The matter of apparatus is more complicated for, as mentioned earlier, three major families were used by the various workers: opposed anvils; multianvils or piston–cylinders utilizing solid pressure-transfer media surrounding the sample; and gas-pressured apparatus. In our work with other types of apparatus or with modified techniques using opposed anvils we have found some indications of cause for discrepancies in results. For example, while our piston–cylinder data generally fitted the curve shown in Figure 1 up to a limiting pressure of about 13 kbars, the cusp in this portion of the curve was apparently lowered both in pressure and temperature. Our interpretation of this behavior is that on approaching the *p–t* conditions of the cusp, the boundary of a very rapid solid–solid transition had to be crossed at which time the sample–apparatus complex responded with an exaggerated volumetric change or "blowout."

Another example was found in the results we obtained on using a modified sample wafer assembly with the opposed anvils. In this series of runs the enclosed platinum–rhodium foils were omitted and instead the faces of the anvils and nickel ring were coated with an abrasive (rouge). The melting curve up to 23 kbars obtained with this procedure was displaced in the up-pressure direction and showed some unusual features. This behavior is attributed to the fact that the use of the abrasive in effect made the containing ring more rigid than in normal usage, so that it could support a greater proportion of the load force and, in general, would be less compliant to volumetric changes of the sample.

Data and further discussion concerning these two examples will be found in ref 14, as will a consideration of the marked deviations of the melting curves of Baak and Bell, *et al.*, from the others shown in Figures 2 and 3.

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An Investigation of the Structure of the Disulfite Ion in Aqueous Solution Using Raman and Infrared Spectroscopies

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The species formed upon preparing saturated solutions of sodium and potassium disulfites ($Na_2S_2O_5$ and $K_2S_2O_5$, respectively) have been studied using Raman and infrared (4000–200 cm^{-1}) spectroscopies. These studies are supplemented by an examination of the corresponding solid salts by both techniques. Fifteen lines which are attributable to the disulfite ion appear in the Raman and infrared spectra, and nine of the Raman lines are found to be polarized. These measurements indicate an assignment of this ion to the C_s point group, consistent with its formulation as an asymmetrical species containing a S–S bond in contradiction to earlier vibrational investigations by Simon and coworkers.[2] There is some evidence for the existence of the hydrogen disulfite ($HS_2O_5^-$) ion. Also, Raman spectra of the sulfite ion (sodium salt) indicate that the degeneracies of the E modes at *ca.* 930 and *ca.* 470 cm^{-1} are removed in concentrated aqueous solution.

In a fundamental review of problems in the hydration of ions in solution, Taube[3] noted the incongruity between the symmetrical $O_2SOSO_2^{2-}$ structure proposed for the disulfite ion on the basis of Raman data[2] and the asymmetrical one, $O_3SSO_2^{2-}$, assigned from a complete X-ray determination by Lindqvist and Mortsell,[4] confirming an earlier study by Zachariasen.[5] Although Raman spectra were obtained for both the solid and concentrated aqueous solutions,[2] structural conclusions were based primarily on the solution measurements. The case for a definitive assignment of structure for this ion in aqueous solution is generated by Woolfolk's bacterial studies,[6] which indicate that disulfite is the metabolized species in assimilatory sulfite reduction with dithionite ($S_2O_4^{2-}$) formed as an intermediate in a reversible initial step. Similarly, the dithionite–disulfite equilibrium is of probable significance in adenosine triphosphate dependent hydrogen evolution[7,8] and $Na_2S_2O_4$-supported nitrogen fixation[8] by extracts of *Clostridium pasteurianum*, as well as in the reduction of tetrahydroporphyrin by sulfite and dithionite.[9] Although a rearrangement to the oxygen-bridged species in solution is possible, this would represent one of the more drastic departures from solid structure upon dissolution, and it would be difficult to formulate a biological mechanism for sulfite reduction[6] incorporating the symmetrical structure.[10,11]

Experimental Procedures

Reagent grade sodium disulfite (J. T. Baker) and potassium disulfite (Fisher) were used without further purification in preparation of saturated solutions. The disulfite concentration was approximately 2.5 *F*. Saturated solutions of sodium sulfite (J. T. Baker) were similarly prepared. Below pH 3.0 the solutions evolved sulfur dioxide and a previously noted yellow color[12] developed, preventing measurement of a Raman spectrum using the 4358-Å mercury line. Above pH 8.0 the spectrum is characteristic of sulfite ion as the predominant species. The spectrum of the solution was measured at several acidities within

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TABLE I

VIBRATIONAL SPECTRA OF $S_2O_5^{2-}$

Raman			Infrared		
$K_2S_2O_5$ (aq soln)[a] ν, cm^{-1}	ρ[b]	$K_2S_2O_5$ (solid) ν, cm^{-1}	$K_2S_2O_5$ (solid)[c] ν, cm^{-1}	$K_2S_2O_5$ (aq soln) ν, cm^{-1}	Assignment
168 s	p (0.25)	147 s			A′ ($S_2O_5^{2-}$)
200 s	p (0.17)	218 s, 195 w	210 s	225 m	A′ ($S_2O_5^{2-}$)
235 vs	p (0.40)	245 vs	236 s	250 m	A′ ($S_2O_5^{2-}$)
309 s	p (0.48)	317 s	313 m	310 vw	A′ ($S_2O_5^{2-}$)
395 w	dp (0.75)			395 w	HSO_3^-
424 s	p (0.36)	433 s	439 vs		A′ ($S_2O_5^{2-}$)
467 m	p (0.48)				SO_3^{2-} and HSO_3^-
510 m	dp (0.74)	517 w, 507 vw	509 s		A″ ($S_2O_5^{2-}$)
558 w	dp (0.65)	558 m	558 s	551 w	A″ ($S_2O_5^{2-}$)
587 w	dp (0.65)	569 w, 564 w[d]	584 w[e]	586 w	A″ ($S_2O_5^{2-}$ and HSO_3^-)
			618 s		SO_4^{2-}
637 w	dp (0.65)	645 w	649 s	626 m	A″ ($S_2O_5^{2-}$ and HSO_3^-)
655 s	p (0.13)	653 s	668 sh	648 m	A′ ($S_2O_5^{2-}$)
685 vw				690 vs, br	HSO_3^-
709 w					HSO_3^-
740 w					HSO_3^-
933 vw					SO_3^{2-}
966 w	p (0.14)	971 w	973 vs	961 s, br	A′ ($S_2O_5^{2-}$ and SO_3^{2-})
1021 s	p (0.12)			1022 s	HSO_3^-
1052 vs	p (0.11)	1059 s	1058 s	1050 vs	A′ ($S_2O_5^{2-}$)
1085 s	p (0.22)	1088 m	1081 vs	1070 m	A′ ($S_2O_5^{2-}$ and $S_2O_6^{2-}$)
1128 m	dp (0.77)		1110 s		HSO_3^-; SO_4^{2-} in solid-state spectra
1170 w	dp (0.78)	1178 m	1176 vs, br	1155 vs, br	A″ ($S_2O_5^{2-}$)
1196 w	dp (0.76)	1202 w[d]	1189 s, sh	1190 s, br	A″ ($S_2O_5^{2-}$)
2494 w					S—H str in HSO_3^- and $HS_2O_5^-$
2521 w					
2543 m					

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad. [b] p, polarized; dp, depolarized; depolarization ratios are given in parentheses. [c] Infrared samples run as carefully dried KBr and CsI pellets. [d] Observed in the spectrum of $Na_2S_2O_5$(s), only. [e] This band is measured at 566 cm^{-1} in the infrared spectrum of $Na_2S_2O_5$.

the range pH 3.0–8.0, and pH determinations were made with a Radiometer Model 22 pH meter. The analysis of the disulfite spectrum was most accurate for solutions of pH *ca.* 5.5, in which the equilibrium-dependent concentration of $S_2O_5^{2-}$ maximizes and the spectral lines are most intense.

The majority of the Raman spectra were measured on a Cary Model 81 Raman spectrophotometer, using the 4358-Å mercury line from a Toronto arc as the exciting frequency. This line was isolated with a Du Pont Rhodamine 5GDN-Extra filter solution and an Eastman Kodak Wratten 2a single-sheet filter. The frequency scale was calibrated in the region 0–4000 cm^{-1} using known frequencies for chloroform, carbon tetrachloride, carbon disulfide, and certain mercury lines. The spectrum of the pH 5.5 aqueous solution was also measured on a recently acquired laser-Raman spectrometer, and good agreement was found between the two sets of spectra. The laser-Raman instrument is a module system consisting of a Spex Model 1400 double monochromator, a Spectra-Physics Model 112 helium–neon laser (43-mW monitored power at 6328 Å) as the exciting source, a FW-130 photomultiplier with S-20 coating, and a Victoreen Model 1010 microammeter. The laser-Raman spectra of the solid potassium and sodium salts were obtained for comparison purposes on multicrystalline pressed pellets mounted on a goniometer head at an angle of 20° to the incident beam.

The reported Raman frequencies are averages obtained from values measured in at least four of the best spectra. These spectra were analyzed using a Du Pont Model 310 curve resolver, and the frequency analyses by two different individuals exhibited a precision within ±3 cm^{-1}. The estimated frequency error is ±5 cm^{-1}.

The depolarization data were obtained using the laser-Raman instrument, and they represent the results of multiple sets of measurements on each peak. Polarized incident radiation was used with subsequent analysis of the scattered light through rotation of a Polaroid film, and a polarization scrambler was placed between the Polaroid analyzer and the entrance slit of the spectrometer. Thus, a depolarized line should theoretically exhibit a depolarization ratio (ρ) of 0.75. The error in these measurements is probably not greater than 10% except for the weakest lines in the spectrum where the errors made in differentiation from background are proportionately greater.

The infrared spectra of the solids were recorded as KBr and CsI pellets in the 4000–200-cm^{-1} region on a Perkin-Elmer Model 621 spectrophotometer equipped with an air dryer accessory. This instrument was calibrated with water vapor, and frequency placements are accurate to 1 cm^{-1}. Although the spectra of both sodium and potassium disulfites were measured, the potassium salt exhibited the best resolution and is recorded in Table I. Slight oxidation to sulfate and dithionate was observed in the potassium salt spectra, and extensive oxidation of both salts occurs on heating in a moist atmosphere at 130° over a period of 24 hr. The infrared absorptions due to $S_2O_5^{2-}$ diminish in intensity, while absorptions due to SO_4^{2-} (620 and 1113 cm^{-1}) and $S_2O_6^{2-}$ (998 and 1243 cm^{-1}) increase in intensity, in agreement with earlier chemical findings.[12] The infrared spectrum of the $K_2S_2O_5$ aqueous solution was also measured on the above instrument using several drops of the saturated solution lightly pressed between KRS-5 plates (Barnes Engineering Co.). Because these absorptions are broad, an accuracy of no more than ±5 cm^{-1} may be anticipated.

Results and Discussion

The Raman spectra of a concentrated aqueous solution of $K_2S_2O_5$ and of the solid salt are contained in Table I. The infrared spectra of $K_2S_2O_5$ in the solid and in aqueous solution are also included, and the solid spectrum is in good agreement with previously published spectra which were measured only above

600 cm^{-1}.[2,13,14] The infrared and Raman spectra of the aqueous solution contain lines due to hydrogen sulfite and sulfite ions, which are in equilibrium with $S_2O_5^{2-}$ in aqueous solution. Also, weak Raman lines are apparent that are attributable to the most intense vibrations of sulfate[15] and dithionate[16] impurities formed on air oxidation of disulfite.[12] Because lines associated with the oxidation impurities are discriminable only at the limit of instrumental sensitivity, it is improbable that weaker SO_4^{2-} and $S_2O_6^{2-}$ vibrational modes contribute significantly to observed intensities in other regions of the spectrum.

After taking into account spectral lines due to other species, 15 frequencies that may be ascribed to the fundamentals of the $S_2O_5^{2-}$ skeleton are observed in the region below 2000 cm^{-1} in the Raman solution spectrum. A thorough discussion of the structures possibly adopted by the $S_2O_5^{2-}$ ion is presented in ref 2 and is not repeated here. Three of these structures are shown in Figure 1. For an S–S bonded structure of C_s symmetry it is anticipated that the vibrations would be divisible into two frequency groups. The higher frequency group would contain five lines principally attributable to sulfur–oxygen stretches, while the lower frequency group would contain ten lines assignable to bending modes and the sulfur–sulfur stretching vibration. For C_s symmetry, vibrations are of either A′ or A″ symmetry, and all are both Raman and infrared allowed. On the basis of the Raman measurements the high- and low-frequency groups may be further subdivided, for the A′ modes should be polarized and the A″ modes should be depolarized. For the S–S bonded structure observed in the solid[4] (Figure 1a), three polarized and two depolarized lines in the high-frequency region and six polarized and four depolarized modes at lower frequencies are expected. For the other possible structure of C_s symmetry (Figure 1b), an identical polarization pattern in the low-frequency region is anticipated, while one depolarized and four polarized lines are predicted in the region of S–O stretches. Electron-pair repulsion considerations indicate that the occurrence of the structure shown in Figure 1b is highly unlikely, however.

The symmetrical ion reported by Simon, *et al.*,[2] (Figure 1c) would have four polarized and seven depolarized lines below 700 cm^{-1} and a single polarized line and three depolarized lines at higher frequencies. An examination of Table I shows that the polarization pattern of the solution species agrees with that predicted for the structure in Figure 1a, which is that found to exist in the solid by X-ray techniques.[4] The number of polarized lines in both the high- and low-frequency regions exceeds the number possible for the C_{2v} structure (Figure 1c), while the observation of two depolarized high-frequency bands attributable to $S_2O_5^{2-}$ tends to exclude the other asymmetrical species. Furthermore, comparison of measured frequencies in the Raman and infrared spectra of the solution phase with those found in the respective spectra of the solid shows good agreement. The correlation of the spectral lines measured in the solid and solution phases is perhaps the strongest evidence indicating that structural modification is small between these phases.

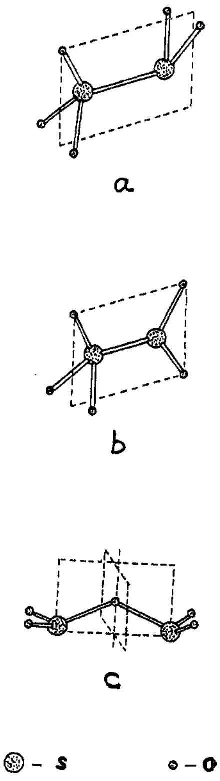

Figure 1.[2]—(a) Structure of C_s symmetry observed in solid.[4] (b) Other possible structure of C_s symmetry (c). Structure of C_{2v} symmetry proposed by Simon, *et al.*[2]

In the earlier vibrational study[2] it was argued that modes which retain the full symmetry of the ion (A′) should be more intense than the A″ modes. We observe that while this is true in general, there does appear to be an exception. We have assigned the polarized band at 966 cm^{-1} as an A′ fundamental of $S_2O_5^{2-}$, and it is weaker than the two A″ modes at 1170 and 1196 cm^{-1}. Although a weak band due to the ν_1 mode of SO_3^{2-} also occurs at *ca.* 970 cm^{-1} in the aqueous solution spectra, the 966-cm^{-1} band persists in both the Raman and infrared spectra of the solid material. No other frequencies possibly attributable to SO_3^{2-} are observed in the infrared or Raman spectra of the solid, where the band in question has shifted slightly to 971 cm^{-1}. Simon and coworkers[2] indicated that the intensity of the Raman line has a strong dilution dependence, and they also proposed that this band is a fundamental of $S_2O_5^{2-}$. Although the third A′ band could lie masked in the region between 1000 and 1100 cm^{-1}, no corresponding frequency is evident in the vibrational spectra of the solids.

In addition to the polarization measurements, the Raman spectra differed with the previously reported spectra[2] as follows. In the low-frequency region, a

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strong band at 168 cm^{-1} is found in addition to the four strong lines reported earlier (235, 309, and 655 cm^{-1}). This polarized band is more intense than would be anticipated for the depolarized hydrogen-bond stretching band of water at 152–175 cm^{-1} [17] which it overlaps. The line at 200 cm^{-1} is a strong line in our solution spectrum, and it was formerly observed as a weak band in the solid state only. The band at 467 cm^{-1} which was attributed to $S_2O_5^{2-}$ is almost certainly due to small amounts of HSO_3^- and SO_3^{2-}. In the high-frequency region (above 950 cm^{-1}) we have assigned the polarized lines at 966, 1052, and 1085 cm^{-1} as A′ vibrations. In the earlier study,[2] the 966- and 1085-cm^{-1} bands were taken to be antisymmetrical modes, and the 1200-cm^{-1} line was reported only in measurements on the solid state.

Further evidence against the adoption of a C_{2v} oxygen-bridged structure upon solution is found in a comparison of the infrared and Raman spectra. In the region from 200 to 2000 cm^{-1} every Raman line is paired in direct correspondence with an infrared absorption in the spectra of the solids. This is true for the solution spectra also, except that the region between 400 and 500 cm^{-1} in the infrared spectrum is obscured by strong water absorption. This is compatible with the results that would be anticipated for a C_s asymmetrical structure for which all modes should be both Raman and infrared allowed, but this observation is inconsistent with the assumption of a C_{2v} oxygen-bridged moiety whose A_2 modes are forbidden in the infrared spectrum. The Raman-active vibrations above 2000 cm^{-1}, which are discussed below, were not observed in the infrared region, and the Raman shift at 168 cm^{-1} lay beyond the low-energy limit of our infrared spectrometer. The infrared absorption at 580 cm^{-1} is the weakest of the lines assigned to the disulfite ion, and it is nearly coincident with a hydrogen sulfite vibration of moderate intensity at 586 cm^{-1} that is observed in an undried pellet. Upon drying, the 586-cm^{-1} peak disappears concurrent with conversion of the hydrogen sulfite to disulfite, while the 580-cm^{-1} line persists. The Raman and infrared modes at *ca.* 590 cm^{-1} in the aqueous solution may be attributed to both of these species.

In summary, three lines of argument may be explored that tend to exclude structural conversion to the $O_2SOSO_2^{2-}$ structure of C_{2v} symmetry upon dissolution. First, the most vigorous of these is the observation that the vibrational spectra are virtually identical for the solution and solid phases. Concomitantly, it seems probable that the C_s structure determined to exist in the solid[4] is also present in aqueous solution. Second, the number of polarized Raman shifts exceeds that predicted for the structure in Figure 1c, but it is consistent with the proposed asymmetrical structure. Finally, since the A_2 vibrations of a C_{2v} symmetry species would not be infrared active, one would anticipate fewer coincident frequencies in the Raman and infrared spectra. Again, for an S–S bonded structure as in Figure 1a, all modes should exhibit both Raman and infrared activity.

With the assumption that the observed spectra in both phases are those associated with an asymmetrical structure (Figure 1a), a few comments regarding specific vibrational assignments are appropriate. Simon[2] attributed the Raman mode at 655 cm^{-1} to the S–O–S symmetrical stretching frequency on the basis of its proximity to that observed for similarly assigned vibrations in molecules known to be oxygen-bridged, such as pyrosulfate. As noted in Table I, this line is one of six strong lines in the low-frequency region. One of these should approximately correspond to an S–S stretch. In thiosulfate this mode is assigned to a band at 447 cm^{-1}, while a line at 670 cm^{-1} is attributed to an A_1 deformation.[18–20] In dithionite the sulfur–sulfur stretch is found at 465 cm^{-1},[21] but Palmer[16] has assigned the polarized Raman shift at 281 cm^{-1} in aqueous solutions of sodium dithionate ($Na_2S_2O_6$) to this mode. Although mixing of the A′ vibrational modes of disulfite will be important, it is possible that the principal contribution to the observed shift at 424 cm^{-1} is due to the S–S stretching vibration and that the band at 655 cm^{-1} is a deformation mode. On the basis of the present measurements, however, one may not dismiss a possible assignment of the S–S stretch to either a lower frequency polarized line or to the band at 655 cm^{-1}.

In the S–H stretching region three Raman lines are apparent at 2494, 2521, and 2543 cm^{-1}. The assignment of these lines cannot be made with certainty on the basis of the present investigation. Simon's photographic spectrum[2] resolved only a single S–H vibration at 2532 cm^{-1}, and he attributed this to the HSO_3^- species. From a pH-dependence study of the equilibria involved in a disulfite solution, Golding[22] concluded that the hydrogen sulfite ion containing a sulfur–hydrogen bond exists in solution in two forms. In one of these forms the sulfur-bonded proton is hydrogen bonded to water, while in the other it is hydrogen bonded to the sulfur of the tautomer $HOSO_2^-$. Thus, two of the shifts may arise from these species, which must have slightly different force constants for the S–H stretch. The third line in this region is more difficult to rationalize. While Golding's ultraviolet absorption studies tend to indicate that the solution species containing two sulfur atoms is $S_2O_5^{2-}$, and not $HS_2O_5^-$ or $H_2S_2O_5$, his measurements were conducted over a limited pH range (pH 3.58–4.60), and it is possible that a protonated species escaped detection. The observation of a third Raman shift in this region does not confirm the existence of the $HS_2O_5^-$ ion, but more convincing explanations have not occurred to us.

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In control measurements on species in equilibrium with disulfite, the Raman spectrum of a concentrated aqueous solution of sodium sulfite was recorded. While our spectrum is in general agreement with that reported by Evans and Bernstein,[23] the degenerate modes ν_3 and ν_4, at 933 and 469 cm^{-1}, respectively, each appear to be split into two components. These are measured at 950 and 930 cm^{-1} for ν_3 and 480 and 460 cm^{-1} for ν_4. The removal of these degeneracies is reminiscent of similar effects for the degenerate frequencies of the nitrate ion in concentrated solutions.[17,24,25] The detailed analysis of this perturbation in terms of contact ion pairing or solvent-separated ion pairing is not apparent, but the sulfite spectrum may be as sensitive to these effects as that of nitrate.

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A New Synthesis of 2-Chloroborazine. The Reaction of a Pyridine Complex of 2,4,6-Trichloroborazine with Lithium Borohydride[1]

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The unsymmetrically substituted 2-chloroborazine $H_2ClB_3N_3H_3$ has been prepared in approximately 50% yield from the reaction of a pyridine complex of 2,4,6-trichloroborazine with lithium borohydride in diethyl ether. Smaller yields of $HCl_2B_3N_3H_3$ (6%) and $H_3B_3N_3H_3$ (12%) were also obtained. The reaction of an analogous pyridine complex of $Br_3B_3N_3H_3$ with $LiBH_4$ gives $H_3B_3N_3H_3$ as the major product, not $H_2BrB_3N_3H_3$. The ^1H and ^{11}B nmr chemical shift data for $H_2ClB_3N_3H_3$ and $HCl_2B_3N_3H_3$ have been compared to $H_3B_3N_3H_3$. The ^1H nmr data suggest that the chlorine is a weak electron-releasing substituent. The preparation of $H_2CH_3B_3N_3H_3$ in a 25% yield from the reaction of $H_2ClB_3N_3H_3$ with CH_3MgI in diethyl ether is also discussed.

One of the most intriguing problems in borazine chemistry is the synthesis of the unsymmetrically substituted derivatives. The logical starting materials for the preparations of the B-substituted compounds are the mono- and dichloroborazines. The chlorine can react with or be exchanged for a large variety of other groups. There are two previously reported preparative routes to $H_2ClB_3N_3H_3$ and $HCl_2B_3N_3H_3$ but both methods have definite drawbacks. In the reaction[2] of $H_3B_3N_3H_3$ with $HgCl_2$, the formation of the hydrogen chloride addition compound of borazine significantly limits the percentage yields of the unsymmetrically substituted chloroborazines. The reaction[3] of $H_3B_3N_3H_3$ with BCl_3 suffers from long reaction times and the small quantities of reagents which can be used in sealed-tube experiments. In addition, both of these reactions require the prerequisite preparation of $H_3B_3N_3H_3$, a tedious step. Therefore, a reaction of the more readily available 2,4,6-trichloroborazine, which would give a good yield of an unsymmetrically substituted chloroborazine, would be a significant improvement over these existing methods. We wish to report the reaction of a pyridine complex[4] of $Cl_3B_3N_3H_3$ with $LiBH_4$ in diethyl ether as a good route to $H_2ClB_3N_3H_3$. The proton and boron-11 nmr spectra of the chloroborazines have been studied in order to monitor the effect of a chlorine atom on the borazine ring.

Experimental Section

All compounds described in this investigation were manipulated in a vacuum system or a purified nitrogen atmosphere. The solvents and reagents were purified by conventional means. The 2,4,6-trichloroborazine[5] was prepared by allowing BCl_3 to react with NH_4Cl in a tube at 200°. The unsymmetrically substituted chloroborazines[2] were identified by their vapor pressures and mass spectra.

Preparation of 2-Chloroborazine.—In a typical experiment, 5.15 g (65.3 mmol) of dry pyridine was added, by means of a vacuum distillation, to 6.043 g (32.6 mmol) of $Cl_3B_3N_3H_3$ which was dissolved in 30 ml of dry diethyl ether. Upon warming the reaction flask from $-196°$ to room temperature, a white insoluble solid, a pyridine complex of $Cl_3B_3N_3H_3$, formed. The suspension was then cooled to 0° and 1.43 g (65.6 mmol) of $LiBH_4$ was added by means of a side-arm addition tube. The mixture was stirred, warmed to room temperature over a period of about 30 min, and then fractionated. Trap temperatures of -46, -63, -78, and $-196°$ separated 0.279 g of $HCl_2B_3N_3H_3$ (5.7% based on $Cl_3B_3N_3H_3$ reacted), 1.758 g of $H_2ClB_3N_3H_3$ (47%), 0.23 g of a mixture of $H_2ClB_3N_3H_3$ and diethyl ether, and a mixture of $H_3B_3N_3H_3$ (4.3 mmol by N analysis) and diethyl ether, respectively. It was very tedious[2] to remove the ether from the $H_2ClB_3N_3H_3$ in the $-78°$ trap. The reaction flask contained a viscous white material which was a mixture of LiCl and pyridine–borane (5.2 g, 56 mmol). It was not possible to detect any unreacted $Cl_3B_3N_3H_3$ or pyridine complexes of chloroborazines but some could have

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