ge$: C, 22.56; H, 5.68; N, 26.30. Found: C, 22.68, H, 5.70; N, 26.34.

Azidotrimethylstannane (III).—A solution of trimethyltin chloride (1.55 g., 8.19 mmoles) in 50 ml. of distilled water was treated with sodium azide (1.0 g., 15.4 mmoles) in 50 ml. of 0.2 *N* HCl. The mixture was allowed to stand for 1 hr. at room temperature and then extracted with two 100-ml. portions of ether. Evaporation of the ether extract gave a crude residue, which was recrystallized from benzene to give 0.93 g. (58%) of III, m.p. 120–121° (lit.[9] 119.5–121.5°).

Anal. Calcd. for $C_3H_9N_3Sn$: C, 17.50; H, 4.41. Found: C, 17.67; H, 4.78.

Azidotrimethylplumbane (IV).—To a solution of sodium azide (3.81 g., 58.7 mmoles) in 200 ml. of 0.02 *N* HCl was added 1.10 g. (3.90 mmoles) of trimethyllead chloride. After standing for 2 hr., the solution was extracted with three 50-ml. portions of ether. Evaporation of the ethereal extract gave a white solid having a strong azide band but no hydroxide peak in the infrared spectrum. This residue was recrystallized from benzene to give 0.44 g. (38.3%) of IV. A sample heated in a capillary tube showed no change up to 150°; at 155°, a white film appeared on the glass walls above the solid. Sintering began at 220°, and decomposition was complete by 300°.

Anal. Calcd. for $C_3H_9N_3Pb$: C, 12.25; H, 3.08; N, 14.28. Found: C, 12.34; H, 3.30; N, 14.15.

Preparation of Anhydrous Silver Azide.—Because of the instability and shock sensitivity of this compound, certain precautions were necessary. An aqueous solution of silver nitrate was added to cooled aqueous sodium azide. After the white precipitate had settled, the water was decanted, and carefully dried acetone was added to remove water. This was repeated, and then the solid was carefully washed with anhydrous ether three times. The silver azide had to be used immediately; after 2 hr. in the dark at room temperature, extensive decomposition had occurred. The solid silver azide–silver residues were destroyed by the addition of strong potassium carbonate solution.

Conversion Series Experiments.—Ethereal solutions of chlorotrimethylsilane and hexamethyldisiloxane were added to dry silver azide at 0°, and the mixtures were allowed to stand in a Dry Ice–acetone bath for 2 hr. The ether layers were decanted and partially concentrated under vacuum to remove any HN_3. Determination of the infrared spectra of the solutions showed that the trimethylchlorosilane had been converted completely to I, but that the siloxane had not reacted.

Treatment of 1 ml. (9.6 mmoles) of chlorotrimethylsilane in 20 ml. ether with 1.5 g. (10.0 mmoles) of AgCNO gave immediate liberation of heat. The mixture was allowed to stand in a refrigerator for 1 hr., after which a sample was run through a gas chromatograph and found to consist only of ether and isocyanatotrimethylsilane. Treatment of this solution with silver azide gave a mixture of azide and isocyanate.

A solution of I in tetrahydrofuran, shown to be chloride-free, was treated with anhydrous silver oxide and silver cyanate. After 6 hr. at room temperature, there was no azide remaining in the solution treated with silver oxide, as determined by the Fe^{+3} test. A mixture of isocyanate and azide was formed after 6 hr. at room temperature, and there was no significant change after 24 hr. of standing. Refluxing for 12 hr. over excess silver cyanate increased the proportion of isocyanate, but some azide remained.

Infrared Spectra.—Spectra in the sodium chloride region were determined on a Perkin-Elmer Model 237 double beam recording spectrophotometer. Sodium chloride plates were used for solid mulls, while a 0.50-mm. sodium chloride cell was used for solutions. The polystyrene peaks at 2850 and 1603 $cm.^{-1}$ were used to calibrate the 4000–1250 range, and the peaks at 1603 and 906 $cm.^{-1}$ were used for the 2000–625 range. All frequencies were accurate to ± 5 $cm.^{-1}$. Spectra between 625 and 300 $cm.^{-1}$ were run on a Perkin-Elmer Model 112 recording spectrophotometer having a cesium bromide prism, using cesium iodide plates and a cesium iodide cell with 0.1-mm. path length. All frequencies are accurate to ± 1 $cm.^{-1}$.

Ultraviolet Spectra.—All spectra were run on a Cary Model 14 recording spectrophotometer. Cell sizes ranged from 2 to 0.05 cm., and concentrations from 0.001 to 11 g./l. Solvents used included water, methanol, 2-propanol, ether, acetonitrile, and isooctane.

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