ON THE STRUCTURE OF TETRABORANE

Sir:

We have reinvestigated gaseous tetraborane by electron diffraction. The butane-like model with tetrahedral bond angles as reported by Bauer[1] is incompatible with our data; values of ∠B–B–B = 90° and ∠B–B–H = 133.5° do bring it into agreement, but the latter angle is out of the question, especially for the "methylenic" hydrogen atoms. No exhaustive investigation of the butane-like structure was attempted, however, because a structure (Fig. 1) plausibly related to the known boron hydride structures[2] was discovered and shown to be in excellent agreement with the diffraction pattern early in our work,[3,4] and has since been established by Nordman and Lipscomb by the crystal structure investigation reported in the following Communication. The atomic arrangement is closely similar to that of the apical groups in decaborane and is comparable to the arrangements in diborane and stable pentaborane.

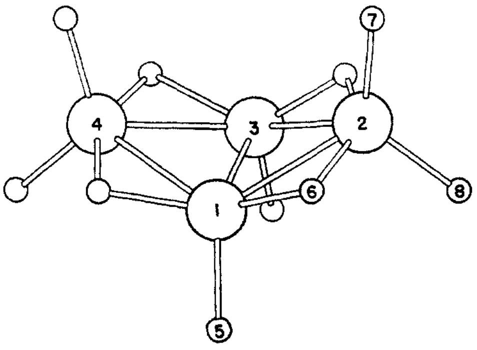

Fig. 1.—The B_4H_{10} structure.

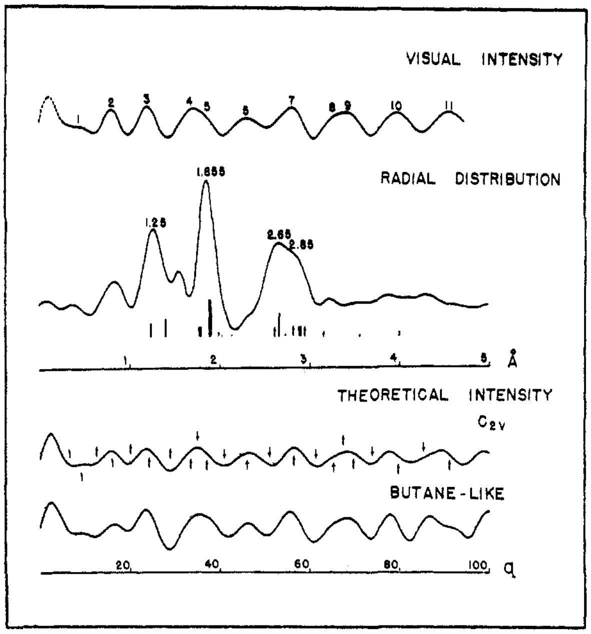

Fig. 2.—Visual, radial distribution and theoretical intensity curves. The theoretical intensity curves are for the butane-like model with ∠ B–B–B = 90° and ∠ B–B–H = 133.5° and for the C_{2v} model described in the text.

Approximate values for the numerous parameters of the C_{2v} model are

B_1–B_2 = 1.85 Å., B_1–B_3 = 1.76 Å.

$B_2 \cdots B_4$ = 2.88 Å. (Dihedral ∠$B_1B_3B_4$–$B_1B_3B_2$ = 124°32′)

B_1–H_5 = B_2–H_7 = B_2H_8 = 1.19 Å.

B_2–H_6 = 1.33 Å., B_1–H_6 = 1.43 Å., H_6 in plane of $B_1B_2B_3$

∠B_3–B_1–H_5 = 118°20′ and ∠$B_{1,3}$–B_2–$H_{7,8}$ = 117°6′

These values were obtained primarily from the radial distribution curve (Fig. 2); they were refined by a (necessarily incomplete) correlation treatment. The H_6 parameters are highly uncertain, but the B–H distance 1.19 Å. and the B–B bond distances warrant comparison with the crystal values.

We are indebted to Professor A. B. Burg and Mr. E. S. Kuljian for the samples of tetraborane and to the Office of Naval Research (Contract N6onr 24423) for support during this investigation.

CONTRIBUTION NO. 1828
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RECEIVED JUNE 30, 1953

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[1] S. H. Bauer, THIS JOURNAL, **60**, 805 (1938).

[2] For references and discussion see K. Hedberg, M. E. Jones, and V. Schomaker, *Proc. Nat. Acad. Sci. U. S.*, **38**, 679 (1952).

[3] K. Hedberg, V. Schomaker and M. E. Jones, Paper E.D. 17, Second International Congress of Crystallography, Stockholm, June 27–July 5, 1951. The structure, although not mentioned in the Abstract, was presented at the meeting.

[4] Quarterly Progress Report, October 23, 1951, Contract N6onr 24423.

THE MOLECULAR STRUCTURE OF B_4H_{10}

Sir:

As a result of a complete analysis of 616 observed reflections from a single crystal of B_4H_{10}, we have determined the molecular structure. There are four molecules in a monoclinic unit cell having parameters a = 8.68, b = 10.14, c = 5.78Å. and β = 105.9°. The space group $P2_1/n$ is unambiguous, and the twelve independent positional parameters of the boron atoms were determined from three-dimensional Fourier analysis. The hydrogen atoms were readily observable, and were also located more precisely from a three-dimensional Fourier series from which the boron atoms had been subtracted.

The molecular structure of B_4H_{10} is shown in Fig. 1. No molecular symmetry elements are required by the space group of the crystal, but the molecular dimensions indicate that the symmetry of the isolated molecule is C_{2v}. For brevity, we

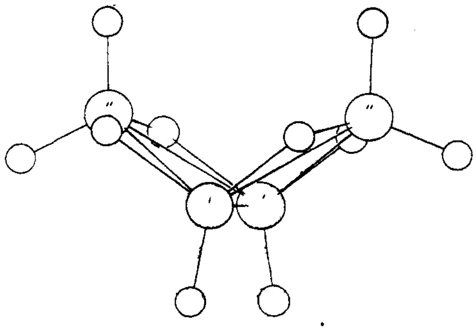

Fig. 1.—The molecular structure of B_4H_{10}.

record average bond distances with their average deviations on the assumptions that the molecular symmetry is C_{2v} and that the two $B'-H$ and the four $B''-H$ distances are all equal. Molecular parameters[1] are four $B'-B'' = 1.845 \pm 0.002$Å., $B'-B' = 1.750$Å., $B''-B'' = 2.786$Å., six $B-H = 1.11 \pm 0.04$, four $B'-H_b$ (bridge) $= 1.21 \pm 0.03$Å. and four $B''-H_b = 1.37 \pm 0.10$Å. Assuming a boron radius of 0.75Å., and therefore single bond distances of 1.50Å. for B–B and 1.10Å. for B–H, bond orders are 0.27 for $B'-B''$, 0.38 for $B'-B'$, 0.01 for $B''-B''$, 0.96 for B–H, 0.65 for $B'-H_b$ and 0.35 for $B''-H_b$. The total bond order for the molecule is thus 11.2, close to the expected value of 11. The assumed boron radius is smaller than that calculated for B_2H_6 (0.79Å.), B_5H_9 (0.78Å.) and $B_{10}H_{14}$ (0.81), and as in B_5H_9 the over-all size of the molecule is smaller than that reported in the preceding electron diffraction study by Jones, Hedberg and Schomaker. A similar effect has been observed in B_5H_9 and in hexamethylenetetramine.

It is of interest that the $B''B'B''$ bond angle is 98° which is a value about midway between the corresponding angle of 90° in the octahedron and 108° in the icosahedron. Thus the boron arrangement may be regarded as a fragment from either the octahedron or the icosahedron. The relatively open structure of this, the first member of the B_nH_{n+6} series compared with the relatively compact higher B_nH_{n+4} structures, probably is a factor relating to the comparatively greater reactivity.

Support of this research by the Office of Naval Research is gratefully acknowledged. All of the three-dimensional Fourier syntheses were carried out on the X-Ray Analogue Computer at Pennsylvania State College through the courtesy of Professor R. Pepinsky. We are also indebted to Dr. L. V. McCarty of the General Electric Company for supplying us with a sample of pure B_4H_{10}.

Details of this investigation will be submitted elsewhere.

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[1] Where the distance is observed more than once we record average deviations, which are comparable with estimated probable errors, except for $B'-B''$ for which a probable error of ±0.01 Å. is estimated.

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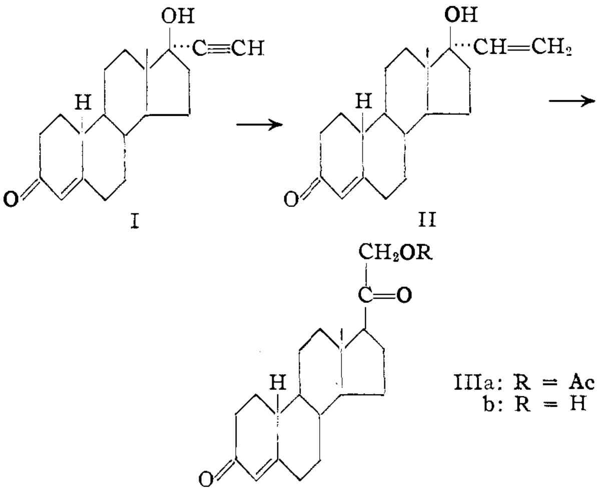
STEROIDS. XLIX.[1] 19-NOR-DESOXYCORTICOSTERONE, A POTENT MINERALOCORTICOID HORMONE

Sir:

19-Nor-progesterone,[1,2] 19-nor-17-methyltestosterone,[3] and 19-nor-17-ethinyltestosterone (I)[3] have all been shown to possess biological activity of a higher order than the parent hormones. It was therefore of considerable interest to make available for biological testing the 19-nor analogs of adrenal cortical hormones, especially in view of the report by Ehrenstein[4] that an amorphous product, believed to be a 19-nor-desoxycorticosterone isomer and obtained by a lengthy degradation from strophanthidin, was devoid of biological activity. In this communication we record the synthesis and physiological activity of 19-nor-desoxycorticosterone (IIIb), which possesses the same configuration at all asymmetric centers as does desoxycorticosterone.



I

II

IIIa: R = Ac
b: R = H

Chromic acid oxidation of 19-nor-testosterone[5] yielded 19-nor-Δ^4-androstene-3,17-dione [m.p. 171–172°, $[\alpha]^{20}D$ +139° ($CHCl_3$), $\lambda_{max.}^{EtOH}$ 240 mμ, log ε 4.24. Calcd. for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.39; H, 8.99] which upon conversion to 19-nor-3-ethoxy-$\Delta^{3,5}$-androstadien-17-one [m.p. 141–143°, $[\alpha]^{20}D$ −87° (pyridine), $\lambda_{max.}^{EtOH}$ 242 mμ, log ε 4.26. Calcd. for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 79.80; H, 9.15], ethinylation with potassium in *t*-amyl alcohol and acid hydrolysis furnished 19-nor-17-ethinyltestosterone (I) [m.p. 203–204°, $[\alpha]^{20}D$ −25° ($CHCl_3$), $\lambda_{max.}^{EtOH}$ 240 mμ, log ε 4.24. Calcd. for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78. Found: C, 80.83; H, 8.80]. Partial hydrogenation in pyridine solution over a 5% palladium–calcium carbonate catalyst[6] led to the corresponding vinyl carbinol II [m.p. 169–170°, $[\alpha]^{20}D$ +25° ($CHCl_3$), $\lambda_{max.}^{EtOH}$ 240 mμ, log ε 4.25. Calcd. for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 79.64; H, 9.27]. This latter compound was hydroxylated with osmium tetroxide,[7] and the product without purification was acetylated and subjected to a Serini reaction in toluene solution.[8] The resulting 19-nor-desoxycorticosterone acetate (IIIa) [m.p. 169–171°, $[\alpha]^{20}D$ +153° ($CHCl_3$), $\lambda_{max.}^{EtOH}$ 240 mμ, log ε 4.26, infrared bands (chloroform) at 1744 and 1718 cm.$^{-1}$ (21-acetoxy-20-ketone) and 1668 cm.$^{-1}$ (Δ^4-3-ketone). Calcd. for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44. Found: C, 73.88; H, 8.23] was saponified with sodium bicarbonate in aqueous methanol

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[1] Steroids. XLVIII, C. Djerassi, L. Miramontes and G. Rosenkranz, THIS JOURNAL, **75**, November (1953).

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[7] *Cf.* A. Serini and W. Logemann, *Ber.*, **71**, 1362 (1938).

[8] *Inter al.* A. Serini, W. Logemann and W. Hildebrand, *ibid.*, **72**, 391 (1939); C. Djerassi and C. R. Scholz, THIS JOURNAL, **71**, 3962 (1949).