The Structure of B-Monoaminoborazine

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Abstract: The molecular structure of B-monoaminoborazine in the gas phase has been investigated by electron diffraction. Molecular parameters were deduced from scattered intensity data obtained over the region $4 < q < 120$ by a least-squares fitting procedure. Three models were considered: a planar ring, the borazine ring in a chair conformation, and the borazine ring in a boat conformation. For all models the amine N was assumed to be coplanar with the NBN group to which it is attached. The least-squares analysis converged in all cases when the mean-square amplitudes for N–H and B–H were constrained to reasonable values. The three models fitted the data equally well. The bonded distances were determined to be: B–N (ring) = 1.418 ± 0.004 Å; B–N (amine) = 1.498 ± 0.008 Å; B–H = 1.25 ± 0.03 Å; N–H (ring) = 1.033 ± 0.02 Å; N–H (amine) = 1.062 ± 0.03 Å. The departure from coplanarity of the heavy atoms in the average structure is small, but its magnitude cannot be determined from this experiment. It appears best to describe the molecule as being essentially planar, with the exception of the amine hydrogens.

The compound B-monoaminoborazine, $B_3N_4H_7$, is a product of the gas-phase photochemical reaction between borazine and ammonia.[1] Its proton magnetic resonance and infrared spectra of the isotopically substituted compound indicate its structure is similar to that of aniline.[2] Because it has been prepared only recently, little information is available on its chemical and physical properties.

Recently structure investigations were completed in this laboratory of a set of related compounds such as boroxine,[3] borazine,[4] hexafluorobenzene, 1,3,5-trifluorobenzene, B-trifluoroborazine, and *s*-trifluorotriazine.[5] These compounds comprise an interesting group which incorporates a six-atom ring with aromatic or semiaromatic properties. Precision determinations of bond lengths and angles should help elucidate the special features of the bonding characteristics of these systems. B-Monoaminoborazine is an extension of this work.

Experimental Section

The sample of B-monoaminoborazine, $B_3N_4H_7$, was prepared photochemically from a gaseous mixture of borazine and ammonia as described previously.[1] The products of reaction were isolated by passing the resulting mixture through a series of cold traps; $B_3N_4H_7$ condensed at −35°. Mass spectral and infrared analyses of the sample prepared and isolated in this manner showed that no impurities condensed with the $B_3N_4H_7$. The compound is a liquid at room temperature and has a vapor pressure of 2.8 mm at 25°.

Sectored electron diffraction photographs were recorded using an electron diffraction apparatus described previously;[6,7] the apparatus was operated in the convergent mode. Diffraction patterns were recorded on 4 × 5 in. Kodak Process plates. During the exposures the sample was maintained at room temperature, but between runs the sample was condensed and pumped on to remove possible decomposition products. Photographs were recorded with a 25-kV electron beam at a plate-to-nozzle distance of 262.4 mm and with a 65-kV beam at two nozzle positions, $L = 262.4$ mm and $L = 129.7$ mm. The precise wavelength of the scattered electrons and the plate-to-nozzle distance were determined by calibration photographs of MgO recorded with each set of gas patterns.

Owing to the small amount of sample that could be prepared at one time, only one exposure was made for each of the three nozzle–voltage conditions. The diffraction patterns were converted to digitized transmittance readings *vs.* distance from the center of the pattern by a Jarrell-Ash microphotometer and a recording digital voltmeter.[8] Because only one exposure was recorded at each nozzle–voltage condition, the data were not corrected for nonlinear darkening of the photographic emulsions. However, since the optical densities of all the photographs were less than 0.65, it is valid to assume that the recorded optical density was linearly related to the intensity of the scattered electrons. The data were corrected for the flatness of the photographic plates.

Refinement of the diffraction data to deduce the molecular portion of the total intensity followed the now conventional procedure.[9] A background was drawn through the intensity curve, a radial distribution curve was calculated, and the background was refined by minimizing fluctuations from the nonstructural regions of the radial distribution curve through reinversion. When the radial distribution curve showed neither negative areas nor significant fluctuations in nonstructural regions, the molecular intensity function, $(\pi/10)qM(q)$, was fitted by a least-squares analysis. For these computations, the experimental points were weighted by a diagonal matrix, $P(q)$, such that

$$P(q) = 0.25 \text{ at } q = 4$$

$$P(q) = 1.00 \text{ from } q = 15 \text{ to } 105$$

$$P(q) = 0.10 \text{ at } q = 120$$

The weighting matrix was assumed to be exponential in the region from $q = 4$ to 15 and from $q = 105$ to 120. Atom form factors of Cromer, Larson, and Waber[10] and the phase-shift correction of Bonham and Ukaji[11] were used in the analysis.

Results

Several models which differed in the degree of planarity of the borazine ring were tested in the analysis of the $B_3N_4H_7$ data. Figure 1 shows the observed intensity curves and the refined background. The experimental molecular intensity curve, $(\pi/10)qM(q)$,

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[1] G. H. Lee, II, and R. F. Porter, *Inorg. Chem.*, 6, 648 (1967).

[2] R. F. Porter and E. S. Yeung, *ibid.*, 7, 1306, (1968).

[3] C. H. Chang, R. F. Porter and S. H. Bauer, submitted for publication.

[4] W. Harshbarger, G. H. Lee, R. F. Porter, and S. H. Bauer, submitted for publication.

[5] S. H. Bauer, K. Katada, and K. Kimura, "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, Co., San Francisco, Calif., 1968, p 653.

[6] S. H. Bauer and K. Kimura, *J. Phys. Soc. Japan*, 17, 300 (1962).

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[8] S. H. Bauer and R. Jenkins, to be submitted for publication.

[9] J. L. Hencher and S. H. Bauer, *J. Am. Chem. Soc.*, 89, 5527 (1967).

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[11] R. A. Bonham and T. Ukaji, *J. Chem. Phys.*, 36, 72 (1962).

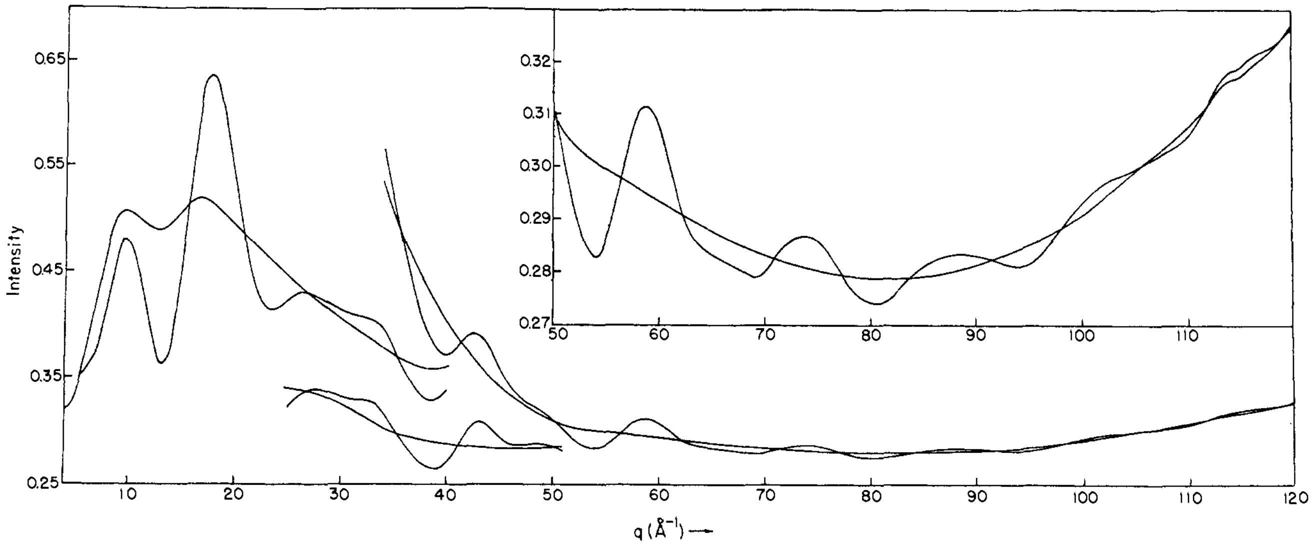

Figure 1. The observed scattered intensity and refined background as a function of angle for $B_3N_4H_7$. The inset shows the observed scattering at large angles on an expanded scale.

Table I. Least-Squares Parameters for Three Models of B-Monoaminoborazine

	Model A	Model B	Model C
N–H	1.032 ± 0.011	1.034 ± 0.011	1.032 ± 0.010
B–H	1.244 ± 0.016	1.255 ± 0.016	1.257 ± 0.015
B–N (ring)	1.4178 ± 0.0005	1.4181 ± 0.0005	1.4184 ± 0.0005
B–N (amine)	1.493 ± 0.005	1.499 ± 0.005	1.504 ± 0.004
N–H (amine)	1.061 ± 0.017	1.062 ± 0.017	1.065 ± 0.016
∠HNH, deg	109.5 ± 2.0	112.7 ± 1.6	114.4 ± 1.4
∠α, deg[b]	0.0[a]	9.5 ± 2.8	13.3 ± 2.1
∠β, deg[c]	0.0[a]	7.3 ± 1.5	5.7[a]
$N_1\cdots N_6$	2.489 ± 0.009	2.480 ± 0.014	2.477 ± 0.011
$B_3\cdots B_5$	2.482 ± 0.008	2.470 ± 0.009	2.470 ± 0.007
^{l}B–N	0.049 ± 0.001	0.048 ± 0.001	0.048 ± 0.001
^{l}N···N[d]	0.073 ± 0.002	0.072 ± 0.002	0.070 ± 0.002
^{l}B···N	0.080 ± 0.004	0.083 ± 0.004	0.084 ± 0.004
^{l}B–H	0.085[a]	0.085[a]	0.085[a]
^{l}N–H	0.070[a]	0.070[a]	0.070[a]
Std dev	0.03156	0.03151	0.03150
Sum of errors squared	0.098198	0.094399	0.090883

[a] Value of this parameter was constrained as listed. [b] α = angle of ring out of plane. [c] β = angle of ring hydrogens out of plane. [d] ^{l}N···N equals ^{l}B···B.

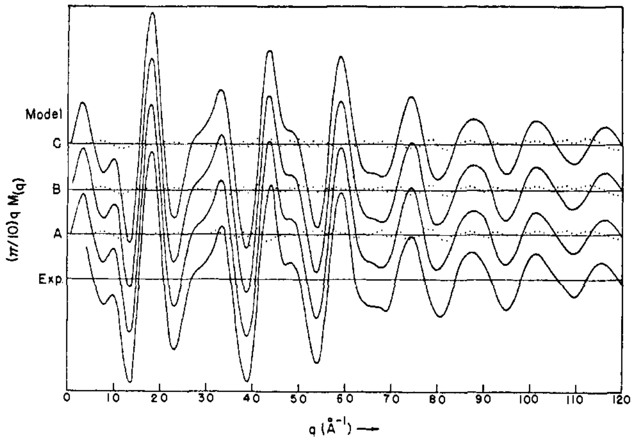

Figure 2. Comparison of the experimental molecular intensity curve with the fitted intensity curves for the three best models. The dotted curves indicate the deviations of the fitted curves from the experimental curve.

is plotted in Figure 2 along with calculated curves for the three best models. The experimental radial distribution curve, calculated with a damping factor $\gamma = 0.00162$, is presented in Figure 3.

The fitted structural parameters for the three models that are in best agreement with the observed molecular intensity curve are listed in Table I. The stated uncertainties for the structural parameters are the standard deviations as calculated from the least-squares analysis. These differ somewhat since they depend on the conformation of the borazine ring. In model A the molecule is entirely planar with the exception of the amine hydrogens. In model B the borazine ring portion of $B_3N_4H_7$ is in a boat conformation, while model C is a chair conformation. These are illustrated in Figure 4, which shows projections of the three structures onto a plane.

Two conclusions follow from the results listed in Table I. First, it should be noted that all three models

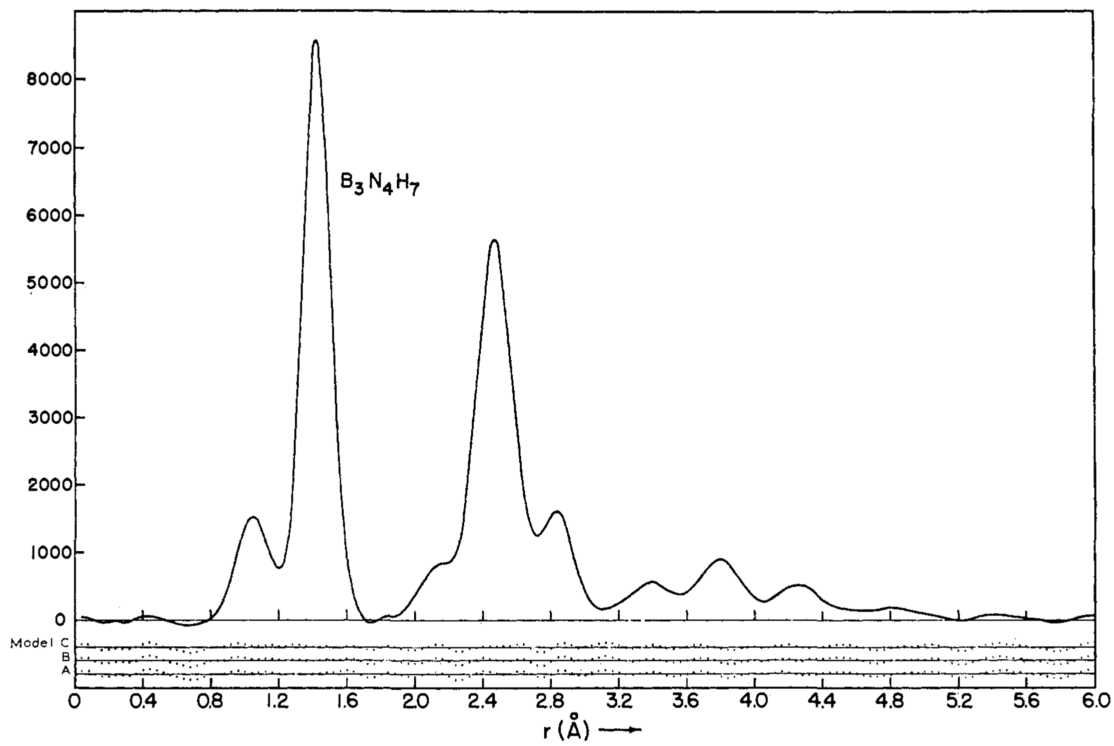

Figure 3. The refined radial distribution curve for B-monoaminoborazine. The dotted curves are the difference curves of the three best models from the experimental radial distribution curve.

fit the data equally well. The standard deviations, σ, differ from model to model by less than 0.2%. Second, values for all fitted parameters, except for those parameters which determine the nonplanarity of the ring and the ring hydrogens, agree from model to model to within two standard deviations. In other words, the least-squares minimizing procedure for the different models converged to essentially the same values for bond distances and bond angles, and differ only as to the postulated conformation of the borazine ring.

Some constraints were necessary in order to obtain convergence in the least-squares procedure. As noted in Table I the bonded B–H and N–H mean-square amplitudes of vibration, l_{ij}'s,were fixed to be 0.085 and 0.070 Å, respectively. The values were estimated from the observed N–H and B–H stretching frequencies for $B_4N_3H_7$[1] and from the observed mean-square amplitudes of vibration of borazine.[3] The B–H amplitude of vibration was constrained because of the uncertainty due to the small contribution by the B–H pairs to the total scattering intensity. The N–H amplitudes of vibration were constrained in order to permit determination of possible differences in bond length between the ring N–H distances and the amine N–H distances. The least-squares analysis shows a large correlation, 0.85, between those two types of bonded N–H distances. Were the amplitudes of vibration for these distances also allowed to vary, the iteration sequence would not converge. The correlation between all other parameters in the least-squares procedure was less than 0.76; these permitted the least-squares calculation to converge for the listed choice of structural parameters.

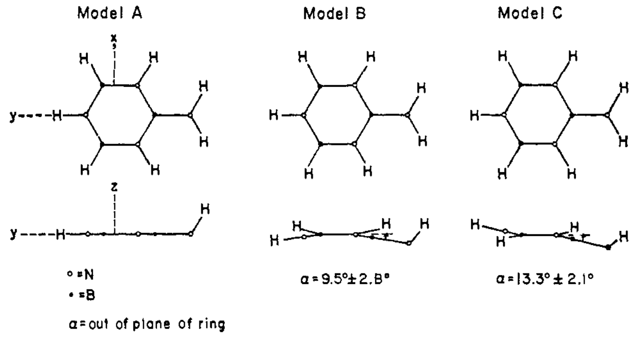

Figure 4. Comparison of the structural conformations of the three models that best fit the B-monoaminoborazine data. The figures are projections on the x, y plane and the y, z symmetry plane, as indicated.

Table I also indicates that the parameter which determined the distortion from the common plane of the ring hydrogens was constrained to 5.7° (0.1 radian) for model C. This parameter was found to be uncertain, and model C did not converge in the least-squares analysis until this constraint was introduced, although the value of the parameter did oscillate around the assumed value. A second assumption made in the analysis was that all of the ring B–N distances were equivalent in length; the amine B–N distance was treated as an independent parameter. It was also assumed that all of the bond angles around the amine nitrogen were equal. In addition, in the least-squares analysis models B and C were not allowed to converge to each other although either could have converged to model A. In other words, the conformation of the borazine ring was fixed in the analysis for each model so that the chair conformation of the ring could not transform to the boat conformation, but could approach a planar structure. A similar constraint was imposed on the boat conformation.

Discussion

Comparison of the molecular parameters for B-monoaminoborazine with the parameters for similar compounds provides some insight into the nature of the bonding in the borazine system. Table II lists the determined B–N bond lengths for borazine and several derivatives. It is thus apparent that the B–N ring distance in borazine is shortened by substitution onto the ring. The fact that all of the substituted borazines have shorter B–N distances is remarkable, considering the range of compounds studied. The valid question arises as to whether these differences are beyond the limits of experimental error. Critical examination of Table II shows that this is the case only for $(ClBNH)_3$ and $B_3N_4H_7$. Nevertheless, all of the quoted values for B–N in the substituted borazines are less than that in borazine. The following is a possible interpretation. Because of the differences in the electronegativities of the boron and nitrogen atoms, the consequent polarization of the B–N bond does not allow as extensive electron delocalization in B_3N_3 as is present in benzene. The immutability of the size of the benzene ring upon substitution appears to be documented.[5] However, substitution onto the borazine nucleus serves to decrease the polarity of the B–N bond, to increase delocalization, and to shorten the B–N distance. Other evidence of this effect is the higher B–N stretching force constants in B-trihalogenated borazines than in the parent compound; the maximum value has been reported for the chloro compound.[12] CNDO molecular orbital calculations for borazine and the methyl-substituted compounds indicate that the methyl group is electron releasing through the π system and electron withdrawing through the σ framework when attached to the boron atoms, but electron releasing through the σ framework when attached to the nitrogen.[13]

Table II. Comparison of Ring Dimensions in Substituted Borazines[a]

Compound	B–N, Å	Ref
$(HBNH)_3$	$1.435_5 \pm 0.002$	4
$(FBNH)_3$	1.426 ± 0.006	5
$(EtBNEt)_3$	1.423 ± 0.015	*b*
$(HBNMe)_3$	1.42 ± 0.02	*c*
$B_3N_4H_7$	1.418 ± 0.004	This work
$(ClBNH)_3$	$1.41_3 \pm 0.01$	*c*, *d*
$(MeBNH)_3$	1.39 ± 0.04	*e*

[a] The limit of error listed for the B–N ring distance in $B_3N_4H_7$ was estimated as the sum of four times the standard error of the least-squares fit and generously assigned experimental errors in the voltage–nozzle position calibration. [b] M. A. Viswamitra and S. N. Vaidya, *Z. Krist.*, **121**, 472 (1965). [c] K. P. Coffin and S. H. Bauer, *J. Phys. Chem.*, **59**, 193 (1955). [d] D. L. Coursen and J. L. Hoard, *J. Am. Chem. Soc.*, **74**, 1742 (1952). [e] K. Anzenhofer, *Mol. Phys.*, **11**, 493 (1966).

The amine B–N distance in $B_3N_4H_7$ at 1.498 ± 0.008 Å is longer than the ring B–N bond distances listed in Table II, yet it is shorter than the reported B–N bond distance of 1.56 Å in the crystal structure of borazane, H_3BNH_3.[14] This indicates a bond order greater than unity for the amine B–N distance and suggests the presence of amine–ring conjugation. The smaller dipole moment of $B_3N_4H_7$ (μ = 1.27 ± 0.07 D)[15] compared with that of aniline (μ = 1.48 D)[16] is further evidence for amine-ring conjugation in the former, in view of the larger electronegativity difference between N and B compared with N and C.

Table III is a summary of various B–H bond lengths and the corresponding B–H asymmetric stretching frequencies. The longer B–H bonds in borazine and $B_3N_4H_7$ show a lower B–H stretching frequency than for boroxine, $B_3O_3H_3$, as anticipated from the structural data. The observed B–H bond distance and stretching frequency for the ring compound $H_2B_2O_3$ extend this correlation.

Table III. Correlation of B–H Bond Lengths and B–H Stretching Frequencies

Compound	B–H, Å	Ref	B–H, cm⁻¹	Ref
$H_2B_2O_3$	1.182 ± 0.003	*a*	2667	*b*
$(HBO)_3$	1.192 ± 0.017	2	2613	*c*
$B_3N_4H_7$	1.25 ± 0.03	This work	2505	1
$(HBNH)_3$	1.259 ± 0.019	4	2520	*d*

[a] W. V. Brooks, C. C. Costain, and R. F. Porter, *J. Chem. Phys.*, **47**, 4186 (1967). [b] J. F. Ditter and J. Shapiro, *J. Am. Chem. Soc.*, **81**, 1022 (1959). [c] F. A. Grimm, L. Barton, and R. F. Porter, *Inorg. Chem.*, **7**, 1309 (1968). [d] K. Niedenzu, W. Sawodny, H. Watanabe, J. W. Davison, T. Totani, and W. Weber, *ibid.*, **6**, 1453 (1967).

It is of interest to note that the N–H bond length in the ring is shorter than that in the amine group (1.033 ± 0.02 Å *vs.* $1.06_2 \pm 0.03_5$ Å). Although the uncertainty for each distance is large, because of the high correlation between the parameters, their relative length is unequivocal. Note also that this amine N–H bond is longer than the N–H bond in aniline (0.998 Å) as determined by microwave spectroscopy.[17] For aniline the reported ∠HNH = 113° 54′ agrees with the observed ∠HNH in $B_3N_4H_7$. The specific magnitude deduced for this HNH angle varies from 109.4 to 114.5°, depending upon the conformation of the borazine ring;

Table IV. Comparison of Bonded and Nonbonded Distances in $B_3N_4H_7$

Distance, Å	Model A	Lot	Model B	Lot	Model C	Wt
B–N	1.417_8	6	1.418_1	6	1.418_4	6
B–N (amine)	1.493	1	1.499	1	1.504	1
B···N[a]	2.783	1	2.784	1	2.789	1
	2.861	2	2.852	2	2.851	2
B···N (amine)	3.806	2	3.809	2	3.804	2
N···N (amine)	4.276	1	4.270	1	4.286	1
$\angle BN_{para}B$, deg	122.8		121.8		121.7	
$\angle BN_{ortho}B$, deg	119.0		119.2		118.7	

[a] Because the symmetry of the borazine ring was allowed to be less than C_{3v}, two values were obtained for the B···N across the ring distances.

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(12) R. E. Hester and C. W. J. Scaife, *Spectrochim. Acta*, 22, 455 (1966).

(13) P. M. Kuznesof and D. F. Shriver, *J. Am. Chem. Soc.*, 90, 1683 (1968).

(14) E. W. Hughes, *ibid.*, 78, 502 (1956).

(15) M. Chakravorty, private communication.

(16) L. G. Groves and S. Sudgen, *J. Chem. Soc.*, 1782 (1937).

(17) D. G. Lister and S. K. Tyler, *Chem. Commun.*, 152 (1966).

it is smaller for the planar ring model, larger for the chair conformation.

The differences between the three models which fit the diffraction data for $B_3N_4H_7$ equally well must be regarded as an indeterminancy of the experiment. As pointed out above, all of the fitted parameters, except the angles determining the degree of planarity of the ring, are very nearly equal for the three models. Comparison of the long nonbonded distances in the molecule for the different models gives some indication of shrinkage effects which are only slightly larger than for benzene[18]. The listing in Table IV documents the argument that the degree of departure from planarity for the average structure, within the limits allowed by models B and C, is inherent to the electron-diffraction technique since the differences observed in the across-the-ring distances between the three models are comparable to the experimental errors. We conclude that in B-monoaminoborazine the borazine ring and the amine nitrogen are essentially coplanar, with the amine hydrogens definitely not in this plane.

Acknowledgments. We wish to thank Mr. Richard Hilderbrandt for his technical assistance in obtaining the diffraction patterns. This work was supported by the Advanced Research Projects, the Army Research Office-Durham, and the National Science Foundation.

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Kinetics of the Reaction of Hydrogen Iodide with 1,1-Difluoroethylene

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Abstract: The gas-phase reaction of hydrogen iodide with 1,1-difluoroethylene produces 1,1-difluoro-1-iodoethane, 1,1-difluoroethane, and iodine. 1,1-Difluoro-2-iodoethane rarely is observed, and never below 230°. The activation energy for consumption of 1,1-difluoroethylene is 27.2 ± 0.7 kcal/mole, and the preexponential factor is 1.5×10^8 l./(mol sec). These values are close to those for the reaction of hydrogen iodide with ethylene. The predominant orientation of hydrogen iodide addition is in keeping with an ion-pair model of the transition state. Calculations based on a point-dipole transition-state model lead to the incorrect prediction that the hydrogen iodide addition is anti-Markovnikov. In the reaction of hydrogen iodide with fluoroethylene, silicon tetrafluoride is produced at both 175 and 305°. Apparently hydrogen fluoride is the product of a side reaction.

Hydrogen iodide reacts with olefins in the gas phase to produce alkyl iodides.[1] Methyl groups adjacent to the double bond have a pronounced effect on the orientation and activation energy of hydrogen iodide addition. The present investigation was undertaken to determine the effects of fluorine substitution adjacent to the double bond. Knowledge of these effects would shed light on the reaction's transition state, which is also the transition state for the reverse reaction, namely dehydroiodination. Relationships between activation energy and structure are known for gas-phase dehydrohalogenations of organic chlorides, bromides, and iodides,[2] but the effects of fluorine substitution on dehydrohalogenation have not been studied.

Experimental Section

Anhydrous hydrogen iodide (Matheson) was degassed and then was freed of iodine and silicon tetrafluoride by bulb-to-bulb distillation from a Dry Ice bath to a *n*-pentane slush. Fluoroethylene, 1,1-difluoroethylene, 1,1-difluoroethane (all from Matheson), and fluoroethane (Air Products) were degassed and then were used without further purification, as no impurities were observed in infrared and gas chromatographic analyses. Authentic samples of 1-fluoro-1-iodoethane and 1,1-difluoro-1-iodoethane were prepared by allowing hydrogen iodide to react at room temperature with fluoroethylene and 1,1-difluoroethylene, respectively. 1,1-Difluoro-2-iodoethane was prepared by heating 2,2-difluoroethyl *p*-toluenesulfonate with sodium iodide in ethylene glycol.[3] The structures of the three organic iodides were verified by their proton nmr splitting patterns.[4] The infrared frequencies of 1,1-difluoro-1-iodoethane agree with previously published values,[5] and those of 1,1-difluoro-2-iodoethane were also determined.[6]

Reactions were carried out in 0.1-l. borosilicate glass vessels, which contained a few glass balls to permit thorough mixing of the reactants. The vessels were flamed while being evacuated to remove water from the inner surface. Stopcocks with Apiezon H grease were the most suitable vessel closures. Reactant pressures were measured with a fused silica spiral manometer sensitive to 0.05 torr. A molten salt bath maintained reaction temperatures constant to

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(3) G. V. D. Tiers, H. A. Brown, and T. S. Reid, *J. Am. Chem. Soc.*, 75, 5978 (1953).

(4) Observed nmr parameters. Chemical shifts are relative to tetramethylsilane. $CHFICH_3$: $J_{HH} = 5.5$, $J_{H1F1} = 49$, $J_{H2F1} = 20$ cps. CF_2ICH_3: δ -2.49 ppm; $J_{HF} = 17$ cps. CHF_2CH_2I: δ_{H1} -5.79, δ_{H2} -3.39 ppm; $J_{HH} = 4$, $J_{H1F1} = 57$, $J_{H2F1} = 16$ cps.

(5) M. Hauptschein, A. H. Fainberg, and M. Braid, *J. Org. Chem.*, 23, 322 (1958). Our frequencies (cm^{-1}) and intensities for CF_2ICH_3: 619 s, 625 s, 632 s, 878 s, 882 s, 888 s, 900 m, 962 s, 1097 vs, 1103 vs, 1107 vs, 1181 vs, 1188 vs, 1387 s, 2943 m, 3015 m (triplet).

(6) CF_2HCH_2I frequencies and intensities: 442 s, 450 s, 540 m, 664 s, 672 s, 702 m, 740 m, 815 m, 975 s, 979 s, 983 s, 1055 vs, 1065 vs, 1115 vs, 1123 vs, 1188 s, 1348 m, 1353 s, 1363 s, 1380 s, 1389 s, 1425 s, 1430 s, 2981 s.

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