Table I. Reaction Sequences Involving the Pentaborane(9) Cation

Reacn mixture	Reacn compn	Press range, mmHg	Pertinent observn of reacn 1	$PA(B_5H_8)$,[a] kcal/mol	Exptl data I_{RD^+}/I_{RH^+}	No. of points	Expected I_{RD^+}/I_{RH^+} for various proton-transfer sites in $B_5H_9^+$ Positions 1-9	Positions 1-5
$B_5H_7D_2/B_5H_8D/B_5H_9/NH_3$	0.12/0.69/0.19/1.0	0.01-0.03	Occurs	<200.7	0.14 ± 0.03	11	0.12	0.24
B_5H_8D/B_5H_9/ethyl acetate	0.33/0.67/1.0	0.017-0.032	Occurs	<198.0	0.027 ± 0.016	12	0.038	0.071
B_5H_8D/B_5H_9/ethyl acetate	0.33/0.67/1.0	0.016-0.031	Occurs	<198.0	0.035 ± 0.015	9	0.038	0.071
B_5H_8D/B_5H_9/acetone	0.33/0.67/1.0	0.012-0.030	Occurs	<194.6	0.036 ± 0.012	15	0.038	0.071
$B_5H_8D/B_5H_9/i\text{-}C_4H_8$	0.33/0.67/1.0	0.011-0.024	Occurs	<193.0	0.038 ± 0.020	11	0.038	0.071
$B_5H_7D_2/B_5H_8D/B_5H_9/i\text{-}C_4H_8$	0.03/2.34/0.63/1.0	0.013-0.018	Occurs	<193.0	0.12 ± 0.03	9	0.10	0.20
$B_5H_7D_2/B_5H_8D/B_5H_9$/ethyl formate	0.01/0.78/0.21/1.0	0.010-0.036	Occurs	<191.2	0.031 ± 0.022	12	0.10	0.20
$B_5H_7D_2/B_5H_8D/B_5H_9$/ethyl formate	0.01/0.78/0.21/1.0	0.011-0.025	Occurs	<191.2	0.038 ± 0.011	20	0.10	0.20
$B_5H_7D_2/B_5H_8D/B_5H_9/CH_3CN$	0.01/0.78/0.21/1.0	0.01-0.016	Occurs	<187.4	0.047 ± 0.020	16	0.10	0.20
$B_5H_8D/CH_3CN/CH_4$	1.0/4.2/3.3	0.022-0.046	Occurs	<187.4	0.038 ± 0.011	5	0.12	0.25
$B_5H_7D_2/B_5H_8D/B_5H_9/C_2H_5OH$	0.01/0.78/0.21/1.0	0.014-0.018	Occurs	<186.8	0.044 ± 0.011	8	0.10	0.20
$B_5H_7D_2/B_5H_8D/B_5H_9/CH_3CHO$	0.01/0.78/0.21/1.0	0.010-0.020	Occurs	<185.4	0.038 ± 0.014	20	0.10	0.20
$B_5H_9/C_6H_6/CH_4$	1.0/0.23/4.2	0.020-0.080	Not obsd	>183.4				
B_5H_9	Neat	0.003-0.054	Not obsd	>170				

[a] Proton affinity taken from ref 1.

below that of acetaldehyde (185.4 kcal/mol). From the appropriate thermochemical cycle ΔH for the reaction

$$B_5H_9(g) \rightarrow B_5H_8(g) + H(g) \qquad (4)$$
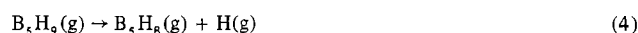
is given by

$$\Delta H = PA(B_5H_8) + IP(B_5H_9) - IP(H) \qquad (5)$$

Using $IP(B_5H_9)$ = 9.87 eV, $PA(B_5H_8)$ = 184 ± 2 kcal/mol from our measurements, and $IP(H)$ = 13.595 eV we obtain for reaction 4 $\Delta H(4)$ = 98.4 ± 2 kcal mol^{-1}. Using the heat of formation of $B_5H_9(g)$ (ΔH_f° = 17.5 kcal/mol)[10] and ΔH_f° = 52 kcal/mol for $H(g)$ we obtain $\Delta H_f^\circ(B_5H_8)$ = 63.8 ± 3 kcal mol^{-1}.

The data in Table I provide some insight into the reaction mechanism for the proton-transfer reactions of $B_5H_9^+$. For each reaction mixture containing deuterium-labeled pentaborane it was possible to calculate the proportion of RD^+ and RH^+ expected if the hydron transferred from $B_5H_8D^+$ originated at the apical position exclusively or from any of the five terminal sites or from all nine sites in the cation. The last two columns of Table I give calculations assuming the hydron has an equal chance of coming from all nine sites (positions 1-9) or only from the apical and basal sites (positions 1-5), respectively. We assume that $B_5H_8D^+$, following its formation, does not have sufficient internal energy for H–D rearrangement since it is produced at an energy close to the adiabatic ionization potential of the precursor molecule. Furthermore, if the ion rearranged prior to its reaction with R we would expect to observe a statistical distribution of RD^+ and RH^+ product ions regardless of the nature of R. We note, for example, that the RD^+:RH^+ ratio observed in the $B_5H_8D^+$ + CH_3CN reaction is well below the calculated statistical value based on all nine reaction sites. On the other hand the RD^+:RH^+ ratio observed in the reaction with the strong base NH_3 is very close to statistical. Our interpretation of these isotope effects is that the least activation energy required is for removal of a basal proton from $B_5H_9^+$ in its reactions with the weaker bases investigated. However, in the more exothermic reactions of $B_5H_9^+$ with strong bases isotope rearrangement probably occurs through the reaction intermediate. Recent photochemical studies with B_5H_9[11] have shown that the preferred product of a Hg-photosensitized reaction is the 2,2-$B_{10}H_{16}$ decaborane, indicating that H was abstracted from a basal B–H bond in forming the B_5H_8 radical intermediate. These photochemical observations are compatible with our

thermodynamic measurements for a B_5H_8 radical formed by loss of a basal proton from $B_5H_9^+$. The value for the (B_5H_8)–H dissociation energy obtained in this study is close to that for the process $HBF_2(g) \rightarrow BF_2(g) + H(g)$ (97.5 ± 6.0 kcal/mol)[10] but is substantially less that for rupture of a B–H bond in borazine (112 ± 3 kcal/mol).[12] The energy required to separate a H atom from B_5H_9 is well below that which could be provided by the $Hg(^3P_1)$ state in photosensitization (111 kcal/mol).

Registry No. B_5H_8, 65930-58-7; $B_5H_9^+$, 65982-52-7; CH_3CN, 75-05-8; $CH_3CNB_5H_7^+$, 65982-51-6.

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Preparation and Structure of Anhydrous Zinc Chloride[1]

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Structures of three crystalline modifications of anhydrous zinc chloride were reported by Brehler[4] and by Oswald and Jaggi.[5] All three are based on pseudo-close-packed anion lattices in which zinc ions occupy tetrahedral interstices. In

Table I. Crystal Data for Orthorhombic $ZnCl_2$

Point group: *mmm*	Probable space group: $C_{2v}{}^9$, $Pna2_1$
$a = 6.443$ (2) Å	4 Zn in 4a: x, y, z; etc.; $x \cong {}^1/_{12}$,
$b = 7.693$ (4) Å	$y \cong {}^1/_8$, $z \cong {}^3/_8$
$c = 6.125$ (4) Å	4 Cl(1) in 4a: x, y, z; etc.; $x \cong {}^1/_{12}$,
$V = 303.6$ (5) Å³	$y \cong {}^1/_8$, $z \cong 0$
Assumed $\rho_{obsd} \cong 3$ g cm⁻³	4 Cl(2) in 4a: x, y, z; etc.; $x \cong {}^1/_{12}$,
$\rho_{x\text{-}ray} = 2.982$ (4) g cm⁻³	$y \cong {}^5/_8$, $z \cong 0$
($Z = 4$)	

the α and γ phases anion layers have a cubic $-$ABCABC$-$ ($-ccc-$) sequence, while in the β phase a four-layered $-$ABCBABCB$-$ ($-chch-$) sequence is followed.

The reported methods of preparation for these materials[4,5] leave little doubt that all three modifications are significantly contaminated by water. All three were prepared from hot, concentrated aqueous solutions. The α and γ phase could be obtained from melts, but the input material for the melts was apparently that crystallized from solutions. Isolation of x-ray diffraction specimens from the room atmosphere was not stringent. In any case, there are good grounds to suspect the presence of nonnegligible numbers of hydroxyl ions substituted for chloride ions in the final products.

In this note we report the preparation of zinc chloride under conditions that exclude water to a greater extent than heretofore achieved. With these conditions our product is monophasic and has a crystal structure different from that of any of Brehler's phases though still based on tetrahedral zinc coordination in a close-packed anion lattice. Our phase transforms to one or more of Brehler's phases if it is imperfectly protected from the ambient atmosphere.

One sample of zinc chloride was prepared as follows: $ZnCl_2$ prepared by a method similar to that of Bjerrum, Boston, and Smith[6] was loaded into a Pyrex tube in a helium-filled drybox with <2 ppm H_2O and <6 ppm O_2. The tube was sealed off under vacuum with rigorous exclusion of moisture, and the zinc chloride was then melted and recrystallized in a temperature gradient according to the Stockbarger method.

Another sample was prepared from Mallinckrodt Analytical Reagent $ZnCl_2$. The material was placed in a long Pyrex tube and heated under vacuum at slowly increasing temperatures. The sample was then kept at about 250 °C until the pressure was constant at about 2 μ, whereupon the temperature was increased to 330 °C and the $ZnCl_2$ was distilled into the colder part of the tube. The distilled material was transferred to another Pyrex tube in the drybox and the procedure was repeated to obtain the final product.

Powders and single crystals from both preparations were loaded into cleaned thin-walled glass capillaries in the helium-filled drybox. Initially the open capillary ends were sealed with wax; later they were fused shut with a Pt hot-wire. Capillaries were removed from the box and exposed to Cu Kα x rays ($\bar{\lambda}$ 1.541 78 Å) in 114.6-mm diameter powder cameras and in various single-crystal diffraction cameras.

Powders of either preparation in capillaries sealed by fusion gave a characteristic x-ray diffraction pattern that did not change with time. Powders in capillaries sealed with wax gave this same pattern if exposures were completed within 24 h after removal from the drybox. Thereafter the gradual appearance of the γ-phase pattern (and eventually the α-phase pattern) was usually noted (Figure 1). Single-crystal diffraction data enabled all reflections in the powder pattern to be indexed on the basis of an orthorhombic unit cell whose dimensions are listed in Table I. The likely contents of this cell, calculated density, and probable space group are also tabulated.

Comparisons of the lattice parameters of the new phase with those of Brehler's phases showed that its structure must be based on a hexagonal $-$ABAB$-$ ($-hhhh-$) sequence of close-packed chloride ion layers lying normal to c. If the space
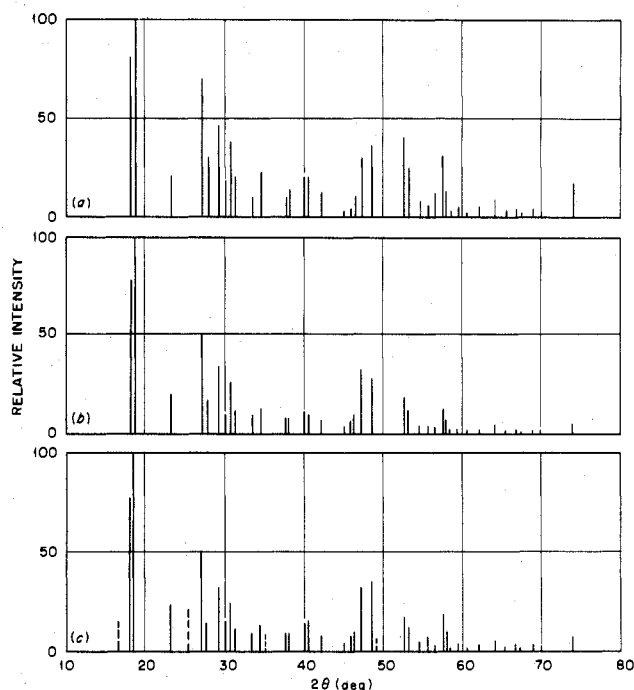

Figure 1. Computed and observed Cu Kα powder diffraction patterns of orthorhombic $ZnCl_2$ (the relative intensity of the 011 reflection is scaled to be 100 in each): (a) pattern computed from parameters in Table I; (b) pattern observed from a sample in capillary sealed by fusion; (c) pattern observed from a sample in a capillary sealed by wax after about 48 h in room atmosphere (reflections of γ-$ZnCl_2$ are dashed).

group were *Pnam*, spatial constraints would require the chloride ion layers to lie in the mirror planes. The 4 zinc ions per cell would then be disordered in the general positions of the group. We considered this arrangement to be improbable and instead devised a model structure based on the polar space group $Pna2_1$. Atom positions of this structure, listed in Table I, were derived by placing chloride ions in hexagonally packed layers and zinc ions in tetrahedral holes such that no two ($ZnCl_4$) groups shared more than one common corner. The powder pattern computed from these positions is shown in Figure 1. It is evident that agreement with the observed pattern is close enough to guarantee the essential correctness of the model.

The proposed structure of our anhydrous $ZnCl_2$ is closely related to those of Brehler's phases. We hypothesize that the $-hhhh-$ stacking sequence is a characteristic of the more nearly anhydrous material and that introductions of relatively small numbers of hydroxyl ions into the structure may trigger slip that leads to cubic sequences. The fact that we observe diffuse streaks parallel to c^* in single-crystal diffraction patterns of our phase indicates faults in the hexagonal stacking which, if our hypothesis is true, may be associated with trace contamination by water.

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