

$C_5C_6C_1^aC_4$ and the phenyl group is 81.5° , with C_5 , C_6 and C_7 on the line of intersection. The planes of $C_5C_6C_1^aC_4C_7$ and of a pyrrole ring are inclined, respectively, 14.2° and 12.0° to (001). The principal circumstances adverse to ideal π -bonding are pinpointed by noting that, in order to achieve exact planarity with $C_5C_6C_1^aC_4$, the pyrrole rings of Fig. 1 would need to be rotated about the bonds $C_5-C_1^a$ and C_5-C_4 by, respectively, 6.5° and 13.6° .

The grouping $NC_4C_5C_1^aN^a$ is not planar and the formally completed chelate ring $MNC_4C_5C_1^aN^a$ is puckered. Bond angles at carbon (and at nitrogen) substantially exceed the ideal value of 120° for σ -bonding in trigonal hybridization. The urge toward reduction of these bond angles through stronger puckering is subject to quasi-rigid constraints set by the character of the pyrrole ring, e.g., the external angles at C_1^a and C_4 should remain sensibly equal and cannot be much less than 125° . There remain quite general grounds, with support from the examination of various models, for concluding that a planar configuration cannot minimize strain for σ -bonding. Inasmuch as the restoring forces associated with π -bonding are zero for initial deformation, one concludes also that some departure from planarity in the porphine skeleton—in *seeming* disproportion with the small energetic gain—is inevitable in a free molecule.

A ruffling of the skeleton in agreement with $\bar{4}$ is plausible for a metal derivative in which $M-N < 2.05 \text{ \AA}$. (cf., ref. 5), with a small energy barrier to reflection of configuration through the mean plane. At sufficiently high temperature, perhaps even at 300°K ., the skeleton should behave as if the configurational potential energy had a single, very broad minimum. The extraordinary deformability normal to the mean plane thus implied finds support in the highly anisotropic thermal parameters of our study. One concludes that, with little energetic prejudice, the skeleton either can simulate exact planarity³ or display considerable ruffling,⁵ as the environment demands.

A convex form (C_4 or C_{4v} symmetry) of the skeleton becomes plausible with longer $M-N$ bonds, by allowing the metal atom to lie far enough outside the plane of the four nitrogens to take care of the added dimensional constraint. This configuration, moreover, could be induced by the additional coordination of an externally constrained ligand to M . The high spin Fe^{+2} and Fe^{+3} derivatives are outstanding candidates for such configurations. Thus Kendrew's⁶ observation that, in myoglobin, the iron atom lies more than 0.25 \AA . out of the mean plane of the heme group is interpretable in simple fashion.

(6) J. C. Kendrew, *Science*, **139**, 1259 (1963), who mentions also that D. Koenig, The Johns Hopkins University, has observed the same phenomenon through structure analysis of hemin.

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On the Crystal Structure of AlB_{10}

Sir:

The higher aluminum borides AlB_{10} , AlB_{12} and its polymorphs are distinct from other higher metal borides in that the former combine exact stoichiometric chemical formulas with an anomalous number of formula units per crystallographic unit cell. Despite extended efforts, no crystal structure of any of the higher aluminum borides has thus far been solved.

We have found a structure for AlB_{10} from an X-ray study of a single crystal prepared earlier at this laboratory.¹ The symmetry is orthorhombic, with $a = 8.88$,

$b = 9.10$ and $c = 5.69 \text{ \AA}$.; chemical analysis and density measurements indicated $5.2 AlB_{10}$ formula units per unit cell.¹ The space group is $B 2/b 2_1/m 2/m$, from which four or eight formula units are to be expected.

The crystal structure found is based on an icosahedral (12-grouping) arrangement, consisting of four boron icosahedra and four inter-icosahedral boron atoms per unit cell. Thus 52 boron atoms are located, in agreement with the chemical analysis. Statistical distribution over several sites must be assumed for the aluminum atoms, which may or may not substitute for boron atoms.

An icosahedral packing of boron atoms was first recognized in $B_{12}C_3$ ² and has also been reported for tetragonal boron,³ in low-temperature α -rhombohedral boron,⁴ and recently for high-temperature β -rhombohedral⁵ boron. It is also favored from some theoretical aspects.⁶

X-Ray analysis of AlB_{10} has been restricted so far to the (100) and (001) projections. The unit cell is thereby reduced to 0.25 and 0.5, respectively, of its full size, thus significantly decreasing the number of parameters to be determined. In (100), therefore, one icosahedron is expected, which was revealed and oriented by applying convolution molecule methods⁷ to the Patterson projection and confirmed by Fourier transform methods using the weighted reciprocal lattice. Fourier and least squares calculations of the icosahedron alone in this projection resulted in an R -factor of 28.5%.

By applying the convolution molecule method to the (001) Patterson projection, the two expected icosahedra were located and their relative orientation and translation parameters determined. Working with icosahedra alone and omitting inter-icosahedral atoms, the combined (100) and (001) projections gave an R -factor of 29.3%.

Using the signs of the least square refinement, Fourier calculations revealed additional peaks, upon

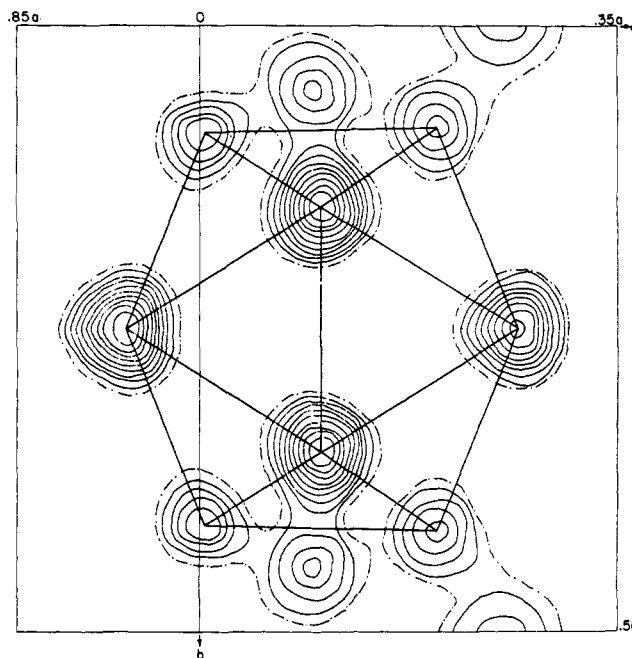


Fig. 1.—Electron density projection of AlB_{10} on (001).

- (1) J. A. Kohn, G. Katz and A. A. Giardini, *Z. Krist.*, **111**, 53 (1958).
- (2) H. K. Clark and J. L. Hoard, *J. Am. Chem. Soc.*, **65**, 2115 (1943).
- (3) J. L. Hoard, R. E. Hughes and D. E. Sands, *ibid.*, **80**, 4507 (1958); cf. J. L. Hoard, S. Geller and R. E. Hughes, *ibid.*, **73**, 1892 (1951).
- (4) L. V. McCarty, J. S. Kasper, F. N. Horn, B. F. Decker and A. E. Newkirk, *ibid.*, **80**, 2592 (1958); B. F. Decker and J. S. Kasper, *Acta Cryst.*, **12**, 503 (1959).
- (5) R. E. Hughes, C. H. L. Kennard, D. B. Sullenger, H. A. Weakliem, D. E. Sands and J. L. Hoard, *J. Am. Chem. Soc.*, **85**, 361 (1963).
- (6) W. N. Lipscomb and D. Britton, *J. Chem. Phys.*, **33**, 275 (1960).
- (7) W. Hoppe, *Z. Elektrochem.*, **61**, 1076 (1957).

which boron atoms were subsequently placed. The *R*-factor then dropped to 20.4%. These additional positions indicate an excess of sites, which can be attributed to a statistical distribution of inter-icosahedral atoms; also, aluminum has not yet been positioned. The exact distribution of the inter-icosahedral atoms is a matter for three-dimensional analysis, which is in progress.

The icosahedra are centered at 4(c) with the coordinates $x/a, y/b, z/c = 0.1, 0.25, 0; 0.9, 0.75, 0; 0.6, 0.25, 0.50$, and $0.4, 0.75, 0.50$.

The symmetry required of the B_{12} configuration by the space group is $mm2$, and no conclusion can be drawn at this time as to what degree the symmetry mmm of a regular icosahedron is approximated. Within the icosahedra, preliminary bond distance calculations reveal boron-boron distances ranging from 1.77 to 1.91 Å., in agreement with bond lengths reported for elementary boron.

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High Resolution Nuclear Magnetic Resonance Spectra of Methylsilicon Compounds

Sir:

There is considerable current interest in the correlation between spin-spin coupling constants and hybridization of the atoms participating in the chemical bondings of the compounds studied. A series of important relations have been established for a number of organic¹⁻⁸ and tin-organic^{9,10} compounds, using the indirect spin-spin interaction of ¹³C and ^{117,119}Sn with protons as a reference. In recent papers^{6,11} these investigations were extended to the interactions of the ²⁹Si isotope (natural abundance 4.7%, spin 1/2) with protons directly bonded to silicon, but the results are not yet as readily understood in terms of hybridization.

¹H-²⁹Si interactions in compounds with protons not directly bonded to silicon, however, are not easily detected in n.m.r. spectra of ordinary resolution because of the small coupling constants, and corresponding data are known only for a small number of organosilicon compounds.^{7,11,12} As a part of our current high resolution n.m.r. studies on alkylsilicon compounds this communication now reports the H-C-²⁹Si and H-¹³C coupling constants of some series of methylsilicon derivatives, which show significant dependence on the nature of the ligands attached to the central silicon atom.

The chemical shifts and coupling constants of tetramethylsilane (I) and the four trimethylsilicon halides (II-V), given in Table I, show a marked decrease in the δ values and an increase in $J(\text{H}-^{13}\text{C})$ and $J(\text{H}-\text{C}-^{29}\text{Si})$ in the sequence $\text{CH}_3, \text{F}, \text{Cl}, \text{Br}, \text{I}$. These relations are in contradiction to customary electronegativity considerations (F > Cl > Br > I > CH₃), from which an opposite trend should be expected. (Proton shielding usually is restricted by an increasing electronegativity of the substituent introduced in a compound, and the spin-spin interactions should be greater

- (1) M. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).
- (2) M. Karplus and D. H. Anderson, *J. Chem. Phys.*, **30**, 6 (1959).
- (3) J. N. Shooley, *ibid.*, **30**, 1427 (1959).
- (4) N. Muller and D. E. Pritchard, *ibid.*, **30**, 768, 1471 (1959).
- (5) E. R. Malinowsky, *J. Am. Chem. Soc.*, **83**, 4479 (1961).
- (6) C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).
- (7) H. S. Gutowsky and C. Juan, *J. Am. Chem. Soc.*, **84**, 307 (1962).
- (8) G. Klose, *Ann. Physik*, **9**, 262 (1962).
- (9) J. R. Holmes and H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 3903 (1961).
- (10) G. P. van der Kelen, *Nature*, **193**, 1069 (1962).
- (11) E. A. V. Ebsworth and J. J. Turner, *J. Chem. Phys.*, **36**, 2628 (1962).
- (12) G. Fritz, E. A. V. Ebsworth, *et al.*, *Z. anorg. allgem. Chem.*, **321**, 10 (1963).


TABLE I
CHEMICAL SHIFTS δ AND COUPLING CONSTANTS J OF SOME TRIMETHYLSILICON DERIVATIVES

Varian A-60, 60 Mc., room temperature, TMS as an internal reference. All compounds in CCl₄ with $c = 5 \pm 1\%$ [v./v.] for δ , and $c = 20 \pm 2\%$ [v./v.] for J values. Standard deviations are ± 1 [c.p.s.] for δ , $J(\text{H}-^{13}\text{C})$, and $J(\text{H}-\text{C}-\text{Sn}, \text{Pb})$, and ± 0.05 [c.p.s.] for $J(\text{H}-\text{C}-^{29}\text{Si})$ and $J(\text{H}-\text{C}-\text{Si}-\text{F})$.

No.	Formula	δ^a	J (H- ¹³ C)	$J(\text{H}-\text{C}-^{29}\text{Si})$	
I	Me ₄ Si	0.0	118.5	6.78	
II	Me ₃ SiF ^a	-12.2	118.8	7.00	
III	Me ₃ SiCl	-25.4	120.5	7.10	
IV	Me ₃ SiBr	-42.5	121.0	7.23	
V	Me ₃ SiI	-47.0	121.5	7.30	
VI	Me ₃ SiOSiMe ₃	-3.5	118.0	6.86	
VII	Me ₃ SiSSiMe ₃	-19.5	119.5	7.10	
VIII	Me ₃ SiSeSiMe ₃	-25.7	120.5	7.15	
IX	Me ₃ SiOGeMe ₃	Me ₃ Si	0.0	117.8	6.80
		Me ₃ Ge	-21.0	126.0	...
X	Me ₃ SiOSnMe ₃ ^b	Me ₃ Si	+2.5	116.8	6.72
		Me ₃ Sn	-20.5	128.5	...
XI	Me ₃ SiOPbMe ₃ ^c	Me ₃ Si	+3.5	115.5	6.69
		Me ₃ Pb	-73.0	136.0	...
XII	(Me ₃ Si) ₃ N	-10.7	118.0	6.76	
XIII	(Me ₃ Si) ₂ NGeMe ₃	Me ₃ Si	-7.2	118.0	6.75
		Me ₃ Ge	-23.5	125.4	...
XIV	(Me ₃ Si) ₂ NSnMe ₃ ^d	Me ₃ Si	-5.0	118.0	6.60
		Me ₃ Sn	-18.8	130.0	...
XV		Me ₃ Si	0.0	117.5	6.78
		Me ₃ Si	-14.0	118.5	7.20
XVI		Me ₃ Si	0.0	118.5	6.80
		Me ₃ Si	-15.0	119.0	7.05
XVII	[(Me ₃ SiO) ₂ Al] ₂	bridges	-19.0	119.0	7.00
		terminal	-4.0	116.0	6.65

^a $J(\text{HCSiF}) = 7.48$. ^b $J(\text{H}-\text{C}-^{117,119}\text{Sn}) = 54.9, 57.4$.
^c $J(\text{H}-\text{C}-^{207}\text{Pb}) = 69.5$. ^d $J(\text{H}-\text{C}-^{117,119}\text{Sn}) = 53.4, 55.8$. ^e In c.p.s., negative values are downfield of TMS.

in the compound having the most polarized silicon-halogen bonding, which would lead the central silicon atom to a maximum $sp^3 \rightarrow sp^2$ rehybridization.) From these considerations trimethylfluorosilane should show the lowest chemical shielding and the highest J -values. The results are readily explained, however, by the assumption of a systematic decrease of $d\pi-p\pi$ -interactions between silicon and the halogens, the magnitude of which is a function of the relative atomic radii of the atoms. These π -interactions provide an increase in polarity of the Si-halogen bonding in the direction $\text{F} < \text{Cl} < \text{Br} < \text{I}$ ("back-donation") and an increase in s -character of the silicon and even the carbon orbitals, being in close relation with each other by the Si-C-bondings, following this sequence. Similar results were obtained for hexamethyldisiloxane and its analogs (VI-VIII),¹³ as presented in the table, and can be interpreted in a corresponding manner, following the sequence O, S, Se. Among other evidences the well

known decrease of the bond angles in the series Si  Si is a good support for this assumption.¹⁴

Tris-trimethylsilylamine (XII) and the cyclic trisilylamine compounds XV and XVI¹⁵ gave surprisingly low values for the Me₃Si- groups and illustrate the unusual

(13) For Me₃SiSeSiMe₃ see: M. Schmidt and H. Ruf, *Z. anorg. allgem. Chem.*, **32**, 270 (1963).

(14) R. J. Gillespie, *J. Am. Chem. Soc.*, **82**, 5978 (1960).

(15) W. Fink, *Angew. Chem.*, **73**, 736 (1961), and *Helv. Chim. Acta*, **46**, 720 (1963); We thank Dr. Fink for providing the samples.