Organic and Biological Chemistry

The Crystal and Molecular Structure of 1-Phenyl-1,2,2,3,4,4-hexamethylphosphetanium Bromide

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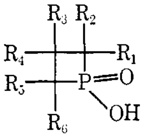
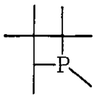
Abstract: The crystal and molecular structure of 1-phenyl-1,2,2,3,4,4-hexamethylphosphetanium bromide has been determined by single-crystal, X-ray diffraction techniques. This represents the first determination[1a] of the geometry and molecular parameters of a phosphetane ring system, a four-membered heterocycle which is the phosphorus analog of the azetidine system. This derivative crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 12.99$, $b = 11.06$, and $c = 13.15 \pm 0.02$ Å with $\beta = 117° 25 \pm 5'$. The phosphetane ring was found to be nonplanar with a dihedral angle of 24°. Long phosphorus–carbon distances of 1.93 Å within the ring offer strong support for the 1–2 ring-opening reactions previously observed. The internal angle at the phosphorus is 83° with adjacent angles averaging to 85° and the internal angle opposite the phosphorus opening up to 103°. The stereochemistry of this particular derivative was determined and the unique hydrogen on the ring was shown to be *trans* to the phenyl ring attached to the phosphorus. A final value of $R = 0.11$ was obtained for the 537 independent reflections observed.

The preparation and characterization of four-membered rings containing phosphorus as a heteroatom is a relatively recent development. Cyclic phosphinic acids (I) were first prepared in 1957.[1b] Recently, phosphetanes (II), which are true azetidine analogs, were prepared[2] from the oxides of these phosphinic acids. As in the azetidines, the 1–2 bonds are equivalent in the symmetrically substituted derivatives so no preference is shown in ring-opening reactions. However, in both systems ring-opening reactions are favored at the 1–2 bond in preference to the 1–4 bond if the ring is unsymmetrically substituted.[2]

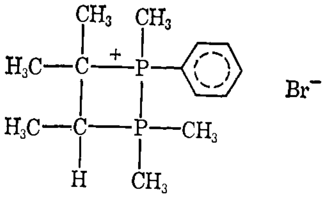


I



II

This laboratory has been previously engaged in a systematic study of three- and four-membered rings containing a heteroatom, usually nitrogen. Such compounds, in addition to their pharmacological significance, are also of chemical interest since their molecular parameters do not conform to the usual hybridization schemes proposed. Thus the structure determination of 1-phenyl-1,2,2,3,4,4-hexamethylphosphetanium bromide (III), a crystalline derivative of phosphetane, was undertaken. Such a study will provide the first set of bond distances and bond angles for a four-membered ring containing phosphorus as a heteroatom; it will determine whether this ring is planar and, if not, the extent of deviation from planarity; and, finally, since the stereochemistry of this particular derivative is not known with certainty, it will determine whether the unique hydrogen on the four-membered ring is *cis* or *trans* to the phenyl group.



III

Crystal Data. A small needle-shaped crystal less than 0.5 mm in diameter and approximately 2.0 mm in length was chosen from the original sample, kindly furnished to us by Professor S. E. Cremer.[3] This crystal was used to obtain the data. An integrating Buerger precession camera with filtered Mo Kα radiation was utilized in collecting the data. Data of the zero and first five levels about the (010) axis, the zero and first six levels about the (001) axis, and the diagonal zone (hkk) were taken. No absorption corrections were applied to the 537 independent reflections which were ultimately obtained.

Extinctions for $l = 2n + 1$ for the ($h0l$) zone and $k = 2n + 1$ for the $0k0$ line uniquely identified the monoclinic space group as $P2_1/c$. The cell dimensions were $a = 12.99$, $b = 11.06$, $c = 13.15 \pm 0.02$ Å, and $\beta = 117° 25' \pm 5'$. The calculated density of 1.248 g/cc assuming four molecules per unit cell was in reasonable agreement with a rough measurement using flotation techniques of the experimental density.

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(1) (a) Two recently published communications on phosphetane ring systems with a neutral phosphorus, corroborate our results [C. N. Caughlan, *et al.*, *Chem. Commun.*, 1051 (1968); 1228 (1968)]; (b) G. M. Kosolapoff and R. F. Struck, *J. Am. Chem. Soc.*, **79**, 3739 (1957).

(2) (a) S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, **32**, 4066 (1967); (b) S. E. Cremer and R. J. Chorvat, *Tetrahedron Letters*, 4066 (1967).

(3) S. E. Cremer, private communication (including sample), 1967.

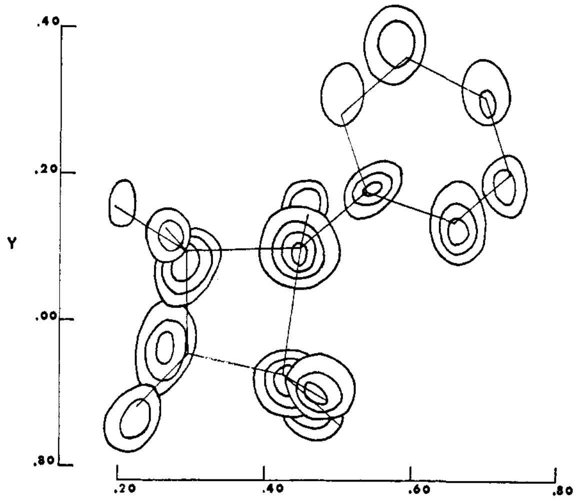

Figure 1. Fourier map based on phases of bromine and phosphorus; projection down the x axis showing organic moiety. Contours were drawn at intervals of 2.0 e$^-$/Å^3 starting with 2.0 e$^-$/Å^3 contour except for phosphorus. Contours for phosphorus were drawn at intervals of 4.0 e$^-$/Å. Final model is superimposed for clarity.

Intensities were measured with a Nonius microdensitometer, and a program[4] modified by us was used in making intrazone correlations, 1/LP corrections, and finally, interzone correlations. The interzone correlations converged in such a manner that the data led to three constants as scale factors for the parity groups ($k + l$ odd) ($k + l$, even with k even) and ($k + l$, even with k odd). Unfortunately, the amount of ($k + l$ odd) data was very limited and of low intensity, hence it was of little use in helping to correlate the data of the other two parity groups. However, our least-squares routine[5] contains a provision for handling data with multiple-scale factors so the data were utilized with each parity group having its own scale factor. Finally, the (hkk) zone was assigned a fourth scale factor and all subsequent refinements utilized these four scale factors as separate variables. It was presumed that ultimately, when the correct structure was determined, these four scale factors should approximate each other.

Structure Determination. A three-dimensional Patterson map was calculated to locate the bromide ion position. An ambiguity in the resulting Patterson peak positions led to eight nonequivalent possible locations for the bromide ion. For each of these choices, the phosphorus–bromine vectors could also be identified. Consequently, three cycles of isotropic least-squares refinement were run on each of the eight two-atom models. Only two of these models led to a reasonable value for R (usual reliability index). The first gave $R = 0.252$, and the second (a disordered variation of the first) led to R 0.268.

Fourier maps were constructed using the observed data and the phases calculated from both of these lattice models. Both models produced essentially the same structure. All of the seventeen atom positions to be expected showed up in the maps and the coordinates thus obtained were refined using least-squares techniques. Figure 1 shows the Fourier from the ordered model ($R = 0.252$) with the final structure superimposed for clarity. Fourteen cycles of isotropic least-squares refinement of the entire structure led to a value of $R = 0.119$.

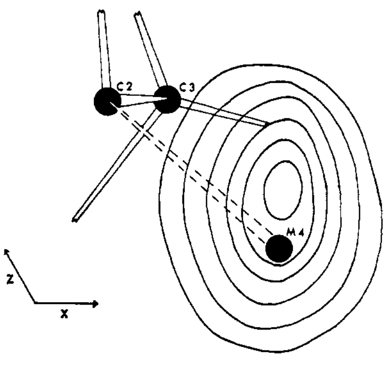

Figure 2. Difference Fourier map based on phases of all atoms excluding M-4, projected down the y axis. Region in the vicinity of M-4 only is shown. Contours at 1.0 e$^-$/Å^3 starting with the first contour.

Since the methyl carbons in addition to the bromide ion showed pronounced evidence of thermal motion, the isotropic temperature factors were converted to anisotropic temperature factors and four cycles of anisotropic least squares were run leading to values of R, r[6] = 0.114, 0.128. However, atom M-4 (see Table I for a definition of symbols) moved toward atom C-2, producing a ring–methyl distance of less than 1.4 Å. A sixteen-atom difference Fourier map excluding atom M-4 was calculated in an attempt to locate the position of atom M-4 more accurately. Figure 2 shows a projection down the b axis of this difference Fourier map in the vicinity of atom M-4. The adjacent portion of the final structure is also shown. The relatively large volume occupied by this peak (almost 1.0 Å in diameter in the XZ plane) illustrates its very large thermal motion and accounts, in part, for our further difficulties with this atom.

The M-4–C-2 distance corresponding to the center of this peak was still less than 1.4 Å. Various attempts were made to place atom M-4 so that it satisfied our prejudices of an anticipated 1.53-Å bond distance. The original position from the isotropic refinement and reasonable variations of the position shown in the difference Fourier map (Figure 2) were tried. Each of these attempts was followed by additional cycles of anisotropic least-squares refinement and all resulted in essentially the same short M-4–C-2 distance.

Finally, the positions for all atoms from the last isotropic refinement were inserted and held fixed, and the temperature factors for all atoms were refined anisotropically. This was then followed by a set of runs where the temperature factors were held fixed and the coordinates were refined. This procedure of alternant

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(4) (a) J. S. Rollet and R. A. Sparks, *Acta Cryst.*, **13**, 273 (1960); (b) D. Smith, private communication, 1967.

(5) W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, Oak Ridge National Laboratories, Publication TM-305, Oak Ridge, Tenn., 1962.

(6) The least-squares program used is a modification of ORFLS (see ref 5) for the IBM 7040. The program uses the full-matrix, fractional shifts and minimizes a weighted residual factor. The expressions for the reliability factor (R) and the weighted reliability factor (r) are

$$R = \frac{\Sigma \lvert\lvert F_o\rvert - \lvert kF_c\rvert\rvert}{\Sigma \lvert F_o\rvert} \qquad r = \left[\frac{\Sigma(wF_o - kF_c)^2}{\Sigma(wF_o)^2}\right]^{1/2}$$

Unit weights were used in this refinement.

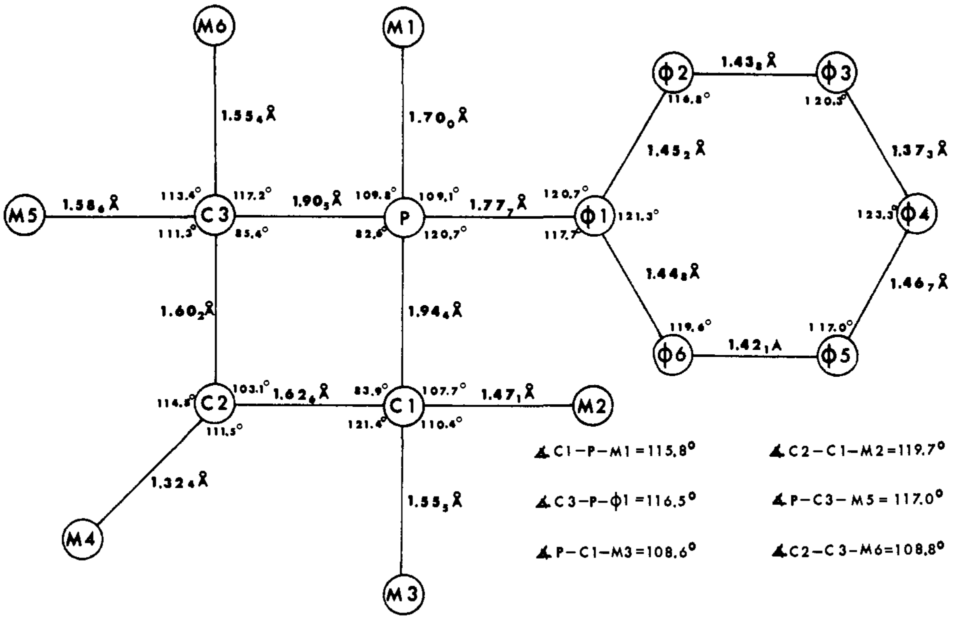

Figure 3. Schematic drawing of molecule with all bond distances and bond angles shown.

cycles of temperature factor and coordinate refinement was repeated until *all* shifts (both temperature factors and coordinates) were less than 0.00001. At this point, refinement was terminated with values of R, r = 0.11_1, 0.12_6. A difference Fourier map substracting out all peaks was calculated. No region of height greater than 1.7 $e^-/\text{Å}^3$ was observed in this final map. Consequently, the determination of the structure was considered completed.

Table I. Final Parameters for 1-Phenyl-1,2,2,3,4,4-hexamethylphosphetanium Bromide

Atom	Symbol	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Bromine	Br	0.1979	0.0050	0.7629	0.0071	0.0096	0.0093	−0.0026	0.0025	−0.0025
Phosphorus	P	0.2165	0.0916	0.4412	0.0035	0.0064	0.0045	0.0001	0.0011	−0.0012
Ring carbon 1	C-1	0.2227	0.9181	0.4207	0.0042	0.0042	0.0032	0.0001	0.0027	−0.0024
Ring carbon 2	C-2	0.1574	0.9515	0.2851	0.0070	0.0072	0.0087	−0.0014	0.0020	0.0006
Ring carbon 3	C-3	0.1824	0.0949	0.2840	0.0206	0.0105	0.0136	−0.0010	0.0108	−0.0091
Methyl 1	M-1	0.3455	0.8821	0.4750	0.0069	0.0071	0.0066	0.0005	0.0031	−0.0057
Methyl 2	M-2	0.1578	0.8534	0.4793	0.0133	0.0083	0.0099	−0.0059	0.0067	−0.0031
Methyl 3	M-3	0.1951	0.8837	0.2260	0.0294	0.0216	0.0227	0.0122	0.0239	0.0131
Methyl 4	M-4	0.2875	0.1190	0.2567	0.0138	0.0119	0.0115	−0.0015	0.0110	0.0024
Methyl 5	M-5	0.0683	0.1587	0.1991	0.0103	0.0094	0.0092	−0.0028	0.0064	0.0044
Methyl 6	M-6	0.1001	0.1420	0.4553	0.0066	0.0148	0.0114	0.0014	0.0060	−0.0025
Phenyl 1	Ph-1	0.3421	0.1720	0.5380	0.0057	0.0072	0.0080	−0.0012	0.0043	0.0011
Phenyl 2	Ph-2	0.3834	0.2758	0.4997	0.0181	0.0148	0.0169	0.0069	0.0062	0.0060
Phenyl 3	Ph-3	0.4753	0.3452	0.5867	0.0161	0.0051	0.0096	−0.0024	0.0045	−0.0002
Phenyl 4	Ph-4	0.5372	0.2995	0.6954	0.0042	0.0087	0.0091	−0.0020	0.0058	−0.0014
Phenyl 5	Ph-5	0.5074	0.1860	0.7333	0.0028	0.0151	0.0123	−0.0021	0.0057	−0.0020
Phenyl 6	Ph-6	0.4077	0.1234	0.6524	0.0041	0.0067	0.0033	−0.0006	0.0019	0.0020

Results and Discussion

The final coordinates and anisotropic temperature factors are shown in Table I. Figure 3 shows a schematic drawing of the molecule with the various bond distance and bond angles resulting from the final parameters. Estimated standard deviations (ESD) were calculated based on the coefficient matrix from the last cycle of least-squares refinement. The bromide ion position involves ESD values of 0.01 Å, whereas all bond distances and bond angles in the organic moiety have ESD equal to 0.04 Å and 2.5°, respectively, with the exception of M-4. For atom M-4, a bond distance ESD value of 0.06 Å and ESD bond angle values of 5° were obtained.

In the benzene ring, average values of 1.43 ± 0.02 Å for the C–C bond distances and 119.7 ± 2.0° for the interior angles were obtained. These are well within one ESD of the accepted values of 1.39_7 Å and 120°, respectively. Only one bond distance is slightly more than one ESD from this average value and all bond angles, taken individually, are within one ESD of the average value.

One can also compare chemically equivalent but crystallographically nonequivalent bonds, to see if the same criteria hold. In the phosphetanium ring, the P–C bonds give an average value of 1.93 ± 0.02 Å and the C–C bonds give an average value of 1.61 ± 0.02 Å. If one excludes the C-2–M-4 distance, the other four ring carbon to methyl distances average 1.54 ± 0.03 Å. All have deviations well within one ESD of the average value with the exception of the C-4–M-4 distance.

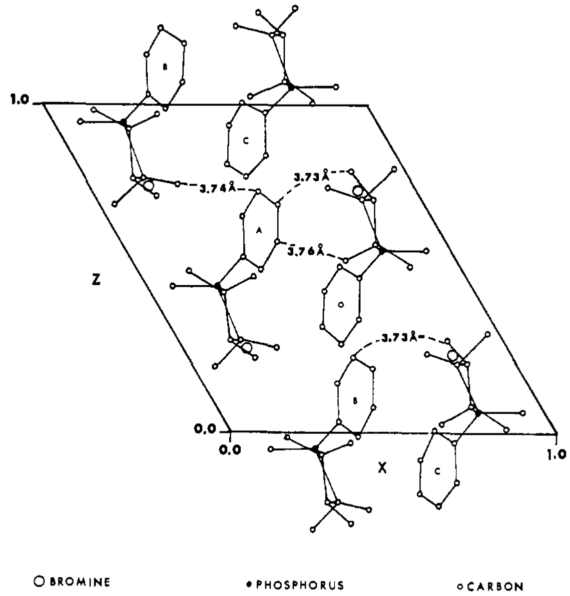

Figure 4. Projection of unit cell contents down the y axis. Nonbromide contacts less than 3.80 Å are indicated.

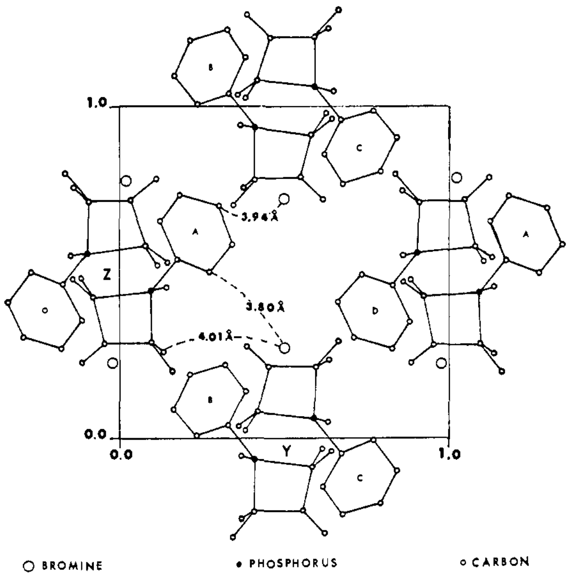

Figure 5. Projection of unit cell contents down the x axis. Bromide contacts to the organic moiety which are 4.0 Å, or less, are indicated.

Similarly, the R, r values of 0.111, 0.126 are comparable to values found in the literature for structure determinations of similar complexity in which film techniques were used. Finally, one can look at the values of the four initially independent scale factors assigned to the various groupings of data. Since the data were taken from one set of films involving the same crystal, these ought to ultimately agree with each other within a reasonable range. Table II shows that this is the case.

This leaves only the M-4–C-2 bond (1.32 Å) with a value significantly different from either the average of the other such distances in this study (1.54 Å) or the usual value for such distances in the literature (1.53 Å).[7] The large anisotropic temperature factor and the large volume occupied by this peak in the difference Fourier map excluding it (Figure 2) suggest that a correction for thermal motion should be made to the bond length. Using the Busing and Levy formulation[8] for such a correction results in a new value for this bond distance of 1.38 Å (a correction of +0.06 Å). As a check, a similar correction applied to the other methyl atoms results in corrections of +0.02 Å or less. This value (1.38 Å) still differs significantly from either our average value of such distances (1.54 Å) or the literature value (1.53 Å), namely a difference of almost three standard deviations. Consequently, it is felt that this difference is a real difference and statistically significant. The possibility that this shortening may be due to crystal packing is readily disproven by the lack of close intermolecular contact distances which are 3.73 Å or greater. This is illustrated in Figure 4 which shows the contents of the unit cell projected down the b axis and gives all nonbromine intermolecular contact distances less than 3.80 Å. Figure 5 shows the unit cell contents projected down the a axis with all bromide contact distances less than 4.01 Å shown.

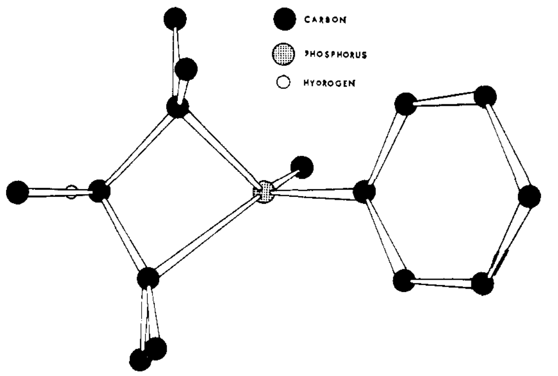

Figure 6. Perspective drawing of the molecule including the calculated ring hydrogen.

Table II. Scale Factors for the Various Parity Groups[a]

Scale factor	Group	Final scale factor	No. of structure factor
k_1	$(k + l)$ even, k even	0.298	264
k_2	$(k + l)$ even, k even	0.352	206
k_3	$(k + l)$ odd	0.325	14
k_4	Diagonal zones	0.388	83

[a] Weighted-average scale factor was 0.331.

Based on geometric considerations (C–H = 1.10 Å, H–C–M-4 = 109°, both HCC angles equal and near 109°) the probable position of the hydrogen on C-2 was calculated. A comparison of the calculated position to the final difference Fourier map shows that it lies in a region of relatively high electron density ($\sim$0.9 e$^-$/Å^3) and hence supports the reasonableness of this choice. Figure 6 shows a perspective drawing of the molecule including the calculated hydrogen atom.

The P–Ph distance of 1.78 Å in this study agrees quite well with similar distances in the tetraphenylphosphonium ion[9] (1.79 Å) and the triphenylmethylphosphonium ion[10] (1.78–1.80 Å). The M-1–P dis-

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(7) A. Langseth and B. P. Stoicheff, *Can. J. Phys.*, **34**, 350 (1956).

(8) W. R. Busing and H. A. Levy, *Acta Cryst.*, **17**, 142 (1964).

(9) P. Goldstein, K. Seff, and K. N. Trueblood, *ibid.*, **B24**, 778 (1968).

(10) C. J. Fritchie, *ibid.*, **20**, 107 (1966).

tance of 1.70 Å in this study is almost 0.08 Å shorter than the only other similar distance in the literature[10] (1.78 Å). Of course, no previous value of a P–C distance in a phosphetane ring is known. However, our average value of 1.925 Å is larger than all previously reported P–C distances which range from 1.78 to 1.84 Å.[9–13]

The phosphetane ring presents some interesting features of its own. First, the unique hydrogen on C-2 is *trans* to the phenyl ring. Secondly, the phosphetane ring is decidedly nonplanar with an angle between the planes defined by (C-1–C-2–C-3) and C-1–P–C-3) of 24°. Thirdly, the internal angle at the phosphorus is 82.6° with the adjacent angles averaging to 84.7 ± 0.7° and the internal angle opposite the phosphorus (at C-2) opening up to 103.1°. Finally, the C–C bonds in the phosphetane ring average to 1.614 Å. These do not differ in a statistically significantly manner from their expected values of 1.54 Å. However, these longer distances coupled with the long P–C distances in the phosphetane ring strongly support the chemical evidence which shows that the ring is highly susceptible to ring opening at the 1–2 positions. It further suggests that a study of an unsymmetrically substituted phosphetane ring should be carried out to see whether these distances would still be equivalent, or whether the 1–2 distance would be longer than the 1–4 distance as is suggested by its ring-opening reactions[2] and in analogy to the azetidine ring studies.[14]

Acknowledgments. The authors wish to express their gratitude to the National Institutes of Health (GM-08348-08) for financial assistance in support of this and subsequent studies; to Professor S. E. Cremer, Department of Chemistry, Illinois Institute of Technology; and to the Computer Centers at Louisiana State University at Baton Rouge and Louisiana State University at New Orleans (NSF-GP-2964).

(11) H. L. Carrell and J. Donohue, *Acta Cryst.*, **B24**, 699 (1968).

(12) N. V. Mani, F. R. Ahmed, and W. H. Barnes, *ibid.*, **21**, 375 (1966).

(13) D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **29**, 914 (1958).

(14) C. Moret and L. M. Trefonas, *J. Heterocyclic Chem.*, **5**, 549 (1968).

Barriers to Internal Rotation in Aminoboranes and in Octamethyloxamidinium Bromide[1]

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Abstract: Barriers to rotation about BN bonds have been studied by nmr spectroscopy in *n*-butyl- and phenylbis(dimethylamino)borane, in tris(dimethylamino)borane, in bis(dimethylamino)methylphenylaminoborane, and in tetrakis(dimethylamino)diborane(4), and about CN bonds in octamethyloxadiamidinium dibromide. Activation parameters are reported for those compounds where the barriers were high enough to be measured.

Since aminoboranes are isoelectronic with olefins, the BN bonds in them are expected to have significant π character;[3] rotation about such bonds should be correspondingly hindered, and with suitable substituents, *cis–trans* isomerism should be observed. Isomerism of this kind was first inferred by Niedenzu and Dawson[4] from the long boiling ranges and vapor pressure characteristics of such compounds, and was subsequently confirmed by standard nmr spectroscopic techniques. The first measurement of this kind was reported for (methylphenylamino)dimethylborane (I), leading to a preliminary estimate[5] of 15 ± 3 kcal/mol for the height of the rotational barriers; this was later revised[6] to 10.8 ± 0.7 kcal/mol, while a third estimate[7] puts the barrier at 18.8 ± 0.3 kcal/mol. Barriers to B–N rotation have also been reported for (dimethylamino)phenylchloroborane (II) (18 ± 2 kcal/mol[8]), for two series of aminoboranes III and IV where the barriers varied from 9.9 kcal/mol for IIIe to 26.6 kcal/mol for IVa, the rest lying between 14 and 19 kcal/mol,[7] and for dimethylaminovinylbromoborane (14.0 ± 0.4 kcal/mol[9]).

In compounds I–IV, either nitrogen or boron carries identical substituents, so *cis,trans* isomerism could not be distinguished. Distinguishable isomers have been detected by nmr spectroscopy in the case of methylphenylaminoethoxymethylborane (V),[10] (methylphenyl-

(1) This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

(2) Israel Mining Industries, Haifa, Israel.

(3) E. Wiberg, *Naturwissenschaften*, **35**, 182 (1948).

(4) K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **82**, 4223 (1960).

(5) G. E. Ryschkewitsch, W. S. Brey, Jr., and A. Saji, *ibid.*, **83**, 1010 (1961).

(6) W. S. Brey, Jr., M. E. Fuller, II, G. E. Ryschkewitsch, and A. S. Marshall in "Boron–Nitrogen Chemistry," K. Niedenzu, Ed., Advances in Chemistry Series No. 42, American Chemical Society, Washington, D. C., 1964, p 100.

(7) H. Watanabe, T. Totani, K. Tori, and T. Nakogawa in "Nuclear Magnetic Resonance and Relaxation in Solids—Proceedings of the XIIIth Colloque Ampére," L. Van Garven, Ed., North-Holland Publishing Co., Amsterdam, 1965, p 374.

(8) P. A. Barfield, M. F. Lappert, and J. Lee, *Proc. Chem. Soc.*, 421 (1961).

(9) K. Niedenzu, J. W. Dawson, G. A. Neece, W. Sarodny, D. R. Squire, and W. Weber, *Inorg. Chem.*, **5**, 2161 (1966).

(10) H. T. Baechle and H. J. Becher, *Spectrochim. Acta*, **21**, 579 (1965).