TABLE III

VISCOSITIES[a] OF PERCHLORC ACID SOLUTIONS—COMPARISON OF EXPERIMENTAL RESULTS WITH LITERATURE[2,3,9]

$HClO_4$, % by wt.	η, 20°C. (Lit.)	η, 20°C. (Exp.)	η, 50°C. (Lit.)	η, 50°C. (Exp.)
10	1.01	1.006	0.572	0.562
20	1.035	1.040	0.610	0.610
30	1.135	1.144	0.682	0.700
40	1.338	1.338	0.808	0.820
50	1.783	1.782	1.068	1.051
60	2.73	2.73	1.60	1.552

[a] η = Absolute viscosity in centipoises.

given values. The value at 50° for 60% concentration shows the greatest deviation (about 3%).

Summary

Measurements of the viscosity of perchloric acid solutions containing 20 to 60% acid have been made over a temperature range from +50 to −58°, except as the measurements were limited by the freezing points. The viscosity of these solutions at 0° is about three times as great as at +50°, but at −50° the viscosity is about thirty times as great.

SEATTLE, WASHINGTON RECEIVED FEBRUARY 21, 1949

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BRITISH COLUMBIA]

The Density and Transition Points of Solid Hexamethylethane

BY WM. F. SEYER,* R. B. BENNETT AND F. C. WILLIAMS

Numerous studies have been made of the various solid phases of *n*-paraffin hydrocarbons. As a result a considerable amount of knowledge has accumulated concerning their crystal structure, transition points and latent heats. In contrast a corresponding knowledge of the branched hydrocarbons is exceedingly small. The reason for this is undoubtedly the great difficulty encountered in preparing these compounds in the pure state. Calingaert, Soroos, Hnizda and Shapiro prepared recently hexamethylethane in a high state of purity.[1] In a series of measurements dealing with the physical chemical properties of this hydrocarbon, they detected the existence of an unstable solid phase just below the melting point. To establish the nature of these solid phases, the above investigators sent two samples of this material to our laboratory, requesting us to measure its densities and coefficient of expansion by the dilatometer method used previously for some of the *n*-paraffin hydrocarbons.[2]

We were informed that the m. p. of both of the samples was 100.63° and that they had a purity of 99.96 ± 0.04%. One of the characteristics of this hydrocarbon is its small liquid range (5.61°) at normal pressures and another is its high sublimation pressure. It was therefore necessary to develop a special technique for transferring this compound from the glass stoppered ampoule in which it was received to the dilatometer.

Experimental Procedure

Preliminary measurements soon verified the observations of the workers from the chemical research laboratories of the Ethyl Corporation. After several unsuccessful methods were tried for filling the bulb, the following was adopted. The bulb, a funnel with a long drawn out stem and the ampoule containing the hydrocarbon were sealed in a glass tube as shown in Fig. 1. To avoid sublimation during the sealing operation, Dry Ice was placed about the lower end of the containing vessel. The sealing process having been completed, the vessel was then exhausted and refilled with hydrogen several times to remove the air. At the last filling, the hydrogen pressure was brought up to about 2.5 atmospheres. The tube was now inverted and heat applied at the upper end while dry ice was placed about the lower end which contained the bulb. In this manner any amount of hydrocarbon could be melted and run into the bulb. The glass tube was then broken in the center, the bulb removed, stoppered and weighed. The procedure from here on was then the same as with the other hydrocarbons.

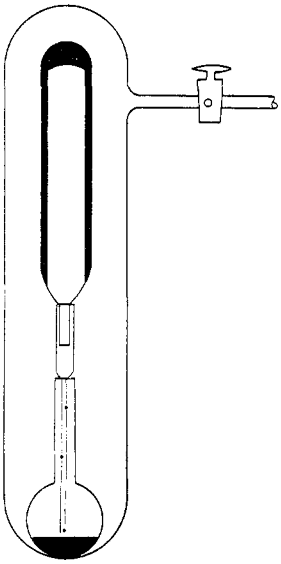

Fig. 1.—Filling the bulb.

A series of density measurements was then made over a temperature range of from 20.69 to 103.50° on the two different lots of materials. Both samples within the limits of accuracy of the measurements gave the same density values. Measurements were first made over intervals of about 2° with both ascending and descending temperatures. In regions near the transition points and rapid density changes the temperature intervals were in the neighborhood of 0.10 to 0.20°, which required an extraordinary amount of bath temperature control. This was found possible with the use of a sensitive thermoregulator and a calibrated Leeds and Northrup platinum resistance thermometer. The absolute density values are considered to be correct to only the third place of decimals while the differential values are within three units of the fourth place. Two phases were found to exist between 20° and the m. p., 100.63°. The density values are given in Table I. The values up to 90° were taken from a large scale plot constructed from the density values obtained in numerous runs. Above 90° to the m. p. actual values of a typical run for phase (1) are given in order to illustrate the manner of approaching a suspected transition or melting point. A similar set of values is given for phase 2.

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(1) Calingaert, Soroos, Hnizda and Shapiro, THIS JOURNAL, **66**, 1389 (1944).

(2) Seyer, Keays and Patterson, *ibid.*, **66**, 179 (1944).

The phase stable above 20° up to 74.25° is referred to as phase 1 and that stable between 74.25 and 99.65°, as phase 2.

It was found that at the low temperatures equilibrium could be reached in about fifteen minutes, above 80° in over thirty minutes; but near the transition temperatures it required as much as seventy-two hours before the mercury level in the capillary tube became constant.

Table I

Phase 1

Temp., °C.	Density, g./cc.	Temp., °C.	Density, g./cc.	
20.0	0.8242	90.0	0.7780	
30.0	.8188	95.89	77.25	
40.0	.8128	98.35	.7690	
50.0	.8065	99.45	.7683	
60.0	.8000	99.96	.7652	
70.0	.7955	100.10	.7641	
73.0	.7913	100.34	.7610	rising
74.4	.7900	100.52	.7538	temp.
80.0	.7858	100.56	.7519	only,
85.0	.7823	100.63 m. p.	.6569	calcd.

Liquid Phase

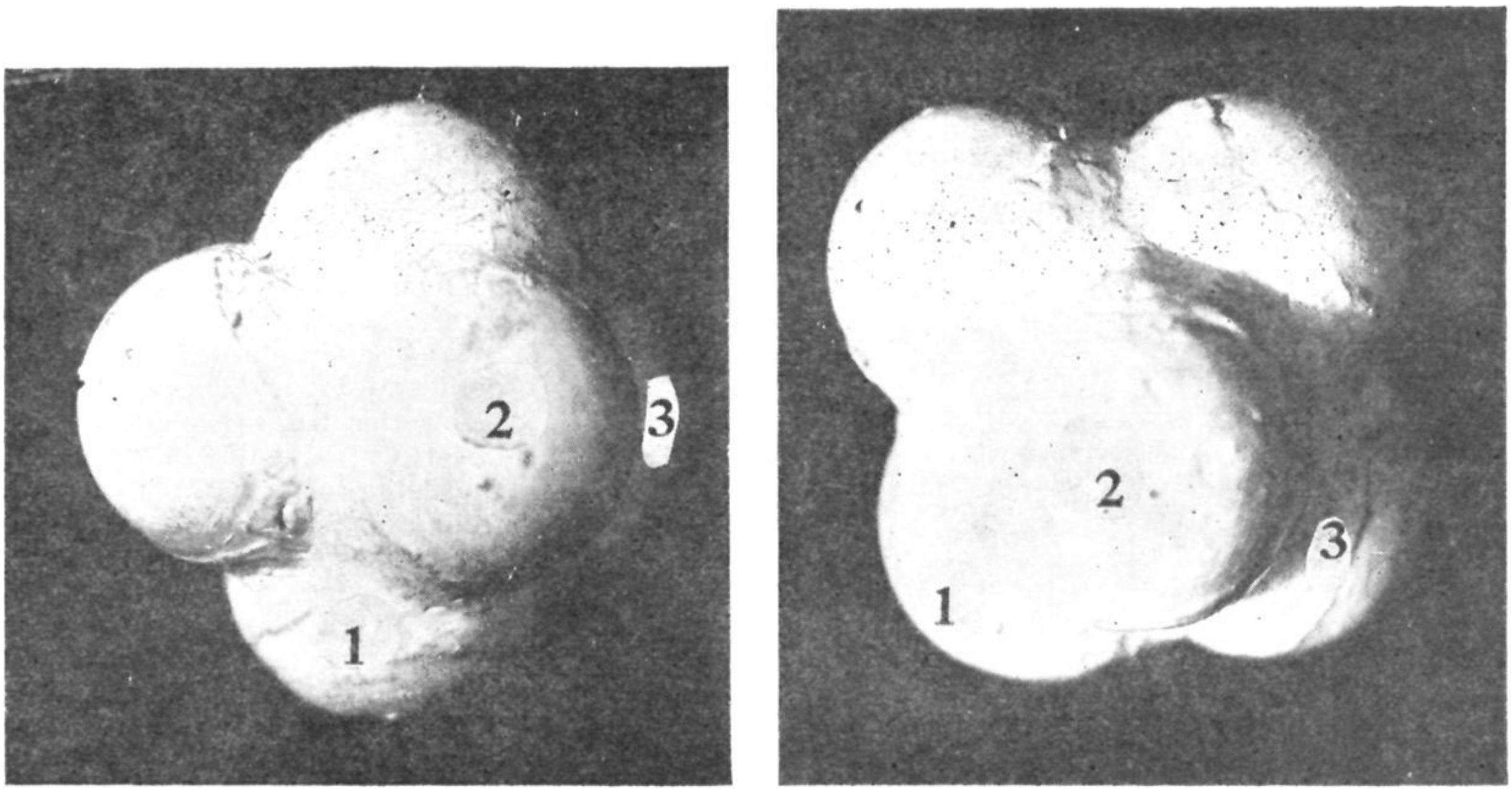
Temp. rising	Density, g./cc.	Temp. falling	Density, g./cc.
100.71	0.6568	100.84	0.6566
101.92	.6557	101.18	.6563
102.28	.6553	102.81	.6549

Phase 2

Temp. rising	Density, g./cc.	Temp. falling	Density, g/cc.
74.85	0.7554	99.65	0.7334
75.02	.7552	97.75	.7353
81.75	.7480	93.52	.7385
84.09	.7456	88.37	.7421
89.67	.7412	86.35	.7435
90.73	.7406	85.71	.7439
91.57	.7398	83.31	.7465
92.95	.7391	79.63	.7502
94.61	.7379	75.96	.7541
95.43	.7372	74.85	.7554
96.55	.7361	74.30	.7558
97.12	.7358	74.25	.7902
98.70	.7343		
99.65	.7334		

Discussion.—The unusual behavior of this hydrocarbon is shown very clearly when densities are plotted against temperatures (Fig. 2). There is an over-all resemblance to the behavior of the even numbered, C_{18}, C_{20}, C_{22}, hydrocarbons of the normal paraffin series, but there is this difference, that the enclosed region for hexamethylethane does not represent a region in which the possible cooling paths with different cooling rates may lie.[2] Here only two definite paths have been found even though the cooling rates in some cases were as low as 0.5° per day. With ascending temperatures, the path was always along ABCD through the melting point to the liquid. Along ABC the path could be retraced at will to the left of C upon either heating or cooling. In general, once beyond C, along CD such was not the case, for increase of temperature led to D, the m. p. The point C was never actually measured. It was established by drawing a line parallel to the density axis through the point F, which was the first equilibrium point that could be obtained upon cooling the hydrocarbon from the liquid state. As mentioned before, measurements in the neighborhood of C and D were made with temperature intervals of less than a tenth of a degree, with heating and cooling rates from 0.1 to 0.5° per day. Yet no transition point could be detected at 74.25° or at 99.65° with an ascending temperature for phase 1, although Calingaert, Soroos, Hnizda and Shapiro, in their communications with us stated that they had twice observed a break in the density–temperature curve, once at 99.59° and once at 99.63° when proceeding toward the melting point on cooling. In our experience both hydrocarbons samples always behaved in the same way. Reproducible points on a large scale curve could readily be obtained for phase 1 with either ascending or descending temperature runs providing the temperature did not exceed 99.96°. Points beyond this were only obtained when proceeding toward the m. p. Whenever the temperature of 99.96° was exceeded it was not found possible to reverse the path toward B because the mercury level in the dilatometer tube never became steady within a time limit of twenty-four hours. At times the mercury column even began to vibrate and it was necessary to cool it below 70° to again obtain a steady state. Why this was so we are unable to explain except to suggest that the time limit of twenty-four hours was too short.

Starting with the liquid and cooling, the hydrocarbon invariably followed the path EDCFGBA instead of the expected one, EDFGBA. There was at no time mistaking this peculiar behavior of the hydrocarbon of first contracting and then when all the liquid had more or less completely solidified suddenly expanding. Before it was understood what was occurring, the rapidity of the expansion was so great as to force some of the mercury out of the dilatometer. In fact, to make measurements at all over this range, it was necessary to construct a special dilatometer with such tube and bulb dimensions that mercury did not overflow into the reservoir upon re-expansion. The action of the hexamethylethane in detail was somewhat as follows: Upon cooling the liquid to 100.5° solidification began and continued for about a period of from one to two hours. After this time as far as one could observe, all the material had solidified, yet the mercury level in the manometer would still keep falling slowly even after seventy-two hours. Lowering the temperatures by decrements of about 0.1° caused further contraction but no steady state. At 99.65° a sudden expansion occurred, causing a change in the mercury level of from 3 to 5 cm., depending upon the dimensions of the particular dilatomer in use. Simultaneously, the solid changed from being opaque to translucent. Furthermore, the above temperature was the first at which equilibrium



(a) Rotation at right angles to 001 plane possible.

(b) No rotation with three methyl groups in 001 plane.

Fig. 2.

could be obtained upon cooling from the liquid phase. The decrease in density between the points C and F was approximately 0.033 or about 4.5%. Further cooling brought about contraction of what is called phase 2 along the line FG until a temperature of 74.25° was reached when transformation into phase 1 took place and the density rose to a value corresponding to point B on the original ABC path.

Once equilibrium had been established just a little to the left of B and the sample then heated, phase 1 did not revert back to phase 2, but persisted in the metastable state along the line BC. Of course it is quite conceivable that had phase been seeded with crystals from phase 2 at the first transformation point (74.25) the latter phase would have formed. However, this was impractical with our present type of apparatus. Furthermore, with all the other hydrocarbons so far investigated this was not necessary to bring about transformation.

Heating phase 2 moved the densities along the line FG. Beyond F to the m. p. no equilibrium states whatever could be obtained. Nor were there any pronounced indications of a contraction equivalent to FC taking place. Thus, as far as could be ascertained with the dilatometer, the path on warming phase 2 was along the path GFD. and not GFCD. In other words, the fusion and solidification processes were not mechanically reversible. A similar situation was recently found when measuring the dielectric constants of *cis* and *trans* decahydronaphthalene, through the melting and freezing regions.[3]

Some sort of transformation, about one degree below the melting point, was observed in the case of several long chain normal paraffins by Piper, *et al.*[4] They inferred the existence of a transition point because of a change in optical properties. The dilatometer method used in this Laboratory for measuring the density of these hydrocarbons in the solid phase failed to show any change in volume at this so-called second transition point.

As a result of the X-ray work of Mueller[5a,b] we have a good knowledge of the crystal structure of the *n*-paraffin hydrocarbons in the various solid phases. There appear to be three forms, one of which is stable in a region 5 to 6° below the m. p. In this form the molecules stand upright on a rectangular base, the 001 plane. Another form common to the even numbered *n*-paraffins has the molecules tilted to the base at an angle of about 60°. There is still another form intermediate between the two mentioned in which the angle of tilt is somewhat less than 60° and the base may be more or less of a rectangle. West, from X-ray data, deduced that hexamethylethane at room temperatures has a cubic body centered dodecahedron crystal structure, which is almost spherical.[6]

Any explanation of the unusual behavior of this compound must of necessity be of a tentative nature until X-ray and specific heat measurements have been made. Hence the following attempted explanations must be considered in this light. While the structural formula would indicate that

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[3] Seyer and Barrow, *ibid.*, **70**, 802 (1948).

[4] Piper, *et al.*, *Biochem. J.*, **25**, 2073 (1931).

[5] (a) Mueller, *Proc. Roy. Soc.* (*London*), **A127**, 417 (1930): (b) **A138**, 514 (1932).

[6] *Z. Krist.*, **88**, 195 (1934).

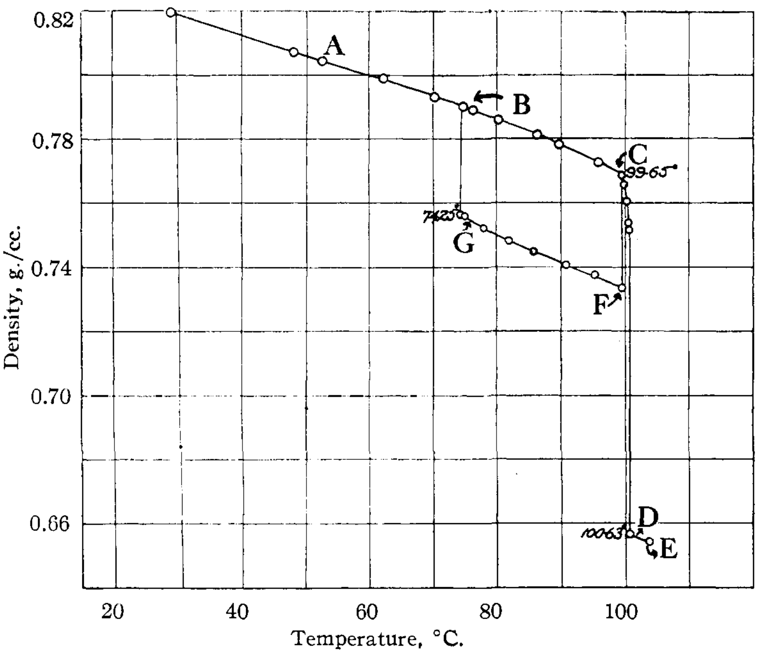

Fig. 3.

hexamethylethane is completely symmetrical, spatial considerations prove that this is not quite so. A geometrical model of the molecule prepared for us by Dr. Robert Delavault with the help of Pauling's data illustrates this clearly in the accompanying photographs. The rounded protuberances represent approximately the volumes swept out by the rotations of the methyl groups attached to the ethane skeleton which is itself buried in the inside of the figure.

West has discussed the crystal modification of C_2X_6 molecules.[6] He reasoned that these derivatives of ethane had not more than one principal axis of rotation. He assumed further that in the cubic modification, there is a large degree of thermal vibration approaching a rotation of the molecules as units, which permits them to simulate a higher degree of symmetry than they actually possess. Consequently, the hexamethylethane molecule might under certain conditions be regarded as a sphere, particularly if it rotated on an axis at right angles to the 001 plane as in Fig. (a) where only one carbon atom of the methyl group lies in this plane.

Unlike the *n*-paraffin hydrocarbons above C_{16} the conditions for the formation of the two solid phases appear to be reversed in the case of this symmetrical octane. Here immediately below the m. p. the stable phase is probably the monoclinic or "tilted form," while at room temperatures the stable one is the cubic form with the long axis at right angles to the 001 plane Fig. 3(a). The former phase could be formed from the latter by merely twisting the molecule through a solid angle of about 30°, so that three of the carbon atoms would lie in the 001 plane (Fig. 3(b)). It is further assumed that in this form no rotation occurs, also that such a form would be anisotropic since that of the cubic form according to West[6] is isotropic.

Hexamethylethane like hexachloroethane appears to be trimorphous. Parks, Huffman and Thomas measured the specific heat of this hydrocarbon from −184.3 to 22.4° and obtained a transition point at −125°.[7] The crystal form below this transition is unknown but from the evidence available, the cubic form is the stable one from this temperature to 74.25°. Let us now assume that the hexamethylethane is heated, that it exists in the form stable above −125.0° which according to West is the cubic form and that rotation of the molecule takes place such as is shown in Fig. 3(a). It is generally considered that the extraordinary stability of solids composed of symmetrical molecules is connected with molecular rotation. Returning again to our Fig. 2, we find that heating causes thermal expansion, only, along the line ABC even beyond the second t. p. 74.25°. Such a belated conversion is not uncommon among the hydrocarbons. At about 99.63° signs of melting appear, the solid becoming soft and more or less plastic in character indicating a loosening up of the polycrystalline mass. This behavior suggests that the melting process is of the type postulated by Mott and Gurney in their discussion on the theory of liquids.[8]

A noteworthy fact was that within the limits of experimental error the amount of expansion at 99.65°, 4.5%, was equal to that found for contraction at 74.25°.

Briefly, the anomalous behavior of hexamethylethane between the temperatures of 101.63 and 99.65° might be regarded as part of the freezing or solid forming process. Were the type of packing in the liquid analogous to that of the GF phase of the solid, this abrupt contraction and re-expansion would probably not take place.

The density of the stable phase at 20° is 0.824. West gave a value of 0.83.[5] The density equation for the liquid phase on the basis of six measurements was established as

$$D_t = 0.6568 - 0.00089\ (t - 100.63)$$

where D_t is density at any temperature t. The extrapolated liquid density at 20° is 0.728 g./cc. Calingaert obtained 0.7219 from solutions of hexamethylethane in *n*-octane.[9]

Their average coefficient $d(D_t)/dt$ for several

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[7] Parks, Huffman and Thomas, THIS JOURNAL, **52**, 1032 (1930).

[8] Mott and Gurney, *Trans. Faraday Soc.*, **35**, 364 (1939).

[9] Calingaert, Beatty, Kuder and Thomson, *Ind. Eng. Chem.*, **33**, 103 (1941).

branched hydrocarbons is 0.000850, a little lower than that of the symmetrical isomer which is 0.00089.

In conclusion, we wish to acknowledge the helpful suggestions offered by G. Calingaert and his co-workers of the Ethyl Corporation, and also that of R. Delavault, who, as mentioned before, took great pains to prepare a model for us.

Summary

1. The density of hexamethylethane has been measured over a temperature range of from 20° to 103.5°.

2. Two transition points were obtained upon cooling from the liquid, one at 99.65° and the other at 74.25°.

3. The contraction and re-expansion of the hydrocarbon between 100.63 and 99.65° might be considered as part of the freezing process.

4. The existence of the two forms can be explained in a similar manner as that of normal paraffins except that in this case the stable form has a cubic structure with the molecule standing upright in the 001 plane instead of being tilted as are the long hydrocarbon chains.

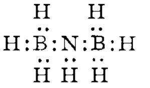
VANCOUVER, B. C. RECEIVED MARCH 17, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

The N-Methyl Derivatives of B_2H_7N[1]

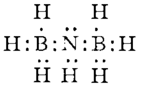
BY ANTON B. BURG AND CARL L. RANDOLPH, JR.

The structure of the aminoboron compound B_2H_7N has not been intelligible in terms of the known chemical facts,[1a] and the application of current theories of electron-deficient bonding has awaited knowledge of the positions of the hydrogen atoms on the B–N–B skeleton. The early electron-diffraction studies[2] suggest an arrangement in which the boron atoms are equivalent, like carbon atoms in dimethylamine. A resonance-structure composed of models such as I and II was suggested but the less symmetrical model III accounts far better for the 1:1 addition compounds formed by B_2H_7N with bases such as ammonia or trimethylamine. On the other hand, the electron-deficiency of the right-hand boron atom in III would demand an irreversible dimerization like that of CH_3BH_2,[3] $(CH_3)_2BH$[4] or $(C_2H_5)_2BH$.[5] Actually B_2H_7N does not dimerize in the least degree.



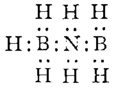
$\mathrm{H{:}\overset{H}{\underset{H}{B}}{:}\underset{H}{N}{:}\overset{H}{\underset{H}{B}}{:}H}$

I



$\mathrm{H{:}\overset{H}{\underset{H}{B}}{:}\underset{H}{N}{:}\overset{H}{\underset{H}{B}}{:}H}$

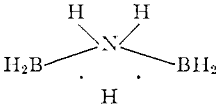
II



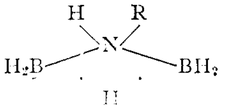
$\mathrm{H{:}\overset{H}{\underset{H}{B}}{:}\overset{H}{\underset{H}{N}}{:}\overset{H}{\underset{H}{B}}}$

III

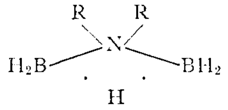
The present paper describes the N-methyl derivatives of B_2H_7N, prepared from diborane and methylamine or dimethylamine. Both are more stable and more volatile than B_2H_7N itself, but present the same structural problem. The existence of the N-dimethyl derivative, $(CH_3)_2NB_2H_5$, narrows the problem by eliminating models I and II, but III remains unsatisfactory unless a way can be found to shift electrons toward the tercovalent boron atom. Earlier concepts of the electronic structure of diborane threw no light on this problem, but the recent proposal that each of the two hydrogen atoms of Dilthey's bridge structure[6] is "half-bonded" to two boron atoms without resonance-relation to the other,[7] justifies the replacement of one bridge-hydrogen atom by nitrogen, thus:



IV



V



VI

These models are like III, except that one hydride unit has moved into a position suitable for sharing electrons equally with the two boron atoms, improving the symmetry and orbital-filling, and achieving a lower energy state by the resonance principle. Base-addition still can occur in terms of structure III, by suppressing one side of the B–H–B bridge linkage in structure IV. Thus structure IV is not only in agreement with the chemical behavior of B_2H_7N, but is also compatible with the suggestion of equivalent boron atoms advanced by Bauer.

The bridge-model for B_2H_7N and its derivatives was suggested by Professor Arthur J. Stosick of this Department in October, 1947.[8] With the as-

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[1] Presented in part in the Symposium on Organometallic Compounds at the Chicago Meeting of the American Chemical Society, April, 1948.

[1a] H. I. Schlesinger, D. M. Ritter and A. B. Burg, THIS JOURNAL, **60**, 2297 (1938).

[2] S. H. Bauer, *ibid.*, **60**, 524 (1938).

[3] H. I. Schlesinger, N. W. Flodin and A. B. Burg, *ibid.*, **61**, 1078 (1939).

[4] H. I. Schlesinger and A. O. Walker, *ibid.*, **57**, 621 (1935).

[5] H. I. Schlesinger, L. Horwitz and A. B. Burg, *ibid.*, **58**, 407 (1936).

[6] W. Dilthey, *Z. angew. Chem.*, **34**, 596 (1921).

[7] R. E. Rundle, THIS JOURNAL, **69**, 1329 (1947).

[8] Essentially the same suggestion has been made independently by E. Wiberg, A. Bolz and P. Buchheit, *Z. anorg. Chem.*, **256**, 286 (1948).