further SCF–LMO and experimental studies on such systems as $B_3C_2H_5$, $B_7C_2H_9$, $B_8C_2H_{10}$, $B_{10}H_{14}$, and the isomers of $B_{10}C_2H_{12}$. Such investigations are now in progress.

Acknowledgments. We thank J. H. Hall, Jr., for helpful discussion and the Office of Naval Research for financial support. D. S. M. and I. R. E. are grateful to the National Science Foundation for predoctoral fellowships. Portions of this study were supported by a grant from the Research Corporation to I. R. E.

Infrared Studies of Matrix Isolated Species in the Hydrogen–Boron–Nitrogen System

Earl R. Lory and Richard F. Porter*

Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York. Received September 21, 1972

Abstract: Infrared spectra of the 1216-Å photolysis products of ammonia–borane (H_3NBH_3) in rare gas matrices indicate that the major product is imidoborane (HNBH). Two of the three Σ^+ vibrations for a linear HNBH structure are observed at 3700 cm^{-1} (ν_1) and 1785 cm^{-1} (ν_3) for the ^{11}B, ^{14}N species in an argon matrix. Calculations based on isotope effects predict a frequency of 2800 cm^{-1} for ν_2. One of the bending vibrations of HNBH is observed at 460 cm^{-1}. A second species appearing after prolonged photolysis of ammonia–borane is identified as HNB. Spectra of the photolysis products of borazine are associated with a species formed by ring opening, loss of hydrogen, and multiple BN bond formation.

Matrix isolation is a valuable technique for study of small molecules that are highly reactive under ordinary experimental conditions. In studies involving reactive boron species we have recently isolated the intermediate HBO.[1] We have now extended this investigation to the H–B–N system, and the main purpose of this paper is to report the isolation and infrared spectra of imidoborane, HNBH. This intermediate is frequently discussed in the chemical literature as a precursor to the more stable trimeric species, borazine. Physical evidence for the existence of imidoborane has not been reported. Recently two theoretical molecular orbital calculations[2,3] have indicated that HNBH should exist in a linear configuration analogous to its organic counterpart HCCH.

Experimental Section

In these experiments we have investigated the photodecomposition products of H_3NBH_3 (ammonia–borane) and $H_3N_3B_3H_3$ (borazine). The procedure is similar to that used by Lory and Porter.[1] The matrix-isolation apparatus has been described.[4] Ammonia–borane was prepared by the reaction of isotopically labeled borane etherate and ammonia.[5] The photolysis source was a microwave-powered (Raytheon Model CMD-4) hydrogen discharge in a quartz tube fitted with a LiF window. The window was baked for several hours at 550° after each experiment to restore its transparency.[6] The lamp body was extended through a sealed flange into the vacuum system to place the lamp window within 4 cm of the target window. Infrared absorption spectra (4000–250 cm^{-1}) were recorded on a Perkin-Elmer 521 spectrometer calibrated with HCl and NH_3. The sample was sublimed into a stream of the matrix gas and the mixture deposited on a cooled (5°K) CsI target window. Simultaneous deposition and photolysis produced more products than did sequential deposition and photolysis. Matrix ratios of 300/1 or higher were used based on a vapor pressure of ammonia–borane of 1 μ at room temperature.[4]

Borazine was prepared by treating *B*-trichloroborazine with $NaBH_4$.[7] Two deposition nozzles were used, one dispensing borazine–matrix gas mixture at room temperature and the other pure matrix gas at 77°K. Matrix ratios of 300 to 800 were used. Photolysis conditions were similar to those described above.

Results

Photolysis of ammonia–borane in argon matrices yielded a species with two strong absorption bands at 3700 and 460 cm^{-1} and a medium absorption band at 1785 cm^{-1}. The band at 1785 cm^{-1} in argon was usually quite broad. Spectra obtained in xenon matrices showed the same absorption bands which were narrow but shifted to slightly lower frequencies (Figure 1). After a considerable period of irradiation and deposition, a second series of weak bands appeared at 3675 and 2035 cm^{-1} (see Figure 1). In most experiments with H_3NBH_3 as precursor, a strong broad absorption centered at 1370 cm^{-1} appeared after prolonged irradiation. This feature did not exhibit an obvious isotope effect in experiments with perdeuterioammonia–borane.

A spectrum of the photolysis products of borazine is shown in Figure 2. The spectrum consists of a small number of narrow well defined bands and a broad poorly defined band structure in the region between about 1800 and 2000 cm^{-1}. The conversion of borazine to products was very high when irradiation and matrix deposition were conducted simultaneously. Irradiation following deposition produced no photolysis products. Experiments with matrix ratios of 300, 500, and 800 showed no change in the sharp features in the spectrum of the photolysis products. The major absorption bands appear at 3700 and 3672 cm^{-1}, the region between 2000 and 2100 cm^{-1}, and in a region near 500 cm^{-1}.

---

(1) E. R. Lory and R. F. Porter, *J. Amer. Chem. Soc.*, **93**, 6301 (1971).

(2) N. C. Baird and R. K. Datta, *Inorg. Chem.*, **11**, 17 (1972).

(3) D. R. Armstrong and D. T. Clark, *Theor. Chim. Acta*, 24, 307 (1972).

(4) A. Kaldor and R. F. Porter, *J. Amer. Chem. Soc.*, **93**, 2140 (1971).

(5) S. G. Shore and R. W. Parry, *ibid.*, **80**, 8 (1958).

(6) A. O. Mosher and R. P. Frosch, *J. Chem. Phys.*, 52, 5781 (1970).

(7) G. H. Dahl and R. Shaeffer, *J. Inorg. Nucl. Chem.*, 12, 380 (1960).

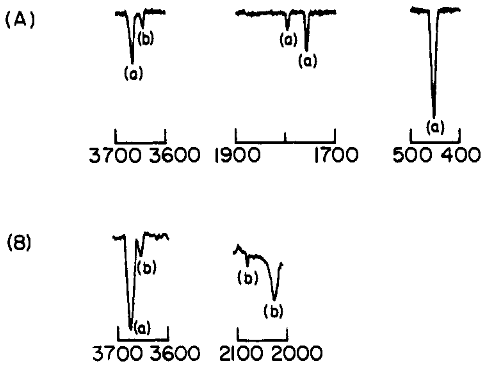

Figure 1. (A) Infrared spectrum attributed to $H^{15}NBH$ in xenon matrix (features denoted by (a)). (B) Infrared spectrum attributed to $H^{15}NB$ in argon matrix (features denoted by (b).

Discussion

In Table I are listed vibration frequencies for the primary photolysis products obtained from several isotopically labeled ammonia–boranes. From information obtained from ten isotopically substituted species, these frequencies are assigned to the isolated molecule HNBH. This conclusion is based on the simulation of frequencies from a set of three force constants for the Σ^+ vibrations for a linear H–N–B–H species as predicted in the theoretical calculations of Baird and Datta.[2] The analysis of the spectrum was complicated by the absence of a frequency that could readily be assigned to ν_2. However, the isotope-substitution experiments clearly indicate that the boron atom is bound to N and H. The calculations show that while substitution of D for H at the N atom results in a modest isotope shift in ν_3 (B–N stretch), a second substitution of D for H at the B atom results in a dramatic shift of almost 150 cm^{-1}. In general the agreement between calculated and observed values of ν_3 is good. Differences in calculated and experimental values for ν_1 can be attributed to anharmonicity effects which are usually quite large for light atom motion. Neglecting stretching–stretching interactions the best choices of force constants for the molecule are k_1(H–N) = 7.50 × 10^5 dyn cm^{-1}, k_2(B–H) = 4.10 × 10^5 dyn cm^{-1}, and k_3(B–N) = 13.14 × 10^5 dyn cm^{-1}.

Table I. Frequencies (cm^{-1}) for Σ^+ Vibrations of HNBH in Ar Matrices

Isotopic species	ν_1 Obsd	ν_1 Calcd	ν_2 Obsd	ν_2 Calcd	ν_3 Obsd	ν_3 Calcd
$H^{14}N^{11}BH$	3700	3700		2800	1785	1785
$H^{14}N^{10}BH$	3700	3700		2823	1822	1822
$D^{14}N^{11}BD$	2790	2762		2194	1595	1583
$D^{14}N^{10}BD$	2790	2767		2237	1610	1596
$H^{15}N^{11}BH$	3684	3689		2799	1762	1762
$H^{15}N^{10}BH$	3684	3689		2822	1799	1799
$D^{14}N^{11}BH$	2840	2836	2730	2713	1734	1731
$D^{14}N^{10}BH$		2858		2715	1772	1767
$H^{14}N^{11}BD$	3695	3699		2225	1624	1618
$H^{14}N^{10}BD$	3695	3700		2275		1629

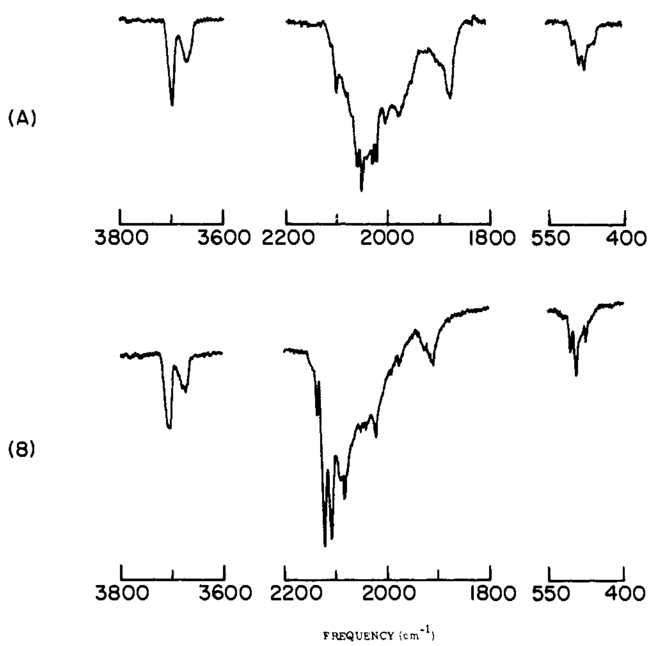

Figure 2. Infrared spectrum of photolysis products of (A) borazine with natural isotope abundance and (B) borazine (^{10}B labeled) in argon matrices.

Table II. Bending Frequencies (ν_4) for HNBH in Ar Matrices

Precursor	ν_4, cm^{-1}	Assignments
$H_3{}^{14}N^{11}BH_3$	460	$H^{14}N^{11}BH$
$H_3{}^{14}N^{10}BH_3$	460	$H^{14}N^{10}BH$
$D_3{}^{14}N^{11}BD_3$	360	$D^{14}N^{11}BD$
$H_3{}^{15}N^{11}BH_3$	456	$H^{15}N^{11}BH$
$D_3{}^{14}N^{11}BH_3$	457	$H^{14}N^{11}BD$
	361	$D^{14}N^{11}BH$
$H_3{}^{14}N^{11}BD_3$	457	$H^{14}N^{11}BD$
	360	$D^{14}N^{11}BD$

Only one of the two degenerate bending vibrations for HNBH has been identified (see Figure 3 and Table II). The products of the photolysis of ammonia–borane and perdeuterioammonia–borane exhibited strong bands at 460 and 360 cm^{-1}, respectively. An isotope effect of less than 1 cm^{-1} was noted for the ^{10}B enriched molecule. Products from the partially deuterated precursors D_3NBH_3 and H_3NBD_3 showed two absorption bands at 457 and 360 cm^{-1}. The close coincidence of these bands with those observed in experiments with isotopically pure precursors and the isotope shifts on the frequencies lead to the following deductions. (1) Hydrogen atom transfer from boron to nitrogen has occurred during photolysis. (2) The bending frequency is primarily H–N rather than H–B motion.

When H_3NBD_3 was photolyzed, the strongest band observed was aligned with the 460 cm^{-1} band in HNBH. When D_3NBH_3 was used as precursor, the strongest band of the product was aligned with the 360 cm^{-1} band in DNBD. Thus, although H–D exchange is evident, it does not appear to occur for every precursor molecule that is photolyzed. The H–N bending frequency (ν_4) in HNBD is actually about 3 cm^{-1} lower than the corresponding band in HNBH. Although this shift is small, it is sufficient to reflect a mass effect due to the isotope substitution at the boron atom. The deuterium isotope effect on ν_4 (460 → 360 cm^{-1}) is approximately that observed for the bending vibration in HNC (474 → 375 cm^{-1}).[8] In other words, the

---

(8) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 47, 278 (1967).

isotope effect in HNBH follows the product rule as if ν_5 (B–H bend)[9] were not strongly coupled to ν_4.

The spectrum of DNBH is noteworthy for the following observations. (1) The frequency ν_1 for this molecule is somewhat higher than that for DNBD. This is reflected in the frequency calculations. (2) A band appears at 2730 cm^{-1}, which has no observable counterpart in the spectra of the other isotopically labeled molecules. This band has been assigned to ν_2 (B–H stretch). A possible explanation for its appearance is that ν_1 and ν_2 of species Σ^+ are nearly coincident in DNBH and resonance due to coupling of the two vibrational modes leads to an intensity variation. The absence of a strong absorption band for ν_2 in HNBH is perhaps not surprising. In the analogous molecule HBO, ν_1 (B–H stretch) is especially weak. The calculated value of ν_2 in HNBH at 2800 cm^{-1} is approximately that reported for ν_1 in HBO and the antisymmetric stretch in BH_3.

In HNBH the N–H stretching frequency at 3700 cm^{-1} is exceptionally high and is in the range of the antisymmetric O–H stretching frequency in matrix isolated water.[10] The best molecule for comparison, HNC,[8] has ν_1 = 3620 cm^{-1}.

The *ab initio* calculation by Baird and Datta[2] predicts a triple B–N bond in HNBH with an energy quite close to the C–C bond in acetylene. Table III lists the multiple bond force constants for a series of isoelectronic molecules including imidoborane and the stable trimers formed by these molecules. The relative change of the multiple bond force constants upon trimerization indicated by the quantity $(k_{\text{mono}} - k_{\text{tri}})/k_{\text{mono}}$ may be taken as a measure of the degree of aromaticity in the trimer. Since trimerization without any aromaticity would mean a bond order change from 3 to 1.5, the smaller the quantity listed in the table the more aromatic character in the trimer. As expected, this criterion shows the two boron-containing species are less aromatic than the carbon-containing species. Also, the lower aromaticity of boroxine ($H_3B_3O_3$) com-

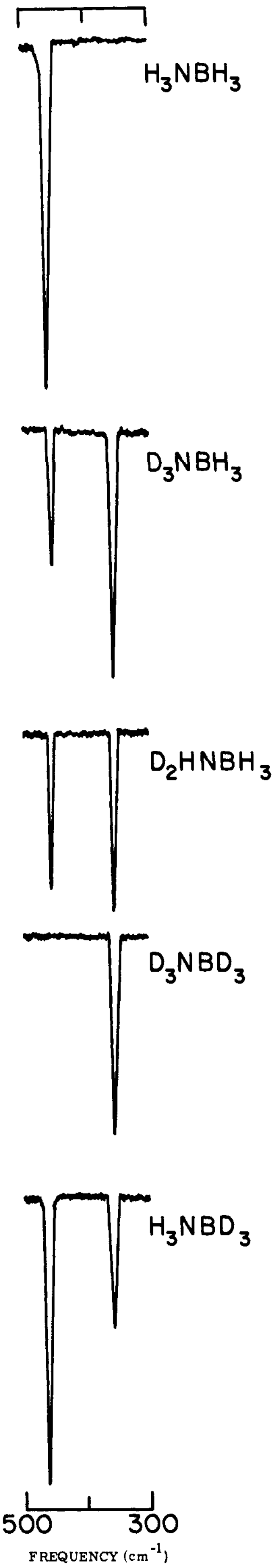

Figure 3. Low-frequency region of the imidoborane infrared spectrum with isotopically labeled photolysis precursors as indicated.

Table III. Comparison of Monomer and Trimer Bond Force Constants[a] for a Series of Isoelectronic Molecules

Monomer		Trimer		(Monomer − trimer)/monomer
HNBH	13.14	$H_3N_3B_3H_3$	5.46[b]	0.58
HBO	14.0[c]	$H_3B_3O_3$	5.64[d]	0.60
HCN	17.9[e]	$H_3C_3N_3$	9.69 or 8.26[f]	0.54 or 0.46
HNC	16.4[g]			
HCCH	15.8[h]	C_6H_6	7.83[i]	0.51

[a] 10^5 dyn/cm^{-1}. [b] K. E. Blick, J. W. Dawson, and K. Niedenzu, *Inorg. Chem.*, **9**, 1416 (1970). [c] E. R. Lory and R. F. Porter, *J. Amer. Chem. Soc.*, **93**, 6301 (1971). [d] F. A. Grimm, L. Barton, and R. F. Porter, *Inorg. Chem.*, **7**, 1315 (1968). [e] G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, Van Nostrand, Princeton, N. J., 1945, p 174. [f] J. E. Lancaster, R. F. Stamm, and N. B. Colthup, *Spectrochim. Acta*, **17**, 155 (1961). [g] D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **47**, 278 (1967). [h] Footnote *e*, p 180. [i] B. L. Crawford, Jr., and F. A. Miller, *J. Chem. Phys.*, **17**, 249 (1949).

---

(9) The bending frequency for $H^{11}BO$ is 754 cm^{-1}.[1] It is possible that in HNBH the second bending vibration ν_5, which is mostly a B–H motion, is higher than ν_4 and the order of numbering of the vibrational modes should be reversed.

(10) E. D. Becker and G. C. Pimentel, *J. Chem. Phys.*, **25**, 244 (1956).

pared with borazine agrees with predictions from electron density calculations by LaBarre.[11]

Consideration of the band structure appearing at 3675 and 2035 cm^{-1} after prolonged photolysis of H_3NBH_3 has led to the assignment of these bands to the species HNB. We have listed in Table IV locations of shifted bands with isotopic substitution in the precursor molecule. The band at 2035 cm^{-1} was generally about the same intensity as the band at 3675 cm^{-1}, but the two bands gained in intensity relative to the HNBH spectrum with irradiation time. Calculated frequencies were determined by solving for the two Σ^+ force constants for a linear HNB molecule from three sets of observed frequencies: 3675 and 2035 cm^{-1} ($H^{14}N^{11}B$), 3675 and 2095 cm^{-1} ($H^{14}N^{10}B$), 3664 and 2009 cm^{-1} ($H^{15}N^{11}B$). Agreement between experimental and calculated frequencies (Table IV) was excellent. Force constant values obtained were 7.38 and 15.72 × 10^5 dyn cm^{-1}. The bending vibration for HNB was not observed. This frequency may be masked by the strong absorption band in HNBH near 460 cm^{-1}. The H–N frequencies of the radical and imidoborane are very close but the multiple bond frequencies and force constants differ significantly with the radical containing the stronger N–B bond. Unfortunately comparable data for the acetylene derived radical, HC_2, are not available. Only one assigned band at 1848 cm^{-1} has been reported for this species.[12] An *ab initio* calculation by Lather, *et al.*,[13] reports a C–C bond length in HC_2 slightly longer than that in acetylene. This result suggests a decrease in the C–C force constant upon hydrogen atom loss, unlike that observed for the boron–nitrogen analogs.

Table IV. Frequencies (cm^{-1}) for Σ^+ Vibration of HNB in Ar Matrices

Isotopic species	ν_1 Obsd	ν_1 Calcd	ν_2 Obsd	ν_2 Calcd
$H^{14}N^{11}B$	3675	3675	2035	2035
$H^{14}N^{10}B$	3675	3675	2095	2093
$H^{15}N^{11}B$	3664	3663	2009	2011
$H^{15}N^{10}B$		3663	2064	2069
$D^{14}N^{11}B$	2770	2762	1963	1953

The observed frequencies and force constants for the radical HNB are very similar to those reported for HNC (7.38 and 15.72 *vs.* 7.10 and 16.40 × 10^5 dyn cm^{-1} for HNC).[8] This species, produced by the vacuum photolysis of HCN, is "expected to be formed by cage recombination of photolytically produced H + CN."[8] A similar situation may be the case with HNB. Mosher and Frosch[6] produced high concentrations of monomeric BN in neon matrices but observed the species only once in argon. It was suggested that neon with a high permeability to hydrogen atoms permitted diffusion away from the photolysis site, leaving BN behind. Consequently, argon and xenon matrices would be favored to produce higher concentrations of HNB by this mechanism. If this is the case, it appears that HNB is thermodynamically favored over NBH. The results of this study, however, do not rule out the sequential photolysis of ammonia–borane first to produce HNBH and then HNB without BN as an intermediate. If sequential photolysis describes the system, it can be concluded that HB bonds in HNBH are selectively photolyzed over HN bonds.

Hydrogen atoms have been observed in preliminary esr spectra of the photolysis products of ammonia–borane in neon, argon, nitrogen, and xenon matrices. However, the NH_2 radical was present in high concentration, presumably produced from ammonia following the partial decomposition of ammonia–borane.[14] It is not expected that hydrogen atoms were present in sufficient quantity to react with any BN present to form the radical HNB. The esr spectrum of a boron-containing radical was observed, but assignment of this spectrum to HNB was not justifiable assuming that the odd electron is mainly σ in character.

The broad absorption at 1370 cm^{-1} observed in experiments with large conversions of precursor to photolysis products could be polymeric BN since no deuterium shift was observed. Infrared absorption which could be attributed to isolated monomeric BN was not observed.

The spectra of the photolysis products of borazine (Figure 2) consist of a surprisingly small number of bands. The H–N stretch region of the spectrum contains two bands very close to the frequencies observed for HNBH and HNB. At least three sharp bands are evident in the 2000 cm^{-1} region, overlapping the BN stretch of the radical, and two absorptions around 500 cm^{-1}. Although no assignment appears possible from these spectra, several conclusions about the species can be made. The almost exact coincidence of the bands in the H–N region and the HNB radical stretch indicate a HNB group is present in the molecule. The multiplicity of the bands around 2050 cm^{-1} suggests BN multiple bonds. The absence of absorptions in the ring motion region of the borazine spectrum (1450 cm^{-1}) leads to the conclusion that the ring has been opened. Consequently, the product molecule appears to be a chain of alternating boron and nitrogen atoms, multiply bonded, with at least one end containing a HNB group. The extent of coupling due to the presence of ^{10}B and ^{11}B atoms in the species is evident from the spectra (Figure 2). The total number of hydrogen atoms in the molecule is unknown, but several must have been lost to raise the bond order to a value comparable with that observed. The spectrum of this photolysis product and that of B_2O_3 in argon matrices,[15] an alternating boron–oxygen chain, are quite similar. The bending frequencies reported for B_2O_3 (454, 477, and 518 cm^{-1}) are close to the two frequencies (495 and 508 cm^{-1}) observed in this study. However, the coincidence of symmetric and antisymmetric BO frequencies observed in B_2O_3 at 2060 cm^{-1} apparently does not occur in the borazine photolysis product since a multiplicity of bands is observed in the BN stretching region. It is evident by comparison of the photolysis products of borazine with those from the ammonia–

---

(11) J. LaBarre, M. Graffeuil, J. Faucher, M. Pasdeleloup, and J. Laurent, *Theor. Chim. Acta*, **11**, 423 (1968).

(12) D. E. Milligan, N. E. Jacox, and L. Abouaf-Marguin, *J. Chem. Phys.*, **46**, 4562 (1967).

(13) W. A. Lather, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971).

(14) P. M. Kuznesof, D. F. Shriver, and F. E. Stafford, *ibid.*, **90**, 2557 (1968).

(15) A. Sommer, D. White, M. J. Linevsky, and D. E. Mann, *J. Chem. Phys.*, **38**, 87 (1963).

borane that borazine does not photolyze, under the conditions of the experiment, to the monomeric imidoborane.

Acknowledgment. We are grateful for support by the National Science Foundation and Advanced Research Projects Agency through the Materials Science Center at Cornell University and the Army Research Office-Durham. We appreciate the help of Professor J. Freed in the esr experiment and Mr. Alan Kilby in programming the calculations of force constants.

Microwave Studies on the Structure and Hydrogen Bonding in 6-Hydroxy-2-formylfulvene[1]

Herbert M. Pickett

Contribution from the Harvard University Chemical Laboratories, Cambridge, Massachusetts 02138. *Received August 25, 1972*

Abstract: The microwave spectrum of 6-hydroxy-2-formylfulvene has been studied in order to determine the symmetry of the molecule and the nature of its hydrogen bond. The nuclear spin statistics observed for the normal isotopic species and the species with a deuterated hydroxyl group in ground and vibrationally excited states put a lower limit of 2×10^{12} sec^{-1} for any rate for tautomerization between asymmetric forms. The data are consistent with a model in which the molecule has C_{2v} symmetry with the proton centered in the hydrogen bond. An anomalous deuterium isotope effect on the moments of inertia indicates the O–H stretching motion is mixed with O–O symmetric stretching motion to yield changes in O–O distance upon deuteration similar to that observed previously for other systems using X-ray techniques.

For some time there has been considerable interest in hydrogen bonding and in the rates of interconversion among hydrogen-bonded tautomeric species. The recently prepared and characterized compound[2,3] 6-hydroxy-2-formylfulvene (HFF, see Figure 1) seemed to be an excellent candidate for a study of hydrogen bonding and tautomerization, especially since the molecule is large enough so that the OHO system can be linear. It is of particular interest to determine whether the symmetric nonclassical structure has least energy or whether it is an intermediate in a tautomeric rearrangement between equivalent asymmetric structures of lower energy.

Experimental Section

A sample of 6-hydroxy-2-formylfulvene was prepared by Mr. Timothy McKeithan and Dr. David Mendenhall following published procedures.[1] The sample was sublimed into the sample tube under vacuum and used without further purification. The singly deuterated species (at the hydroxyl hydrogen) was prepared from 6-dimethylamino-2-(*N*,*N*-dimethylformimmonium)fulvene perchlorate, an intermediate in the synthesis of the parent compound, as follows. A 4 *M* solution of NaOH in 1 ml of D_2O was added dropwise to 0.37 g of this perchlorate salt in 1 ml of D_2O. When addition was complete, nitrogen was bubbled through the solution while heating to 50°. When no more dimethylamine was evolved, the solution was cooled and then acidified with 1 *M* D_2SO_4 in D_2O. The precipitated product was filtered off and sublimed into a sample tube. Spectra were taken after preseasoning the sample cell with D_2O.

Broad-banded gas-phase microwave spectra in the region 26.5 to 40 GHz were recorded at room temperature on a Hewlett-Packard 8400C spectrometer at the Arthur D. Little Co. and on a Hewlett-Packard 8460A spectrometer at Harvard. More detailed studies of selected lower frequency regions were done at Harvard using standard Stark spectrometers.

Spectral Analysis. The HFF molecule is large compared to many molecules studied by microwave spectroscopy, and one may expect that the rotational energy spacings will be closer. Because there are more rotational energy levels populated at room temperature, the spectrum will be richer and individual lines will be less intense. The most intense lines will be those originating from states of high total angular momentum, J, primarily because of the $2J + 1$ degeneracy of states which differ only in spatial orientation of the angular momentum. Conventionally, microwave spectra have been assigned with the aid of the electric field Stark effect which splits the degenerate states into $J + 1$ different levels. The intensity is divided among the components, and it is often impractical for this and other technical reasons to assign the high J lines by their Stark effect. Thus, one is forced to rely on the use of patterns in position and intensity of the lines. Once an assignment is made, the lines must fit the very over determined rotational Hamiltonian within an experimental accuracy which is typically 0.1 MHz or 0.0003%. This Hamiltonian may include centrifugal distortion effects, but for large and moderately rigid molecules these effects can be safely neglected in many cases.

The approach to an assignment used here was to recognize that at high J many of the rotational energies are represented quite successfully by perturbation theory expansions from either a prolate or oblate symmetric rotor, even though the shape of the molecule is not close to either limit.[4] Generally, if the rotational energy is greater than $BJ(J + 1)$, or equivalently $E(\kappa) \gg J(J + 1)\kappa$, the prolate limit applies. If the converse is true, the oblate limit applies. Thus, levels for which K_{-1} is small are well represented in the oblate limit, even for quite prolate molecules. For a planar molecule such levels involve rotation almost exclusively around an axis perpendicular to the plane, and rotational transitions from them can be expected to have the largest intensity. (Classically this is because the rotating component of the dipole moment is largest.) For a $\Delta J = 1$, $\Delta K_{+1} = 1$ transition, the zero-order oblate-top expression for the resonant frequency is

$$\nu = (A + B)J' + (2C - A - B)(K'_{+1} - 1/2) \quad (1)$$

---

(1) Supported in part by a grant extended to Harvard University by the National Science Foundation, GP-14012X, and by a National Institutes of Health Postdoctoral Fellowship during 1970. Portions of these results were presented at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, Sept 1970, and at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.

(2) K. Hafner, K. H. Vopel, G. Ploss, and C. Konig, *Justus Liebigs Ann. Chem.*, 661, 52 (1963).

(3) K. Hafner, H. E. A. Kramer, H. Musso, G. Ploss, and G. Schultz, *Chem. Ber.*, 97, 2066 (1964).

(4) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York, N. Y., 1955, Chapter 4.