The system as described is a good one for synthesizing laboratory-scale quantities of the smaller *closo*-carboranes. Even at 10 mm operating pressure it was capable of producing about 3 g/hr of the combined products $C_2B_3H_5$, $C_2B_4H_6$, and $C_2B_5H_7$. One very important feature of this nearly quantitative process is its relative cleanliness. Solid residues do not build up in the reactor chamber, and the equipment does not require the frequent disassembly and cleaning that has been our experience with the batch process.

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The Preparation of B-Methyl Derivatives of $C_2B_4H_8$. The Correlation of Proton Nuclear Magnetic Resonance Chemical Shift Measurements in $C_2B_4H_8$ Derivatives by Employing "Ring-Current" Contributions

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By the reaction of methylpentaborane with acetylene and 2-butyne, all of the B-methyl derivatives of 2,3-$C_2B_4H_8$ and of 2,3-$(CH_3)_2$-2,3-$C_2B_4H_6$, respectively, have been prepared. The proton nmr of the terminal substituents on boron are correlated by an empirical consideration of ring-current contributions. In this approach the relative magnitude, as well as the direction, of the chemical shifts can be reasonably predicted.

Introduction

Although some C-alkyl derivatives of $C_2B_4H_8$ are known, no boron-substituted derivatives have heretofore been reported except for B-deuterio compounds.[1,2] In the present study the 1-, 4-, and 5-methyl derivatives are reported and the observed proton nmr resonances correlated. Earlier, it had been suggested that a ring current might be one of several effects to account for the high-field position of the $C_2B_4H_8$ apical boron in the ^{11}B nmr.[3] A quantitative approach has been taken in this paper and can satisfactorily account for the magnitude of the chemical shifts for boron-attached hydrogens and alkyl derivatives.

Experimental Section

Materials.—1-Methyl- and 2-methylpentaboranes were prepared using previously reported procedures.[4] Acetylene (Airco) was vacuum fractionated through a trap at −100° to remove acetone. 2-Butyne (Columbia) was used without further purification. All chemicals were handled in standard high-vacuum equipment.

Mass spectra were recorded using a Consolidated Electrodynamics Corp. 21-620 mass spectrometer.

Infrared spectra were recorded by a Beckman IR-5 spectrophotometer and also, in the case of the B-methyl derivatives of $C_2B_4H_8$, by a Beckman IR-12 spectrophotometer.

Gas Chromatography.—A 30% Apiezon L on firebrick column operating at 100° was used in the final purification of the products from the acetylene experiment and a 30% Kel-F on firebrick column was used for the products from the 2-butyne experiment.

Nuclear Magnetic Resonance.—Boron-11 nmr spectra (Table I) were obtained at 12.8 Mc with a Varian V-4300 high-resolution spectrometer and also at 32.1 Mc with a Varian HA-100 spectrometer. Proton nmr spectra (Table II) were obtained using a Varian A-60 spectrometer.

B-Methyl Derivatives of $C_2B_4H_8$.—A mixture of 1-methylpentaborane (16 mmol) and acetylene (185 mmol) was sealed in a 2-l. flask and heated to 220° for 68 hr and then to 250° for 20 hr. The volatile fraction was distilled away from the large amount of dark brown solids that had formed and was vacuum fractionated through traps at −20, −100, and −190°. The contents of the −100° trap were gas chromatographed at 100° to yield 1.25 mmol (7.8%) of 2,3-dicarbahexaborane(8) (retention volume 1.00), 0.70 mmol (4.4%) of 1-methyl-2,3-dicarbahexaborane(8) (retention volume 1.41), and 1.0 mmol (6.3%) of a mixture of 4-methyl-2,3-dicarbahexaborane(8) and 5-methyl-2,3-dicarbahexaborane(8) (retention volume 1.78) in a mole ratio of 2:1. The mass spectra of the latter two fractions exhibited a sharp cutoff at *m/e* 90, corresponding to the $^{12}C_3{}^{11}B_4{}^1H_{10}$ parent ion. The identification of the last fraction as an inseparable mixture of the 4- and 5-methyl isomers was obvious from a complete analysis of both the 12.8- and 32.1-Mc ^{11}B nmr spectra and also of the proton nmr spectra.

The infrared spectrum of the purified 1-methyl-2,3-dicarbahexaborane(8) exhibited bands at (cm^{-1}): 2982 m (C–H stretch), 2950 m (C–H stretch), 2880 m (C–H stretch), 2634 vs (terminal B–H stretch), 1967 m (bridge hydrogen symmetric stretch), 1500 s (bridge hydrogen asymmetric stretch), 1345 m, 1210 m, 1165 w, and 925 m.[5] The infrared spectrum of the mixture of basal boron-substituted isomers was similar to but not identical with that of the 1-methyl isomer. Unfortunately, the unavailability of pure basal isomers or of mixtures of different com-

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(1) J. R. Spielman, R. Warren, G. B. Dunks, J. E. Scott, and T. Onak, *Inorg. Chem.*, **7**, 216 (1968).

(2) T. Onak and G. B. Dunks, *ibid.*, **5**, 439 (1966).

(3) W. E. Streib, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 2331 (1963).

(4) T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, **6**, 1465 (1967), and references therein.

(5) Since it was difficult to remove the last traces of benzene, a side product of the reaction, from the 1-methyl derivative, compensation techniques were used to subtract out benzene infrared contributious.

TABLE I

^{11}B NMR CHEMICAL SHIFT VALUES AND COUPLING CONSTANTS[a]

Compound	Atoms	δ, ppm[b]	J_{B-H_t}, cps	J_{B-H_b}, cps
1-Methyl-2,3-dicarbahexaborane(8)	B(1)–CH_3	+45.2		
	B(4,6)–H	+6.3	152	37
	B(5)–H	~+6[c]	~150[c]	
4-Methyl-2,3-dicarbahexaborane(8)[d,e]	B(1)–H	+52.9	174	
	B(4)–CH_3	−6.3		~30
	B(5)–H	+4	155	
	B(6)–H	+4	155	34
5-Methyl-2,3-dicarbahexaborane(8)[d]	B(1)–H	+52.9	174	
	B(4,6)–H	+4	155	34
	B(5)–CH_3	−10.2		
1,2,3-Trimethyl-2,3-dicarbahexaborane(8)	B(1)–CH_3	+40.3	...	...
	B(4,5,6)–H	+2.5	148	...[f]
2,3,4-Trimethyl-2,3-dicarbahexaborane(8)[d,e]	B(1)–H	+49.0	180	...
	B(6)–H	+6	150	48
	B(5)–H	+7	150	...
	B(4)–CH_3	−3.3	...	...
2,3,5-Trimethyl-2,3-dicarbahexaborane(8)[d]	B(1)–H	+49.0	180	...
	B(4,6)–H	+6	150	48
	B(5)–CH_3	−8.8	...	...

[a] All spectra were taken at 12.8 Mc and also, except for that of 1-methyl-2,3-dicarbahexaborane(8), were taken at 32.1 Mc. [b] δ relative to boron trifluoride ethyl etherate. [c] Overlap with other resonances makes a more exact determination difficult. [d] Because of isomer separation difficulties (see Experimental Section) exact δ and J values are difficult to obtain for the overlapping resonances of the basal borons with attached terminal hydrogens. [e] Racemate. [f] Cannot be accurately determined because of ill-defined separation of coupled resonances.

position makes it impossible to make individual assignments for the 4- and 5-methyl isomers.

Preparation of B-Methyl-2,3-dimethyl-2,3-dicarbahexaborane(8) Derivatives.—2-Butyne (202 mmol) and 1-methylpentaborane (19.2 mmol) were sealed in a 2-l. flask and first heated at 157° for 16 hr and subsequently heated at 205° for 18 hr. The volatile fraction of the reaction product was separated into three parts by fractional condensation through traps at 0, −70, and −196°. The efficiency of the separation was further aided by first immersing the cold finger of the reaction vessel into a −60° bath, which was later exchanged for a 0° bath, and finally without a cooling bath. The contents of the 0° trap were not further investigated. The −196° trap contained 98.1 mmol of unreacted 2-butyne. A gas chromatogram of the contents of the −70° trap gave 2.72 mmol of *cis*-2-butene, 2.82 mmol (14.7%) of 2,3-dimethyl-2,3-dicarbahexaborane(8) (retention volume 1.0), 0.97 mmol (5.0%) of 1,2,3-trimethyl-2,3-dicarbahexaborane(8) (retention volume 1.4), and 1.9 mmol (9.5%) of a mixture of isomers containing 55% 2,3,4-trimethyl-2,3-dicarbahexaborane(8) and 45% 2,3,5-trimethyl-2,3-dicarbahexaborane(8) (retention volume 1.7). The components of the last fraction were easily identified and analyzed by 12.8- and 32.1-Mc ^{11}B nmr spectra and also by the proton nmr spectra. The mass spectra of all of the B-methyl isomers exhibited sharp cutoffs at m/e 118, corresponding to the $^{12}C_5{}^{11}B_4{}^1H_{14}{}^+$ parent ion. In addition to the above-mentioned compounds, 2.1 ml of a material of lower volatility was formed but not characterized.

The infrared spectrum of the purified 1,2,3-trimethyl-2,3-dicarbahexaborane(8) exhibited bands at (cm^{-1}): 2940 s (C–H stretch), 2580 vs (terminal B–H stretch), 1935 m (bridge hydrogen symmetric stretch), 1450 s (bridge hydrogen asymmetric stretch), 1385 s, 1325 s, 976 m, b, 904 m, and 752 m, b. The infrared spectrum of the mixture of basal boron-substituted isomers was quite similar to but not identical with that of the 1,2,3-trimethyl-2,3-dicarbahexaborane(8); individual assignments for the 4- and 5-methyl derivatives were, of course, not possible.

TABLE II

^1H NMR CHEMICAL SHIFT VALUES AND COUPLING CONSTANTS

Compound	Atoms	τ, ppm[a]	J_{H-B}, cps,[b]
1-Methyl-2,3-dicarbahexaborane(8)	H_3C–B(1)	10.30	
	H–C(2,3)	3.4	
	H–B(4,5,6)	6.44	162
	H_{bridge}	12.3 ± 1	
4-Methyl-2,3-dicarbahexaborane(8)[c]	H–B(1)	10.8	175
	H–C(2,3)	3.7	
	H_3C–B(4)	9.2	
	H–B(5,6)	6.9	157
	H_{bridge}	12.3 ± 1	
5-Methyl-2,3-dicarbahexaborane(8)[c]	H–B(1)	10.8	175
	H–C(2,3)	3.7	
	H–B(4,6)	6.9	157
	H_3C–B(5)	9.2	
	H_{bridge}	12.3 ± 1	
1,2,3-Trimethyl-2,3-dicarbahexaborane(8)	H_3C–B(1)	10.53	
	H_3C–C(2,3)	7.96	
	H–B(4,5,6)	6.67	149
	H_{bridge}	12.3 ± 1	
2,3,4-Trimethyl-2,3-dicarbahexaborane(8)[c]	H–B(1)	10.8	177
	H_3C–C(2,3)	8.0	
	H_3C–B(4)	9.3	
	H–B(5,6)	6.8	149
	H_{bridge}	12.3 ± 1	
2,3,5-Trimethyl-2,3-dicarbahexaborane(8)[c]	H–B(1)	10.8	177
	H_3C–C(2,3)	8.0	
	H–B(4,6)	6.8	149
	H_3C–B(5)	9.3	
	H_{bridge}	12.3 ± 1	

[a] τ(tetramethylsilane) 10.00 ppm. [b] Hydrogen–boron coupling constants refer to H–^{11}B coupling only. Most of the quartet peaks assigned to the ^{11}B-attached terminal hydrogens are usually well defined, whereas the smaller septets of the ^{10}B [20% of the naturally occurring boron, I = 3, magnetogyric ratio = 0.336^{11}B value] attached hydrogens are buried under the labyrinth of all other resonances. [c] Because of separation difficulties (see Experimental Section), exact δ and J values are difficult to obtain. This is largely due to the inherently broad line width of the overlapping resonances.

Results and Discussion

Both 1-methylpentaborane and 2-methylpentaborane give, from the thermal reaction with acetylene, a nearly identical distribution of volatile carboranes, 2,3-dicarbahexaborane(8), 1-methyl-2,3-dicarbahexaborane(8), and also the 4- and 5-methyl isomers of 2,3-dicarbahexaborane(8). A similar comparison of the product distribution is found when 2-butyne is used for the alkyne. In all cases the temperature required for the conversion is slightly higher than when pentaborane[6a] itself is used and is also higher than the conditions needed to rearrange 1-methylpentaborane to the 2-methyl isomer.[6b] Therefore, it seems quite likely that all of the products are the result of an interaction of the alkyne with 2-methylpentaborane.

While the over-all yields of the B-methyl derivatives are not very high, the major volatile side product,

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(6) (a) T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964); (b) T. Onak and F. J. Gerhart, *ibid.*, **1**, 742 (1962).

the valued parent 2,3-dicarbahexaborane(8) (or the 2,3-dimethyl derivative from the 2-butyne reaction), can be stockpiled during these preparations.

Several attempts were made to prepare the B-methyl derivatives by a modified Friedel–Crafts reaction on the parent compound or by a Lewis base catalyzed reaction between a methylpentaborane and an alkyne, with little success. In the former case, it is believed that the hydrogen chloride produced from the reaction destroys the carborane under the conditions of the reaction. In the latter type of reaction, a Lewis base has not yet been found to promote the reaction at a reasonable rate without producing extensive decomposition or complexing of the methylpentaborane.

Nuclear Magnetic Resonance Spectra.—The ^{11}B and ^{1}H nmr data for the B-methyl derivatives of 2,3-dicarbahexaborane(8) are given in Tables I and II. Of considerable interest in the proton nmr is the significant chemical shift difference between boron-bonded apical and basal methyl hydrogens, coupled with the upfield shift of the former relative to the latter. The latter observation is particularly important when it is noted that the proposed charge distribution[7] on the attached boron atoms would lead to a shift opposite to that observed. Thus, the apical boron has been assigned a slightly higher positive charge than either of the basal boron atoms which, if this were the only consideration, would have the effect of producing a downfield shift for the 1-substituted derivative. Furthermore, an upper limit of about 0.2 ppm can be assigned for the magnitude of such an inductive effect on the boron-attached methyl hydrogens of $C_2B_4H_8$.[8]

The most convenient approach we have found to account for the relative proton chemical shifts, as well as the magnitude of such a shift, is by employing a classical free-electron model[9,10] as has been used successfully for benzene derivatives. In order to compute $\Delta\tau$ (Table III) from ring-current contributions, the following model was adopted.

TABLE III

RING-CURRENT CONTRIBUTIONS TO THE $C_2B_4H_8$ PROTON CHEMICAL SHIFTS

Compound	Nucleus under consideration	$\Delta\tau$(exptl),[a] ppm	$\Delta\tau$(calcd),[a] ppm
2,3-$C_2B_4H_8$	Boron-attached terminal hydrogens	4.6[b]	4.6
2,3-$(CH_3)_2$-2,3-$C_2B_4H_6$	Boron-attached terminal hydrogens	4.1[c]	3.7 (3.9)[d]
B-CH_3-2,3-$C_2B_4H_7$	Boron-attached methyl hydrogens	1.1	1.3
B-CH_3-2,3-$(CH_3)_2$-2,3-$C_2B_4H_5$	Boron-attached methyl hydrogens	1.2	1.3

[a] $\Delta\tau$(exptl) (and $\Delta\tau$(calcd)) = δ'(base) − δ'(apex). For example, δ'(apex) of B-CH_3-2,3-$C_2B_4H_7$ is measured using 1-methyl-2,3-dicarbahexaborane, and δ'(base) is measured using both 4- and 5-methyl-2,3-dicarbahexaborane. No distinction is made between the two different (4, 5) basal positions. Both in the parent molecule and the B-methyl derivatives the chemical shift difference between the 4 and 5 positions is too small to be measured. Although the above chemical shifts were not measured at infinite dilutions, mixtures of the appropriate B-methyl isomers were used for the chemical shift comparison reported here. [b] T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964). [c] T. Onak, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, **85**, 3378 (1963). [d] The value in parentheses is for a B(4)–H bond distance of 1.2 Å. The reported bond distance of 1.4 Å from the X-ray data for this particular compound is surprisingly higher than any other comparable B–H_t bond; therefore, it is not difficult to justify a value which is more reasonable for such systems. For X-ray data, see W. E. Streib, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 2331 (1963); *Inorg. Chem.*, **3**, 1666 (1964).

From previous X-ray data[7] the height of the nearly planar base to the apex is found to be 1.1 Å for both the parent and 2,3-dimethyl derivatives of 2,3-dicarbahexaborane(8). It is to be noted that for 2,3-dimethyl-2,3-dicarbahexaborane(8), the B–H bond distances appear to be consistently larger than those in the parent compound.[7] It is convenient to treat the pentagonal-pyramidal framework as approximating a cone. A weighted "radius" at the basal plane of the cone is about 1.36 Å for each compound. For the B-methyl derivatives, a methyl C–B bond distance of 1.56 Å and a C–H distance of 1.1 Å (bond angle of 109.5°) are assumed.[11] Essentially free rotation of the alkyl group is assumed. A calculated δ' for the alkyl hydrogens is taken as an average of δ' values for a representative number of conformations of the nucleus in question. The angle of the B–C_{alkyl} bond relative to the carborane framework is assumed not to differ greatly from the corresponding B–H bond in the parent system.

The six electrons bonding the apex to the base of five atoms are treated in a manner similar to the free-electron approach used for benzene.[12] Obviously, the ring current must be placed somewhere between the apex and the basal plane, but preferably parallel to the plane of the base. There are several ways to approach a reasonable height.

(1) By using the ^{11}B nmr chemical shift information as an input to the equation, an approximate height of

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[7] W. E. Streib, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 2331 (1963); *Inorg. Chem.*, **3**, 1666 (1964).

[8] *Cf.* apical and basal attached methyl hydrogen resonance positions for methyl pentaboranes.[6a] Various estimates for the charge distribution of pentaborane are summarized by W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p 110.

[9] Ring currents have been used in many instances satisfactorily to predict chemical shifts in aromatic compounds.[10] Although this approach has been subject to some scrutiny,[10e] such a system is considered empirically valid and useful as long as the limitations are realized.

[10] (a) J. S. Waugh and R. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957); (b) (correction to ref 10a), J. S. Waugh and R. Fessenden, *ibid.*, **80**, 6697 (1958); (c) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958); (d) see also numerous references by J. W. Emsoly, J. Feeney, and L. H. Sutcliffe, "High-Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Inc., New York, N. Y., 1966; (e) J. I. Musher, *J. Chem. Phys.*, **43**, 4081 (1965); *Advan. Magnetic Resonance*, **2**, 177 (1966).

[11] The adopted values appear quite reasonable when compared to related systems: T. Onak, L. B. Friedman, J. H. Hartsuck, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 3439 (1966); L. B. Friedman and W. N. Lipscomb, *Inorg. Chem.*, **5**, 1752 (1966).

[12] The method for a single current loop[10a] was employed. The offered corrections[10b,c] to the original set of data and formulas[10a] are somewhat ambiguous. The expression given for H'_{eff} in ref 10a should be multiplied by $4\pi k$ as mentioned in ref 10c; however, a numerical result derived from an evaluation of H_{eff} by using B_0 values in ref 10a should be multiplied by 4π only. Thus the ring-current contribution, δ', to the chemical shift is expressed by[10c]

$$10^{-6}\delta' = \frac{ne^2}{6\pi mc^2 a}\,\frac{1}{[(1+\rho)^2+z^2]^{1/2}}\left[K + \frac{1-\rho^2-z^2}{(1-\rho)^2+z^2}E\right]$$

See footnote *a* in Table III for the treatment of δ' values.

0.1 Å above the base is calculated. This is probably very approximate, owing to the oversimplification of the ring current as a single loop. Deviations from this simple model would have the greatest effect on atoms very close to the current loop such as the boron atoms. As one moves further away from the loop, such deviations are expected to be more negligible. Also, it is quite optimistic to hope that ring-current contributions are the only major factors when considering boron atoms in several different bonding environments.

(2) A crude assumption is to project the electron cloud bonding the apex to the base along the curved surface area of the cone and to use the ring which bisects this surface area. This approach is based on nearly equal sharing of the bond electrons. This places the ring current at 0.33 Å above the basal plane.

(3) Considering that the apical boron has about a net +0.35 charge, the ring current may well be closer to the base than the 0.33 Å derived in (2) above.

From the above considerations, it is not surprising to find that the best $\Delta\tau$ fit for all compounds places the ring height at about 0.2 Å above the base. Not only does this approach account for the chemical shift difference for the apical and basal boron-attached methyl hydrogens, but it also correlates the relative magnitude of $\Delta\tau$ for the boron-bonded hydrogens in the parent compound and for the 2,3-dimethyl derivative reasonably well (Table III). There is some indication that this approach may work for other structurally related systems. A per-B-ethyl derivative of CB_5H_9 (isoelectronic and presumed isostructural with $C_2B_4H_8$) has been recently reported.[13] A comparison of $\Delta\tau$ (apex, base) values for methylene and methyl hydrogens gives $\Delta\tau_{CH_2} \sim 1.2$ and $\Delta\tau_{CH_3} \sim 0.54$ ppm. Since $\Delta\tau$ values of the α hydrogens are nearly identical for both $C_2B_4H_8$ and CB_5H_9 alkyl derivatives (~ 1.2 ppm), it should be possible to correlate β hydrogens for the ethyl derivatives of the two systems if nearly identical ring-current contributions are operating. A calculated value for the β hydrogens for the B-ethyl derivative of $C_2B_4H_8$ based on a ring-current contribution gives 0.57 ppm for $\Delta\tau_{CH_3}$. This is in quite good agreement with the value (*vide supra*) found for the CB_5H_9 derivative.

Also, for B_6H_{10} a calculated $\Delta\tau$ of 4.8 ppm agrees quite well with the observed $\Delta\tau$ 5.0 ppm[14] for the terminal hydrogens. The structural parameters of B_6H_{10} are taken from previous X-ray data.[15] Since the most recent charge distribution estimates give the apex boron close to zero charge,[16] the ring loop current is positioned so that it bisects the nearly conical surface between the apex and basal plane.

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[13] M. A. Grassberger, E. G. Hoffmann, G. Schomburg, and R. Köster, *J. Am. Chem. Soc.*, **90**, 56 (1968).

[14] Observed value taken from a ^{11}B-decoupled proton spectrum: J. Spielman, unpublished results.

[15] F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert, and W. N. Lipscomb, *J. Chem. Phys.*, **28**, 56 (1958).

[16] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p 110.

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The Crystal Structure of Dicalcium Nitride

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The structure of a nitride of the stoichiometry Ca_2N has been determined from single-crystal X-ray data. Dicalcium nitride is rhombohedral with unit-cell dimensions $a = 6.603$ Å, $\alpha = 31° 59'$, $D_m = 2.17$ g cm^{-3}, $Z = 1$, $D_c = 2.18$ g cm^{-3}, the space group being $R\bar{3}m$. Full-matrix least-squares refinement has reached $R = 0.13$ for 71 visually estimated reflections. Ca_2N has a layer structure of the *anti*-$CdCl_2$ type. The layers are widely separated, their closest approach being a Ca–Ca distance of 4.35 Å, much larger than those in the metal. The nitrogen atoms lie at centers of symmetry, within the layers, and have distorted octahedral coordination. The electrical properties of Ca_2N are discussed in relationship to the structure and with reference to other M_2X compounds.

In a preliminary communication,[1] we reported the crystal structure of a novel subnitride, Ca_2N, first prepared by Ahmad and Tomlinson.[2] The analogous compounds of strontium, Sr_2N, and barium, Ba_2N, had been known previously.[3]

The more usual nitride of calcium is Ca_3N_2, four forms of which have been reported. Below 350°, black β-Ca_3N_2 is formed, which is pseudo-hexagonal.[4] α-Ca_3N_2 is prepared at temperatures up to 1050°. It has a bcc lattice with $a = 11.40$ Å and has an *anti*-Mn_2O_3 structure.[5] Yellow γ-Ca_3N_2 is formed above 1050°.[4,6] A

[1] E. T. Keve and A. C. Skapski, *Chem. Commun.*, 829 (1966).

[2] I. Ahmad, Ph.D. Thesis, London, 1963; I. Ahmad and J. W. Tomlinson, to be submitted for publication.

[3] S. M. Arya and E. A. Prokofyeva, *J. Gen. Chem. USSR*, **25**, 813 (1955).

[4] Y. Laurent, J. David, and J. Lang, *Compt. Rend.*, **259**, 1132 (1964).

[5] M. von Stackelberg and R. Paulus, *Z. Physik. Chem.*, **B22**, 305 (1933).

[6] Y. Laurent, J. Lang, and M. Th. Le Bihan, *Acta Cryst.*, **B24**, 494 (1968).