We are indebted to Professor H. I. Schlesinger and Dr. I. Shapiro for samples of pentaborane and to the Office of Naval Research (Contract N6onr 24423) for support during most of this investigation.

CHEMISTRY DEPARTMENT
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA 4, CALIFORNIA

KENNETH HEDBERG
MORTON E. JONES
VERNER SCHOMAKER

RECEIVED JUNE 7, 1951

THE MOLECULAR STRUCTURE OF PENTABORANE

Sir:

If one compares the recently-determined structures of boron carbide[1] and decaborane[2] on the one hand with the structure of calcium boride[3] and possible structures of pentaborane on the other, the most reasonable structure of B_5H_9 (M. V. King and W. N. Lipscomb, unpublished) that can now be predicted is a tetragonal pyramid of molecular symmetry C_{4v}, such as that shown in Fig. 1. Apparently a molecule of this structure was overlooked in the earlier electron diffraction study,[4] because a recent study by Hedberg, Jones and Schomaker[5] shows that the electron diffraction pattern is consistent with such a model, but is also not inconsistent with some quite different, but chemically less reasonable, models.

We have completed an X-ray diffraction study of single crystals of pentaborane. The crystals are pyroelectric, and belong to the tetragonal space group C^9_{4v}–I4mm., with two molecules in a unit cell of dimensions a = 7.16 Å. and c = 5.38 A. Evaluation of parameters from three-dimensional sections leads to the values:

B_2–B_2 = 1.77 ± 0.02 Å.
B_1–B_2 = 1.66 ± 0.02 Å.
B_1–H_1 = 1.21 ± 0.05 Å.
B_2–H_2 = 1.20 ± 0.07 Å.
B_2–H_3 = 1.35 ± 0.04 Å.

$H_3 \ldots H_3$ = 1.95 ± 0.09 A.
$\angle B_1,B_2, H_3 = 115 \pm 5°$
External dihedral angle between planes $B_1B_2B_2$ and $B_2B_2H_3$ = 190 ± 5°

As in decaborane the intermolecular approaches are all between hydrogen atoms. These approaches range from 2.46 to 2.96 Å. which appear reasonable in view of the very large temperature factor in the crystal. The diagonal of the base of the pyramid has the direction of the a axis. It may be noted that the average boron-boron distance in the molecule is apparently about two per cent. smaller in the solid state than in the gaseous state, a situation previously observed only in hexamethylenetetramine.[6]

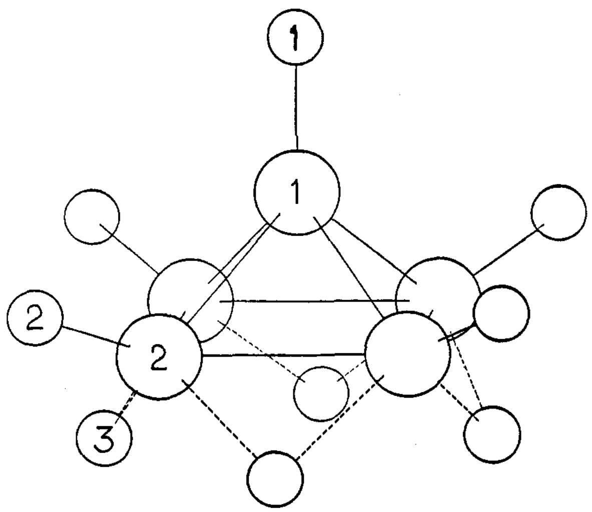

Fig. 1.—The pentaborane molecule: boron and hydrogen atoms are represented by large and small circles, respectively.

The interatomic binding in pentaborane, which is similar to decaborane, is of the 'metallic' type and in such a case we may expect Pauling's relation[7] $r = r_1 - 0.3 \log n$ to be reasonably valid. If we choose a covalent radius for hydrogen equal to 0.36 Å., then the total bond order for the molecule, which should be twelve, will depend upon the choice of the boron single-bond radius. A value of 0.78 Å. for this boron radius satisfies these conditions, thus leading to a total bond order of 12.03. The individual bond orders are $n_{12} = 0.681$, $n_{22} = 0.447$, $n'_{11} = 0.764$, $n'_{22} = 0.794$ and $n'_{23} = 0.447$, where the prime refers to B–H bonds. These orders suggest that the hydrogen atoms are somewhat positively charged and the boron atoms are somewhat negatively charged. This distribution of charge indicates a dipole moment of about 0.6 Debye. Similar calculations lead to a single-bond radius for boron of 0.79 Å. from the diborane molecule, and of 0.81 Å. from the decaborane molecule.

We wish to thank Dr. R. R. Miller of the Naval Research Laboratory and Dr. A. E. Newkirk and Dr. L. V. McCarty of the General Electric Company for samples of pentaborane. Support of this research by the Office of Naval Research and by a Fellowship (to W.J.D.) from the Minnesota Mining and Manufacturing Company is gratefully acknowledged.

---

[1] G. S. Zhdanov and N. G. Sevast'yanov, *Compt. rend. acad. sci. U.S.S.R.*, **32**, 432 (1941); H. K. Clark and J. L. Hoard, THIS JOURNAL, **65**, 2115 (1943).

[2] J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Cryst.* **4**, 436 (1950).

[3] L. Pauling and S. Weinbaum, *Z. Krist.*, **87**, 181 (1934).

[4] S. H. Bauer and L. Pauling, THIS JOURNAL, **58**, 2403 (1936).

[5] K. Hedberg, M. Jones, and V. Schomaker, private communication. A preliminary report on this determination was made at the Chicago meeting of the American Chemical Society, September, 1950. We are indebted to these authors for making available to us their results, described in the preceding letter.

[6] V. Schomaker and P. A. Shaffer, Jr., THIS JOURNAL, **69**, 1555 (1947); P. A. Shaffer, Jr., *ibid.*, **69**, 1557 (1947).

[7] L. Pauling, THIS JOURNAL, **69**, 542 (1947). The details of the present method of applying Pauling's relation were suggested to us by K. Hedberg and V. Schomaker. Following their suggestion also we have taken the revised covalent radius for hydrogen (V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1940)) corrected for the electronegativity difference between boron and hydrogen.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS 14, MINNESOTA

WILLIAM J. DULMAGE
WILLIAM N. LIPSCOMB

RECEIVED JUNE 5, 1951

PHOTOGRAPHY IN ELECTROPHORESIS OF HEMOLYZED SERA

Sir:

The occasional necessity for the examination by electrophoresis of hemolyzed sera, or of solutions of hemoglobin or other proteins having high optical density except for red or infrared light, has presented a technical problem in photography. The customarily used mercury vapor arc lamp has strong green and yellow lines, but its red intensity

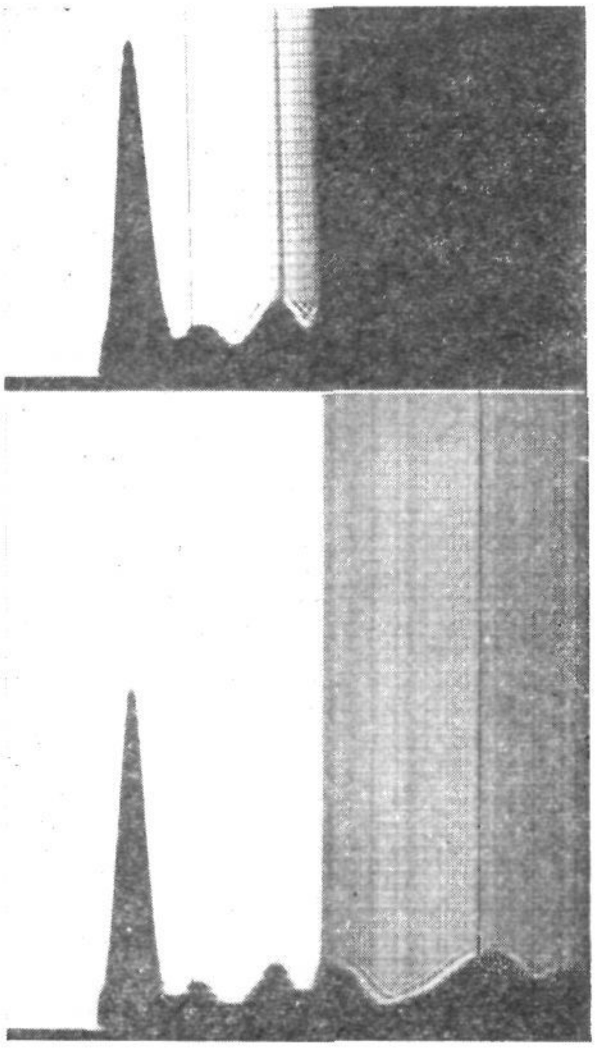

Fig. 1.

is relatively low. For this reason, special infrared sources have been employed,[1] and special adapters have been designed,[2] to permit the interchangeable use of overvoltage tungsten filaments illuminating a slit in the correct focal plane for the schlieren optical system. In an extended study of the sera of a leukemia patient,[3] the critical demand for the analysis of a serum sample which was irreplaceable, but had been hemolyzed when drawn led us to the accidental discovery of a very simple technique for photography, in the absence of a specially designed source of red light. We found that with a Wratten No. 105 (hemoglobin analysis) filter to reduce contrast, Eastman Spectroscopic Type 103F plates are sufficiently sensitive to the mercury red lines to permit satisfactory schlieren scanning photographs[4] in the normal exposure range. Moreover, the lens system used[5] is sufficiently achromatic that satisfactory longitudinal focusing is obtained without shifting the source slit. In the accompanying figure, the upper schlieren scanning photograph of a badly hemolyzed sample was made, after 7200 seconds electrophoresis at 6.29 volts/cm. in 0.1 molar sodium diethylbarbiturate buffer at *p*H 8.60, by use of a Wratten No. 77A (monochromat green) filter and a Kodaline CTC photographic plate. At the position conjugate to the incidence of hemoglobin in the cell, the pattern of the rising boundaries vanishes. The lower schlieren scanning diagram of the same boundaries was obtained with the 105 filter and 103F plate and permits the observation of the globulin and δ-boundaries in the cell. However, since hemoglobin refracts as well as absorbs light its quantitative effect upon the globulin components with which it is associated must not be overlooked in analyzing the pattern. The same light source, filter and photographic plate combination has been used to obtain continuous scanning records[6] of the chromatographic resolution of artificial mixtures of proteins containing hemoglobin as a component,[7,8] and also to obtain cylindrical lens schlieren diagrams in the ultracentrifuge[9] with purified human carbon monoxide hemoglobin solutions up to 2% concentration.

---

[1] H. P. Treffers and D. H. Moore, *Science*, **93**, 240 (1941).

[2] L. G. Longsworth, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 219 (1946).

[3] F. J. Gutter, J. Krevans, G. A. Moulton and G. Kegeles, *J. Nat. Cancer Inst.*, in press.

[4] L. G. Longsworth, THIS JOURNAL, **61**, 529 (1939).

[5] Klett Mfg. Co., New York, N. Y.

[6] G. Kegeles and H. A. Sober, Abstracts of 119th National Meeting, American Chemical Society, April, 1951.

[7] H. A. Sober, G. Kegeles and F. J. Gutter, Abstracts of 117th National Meeting, American Chemical Society, April, 1950.

[8] H. A. Sober and G. Kegeles, *Fed. Proc.*, **10**, 299 (1951).

[9] G. Kegeles and F. J. Gutter, THIS JOURNAL, in press.

NATIONAL CANCER INSTITUTE
NATIONAL INSTITUTES OF HEALTH
U. S. PUBLIC HEALTH SERVICE
BETHESDA, MD.
GERSON KEGELES
FREDERICK J. GUTTER

RECEIVED MAY 9, 1951

STEROIDS. XXII. THE SYNTHESIS OF 19-NORPROGESTERONE

Sir:

In 1944, Ehrenstein[1] reported the twelve-step degradation of strophanthidine in 0.07% yield to a resin, $[\alpha]_D$ +89°, believed to be 19-norprogesterone (IIIb). The material represented a mixture of stereoisomers, most likely possessing the "unnatural" configuration[2] at C-14(β) and C-17(α) and was reported[3] to exhibit the same biological activity as progesterone. Subsequent work[4] has shown that the "unnatural" configuration at C-14 and C-17 *per se* does not confer progestational activity and it remained, therefore, to be seen whether the lack of an angular methyl group at C-10 in IIIb was responsible for this pronounced biological effect, so surprising in view of the extreme specificity of this type of hormonal activity.[2a]

A modified[5] Birch reduction[6] on 3-methoxy-17-acetyl-1,3,5-estratriene (I)[7] produced $\Delta^{2,5(10)}$-19-nor-3-methoxy-20-hydroxypregnadiene (II), (m.p. 135–138°, $[\alpha]^{20}_D$ +88° (all rotations in chloroform), no selective absorption in the ultraviolet, free hydroxyl band in infrared. Calcd. for $C_{21}H_{32}O_2$: C, 79.69; H, 10.19; methoxy, 9.80. Found: C, 79.33; H, 10.47; methoxyl, 9.15), which without isolation upon boiling with alcoholic hydrochloric acid yielded Δ^1-19-norpregnen-20-ol-3-one (IIIa),

---

[1] M. Ehrenstein, *J. Org. Chem.*, **9**, 435 (1944).

[2] (a) M. Ehrenstein, *Chem. Rev.*, **42**, 457 (1948); (b) *J. Org. Chem.* **16**, 355 (1951).

[3] W. M. Allen and M. Ehrenstein, *Science*, **100**, 251 (1944).

[4] Pl. A. Plattner, H. Heusser and A. Segre, *Helv. Chim. Acta*, **31**, 249 (1948).

[5] A. L. Wilds and N. Nelson, to be published. We are greatly indebted to Prof. A. L. Wilds, University of Wisconsin, for advance information on this modified procedure.

[6] A. J. Birch, *Quart. Rev.*, **4**, 69 (1950); *J. Chem. Soc.*, 2531 (1949).

[7] C. Djerassi, G. Rosenkranz, J. Iriarte, J. Berlin and J. Romo, THIS JOURNAL, **73**, 1523 (1951).