

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

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Microwave Studies on the Structure and Hydrogen Bonding in 6-Hydroxy-2-formylfulvene¹

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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 $2 \times 10^{12} \text{ sec}^{-1}$ 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 D₂O was added dropwise to 0.37 g of this perchlorate salt in 1 ml of D₂O. 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* D₂SO₄ in D₂O. The precipitated product was filtered off and sublimed into a sample tube. Spectra were taken after preseasoning the sample cell with D₂O.

(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 Liebig's Ann. Chem.*, **661**, 52 (1963).

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

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

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

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

Table I. Observed Frequencies, MHz

Transition	HFF-gnd	HFF-exctd	d-HFF-gnd
6 _{2,4} -5 _{2,3}	17,433.40 (0.11) ^a		
8 _{0,8} -7 _{0,7}	17,444.70 (0.14)	17,457.00 (0.24)	
8 _{1,8} -7 _{1,7}	17,438.90 (0.07)	17,451.20 (0.06)	
8 _{3,5} -7 _{3,4}	23,494.40 (0.14)		
8 _{5,3} -7 _{5,2}	22,051.10 (-0.09)		
9 _{0,9} -8 _{0,8}	19,493.80 (0.06)	19,507.60 (-0.04)	
9 _{1,9} -8 _{1,8}	19,491.80 (-0.01)	19,505.80 (0.06)	
9 _{2,7} -8 _{2,6}	24,045.90 (0.08)	24,052.20 (0.32)	
9 _{3,6} -8 _{3,5}	26,186.05 (0.02)		
9 _{4,5} -8 _{4,4}	26,228.70 (0.11)	26,258.00 (0.15)	
9 _{5,4} -8 _{5,3}	25,133.20 (-0.38)	25,161.60 (-0.20)	
10 _{1,0} -9 _{1,0}	21,544.30 (0.14) ^a		
10 _{1,9} -9 _{1,8}	23,624.70 (0.13)		
10 _{2,9} -9 _{2,8}	23,598.10 (0.14)	23,611.75 (0.08)	
10 _{2,8} -9 _{2,7}	25,931.65 (-0.02)	25,939.40 (-0.21)	
10 _{3,8} -9 _{3,7}	25,563.60 (0.00)	25,577.80 (0.06)	
10 _{3,7} -9 _{3,6}	28,515.40 (-0.07)	28,525.20 (-0.08)	
10 _{4,7} -9 _{4,6}	27,024.50 (0.00)	27,042.50 (-0.09)	
10 _{4,6} -9 _{4,5}	29,439.15 (-0.05)	29,466.60 (0.00)	
10 _{5,6} -9 _{5,5}	27,576.60 (0.08)		
10 _{5,5} -9 _{5,4}	28,414.10 (0.15)	28,448.70 (0.00)	
10 _{6,5} -9 _{6,4}	27,494.05 (0.06)		27,124.00 (0.00)
10 _{6,4} -9 _{6,3}	27,593.80 (-0.07)		27,218.50 (-0.66)
10 _{8,-} 9 _{8,-}			26,784.00 (-0.65) ^a
11 _{1,1} -10 _{1,0}	23,595.60 (0.08) ^a	23,612.85 (0.08) ^a	
11 _{1,10} -10 _{1,9}	25,663.75 (0.03)	25,678.80 (0.08)	
11 _{2,10} -10 _{2,9}	25,653.70 (-0.04)	25,669.00 (0.01)	
11 _{2,9} -10 _{2,8}	27,861.05 (-0.19)	27,871.75 (-0.29)	
11 _{3,9} -10 _{3,8}	27,685.32 (-0.04)		
11 _{7,5} -10 _{7,4}	30,164.95 (-0.16) ^c		
11 _{9,-} 10 _{9,-}	29,837.65 (-0.35) ^{a,b}		
11 _{10,-} 10 _{10,-}	29,743.50 (-0.60) ^{a,b}	29,770.17 (-0.81) ^{a,b}	
12 _{1,2} -11 _{1,1}	25,647.00 (-0.01) ^a	25,666.00 (0.08) ^a	25,327.64 (0.07) ^a
12 _{1,11} -11 _{1,10}	27,709.33 (-0.09)	27,726.10 (-0.08)	27,364.60 (0.11)
12 _{2,11} -11 _{2,10}	27,705.71 (-0.10)	27,722.60 (-0.08)	27,360.90 (0.14)
12 _{2,10} -11 _{2,9}	29,843.42 (-0.11)		
12 _{3,10} -11 _{3,9}	29,766.85 (-0.02)	29,781.90 (-0.19)	
12 _{7,6} -11 _{7,5}	33,069.30 (-0.30) ^{b,d}		
12 _{7,5} -11 _{7,4}	33,144.60 (-0.30) ^{b,d}		
13 _{1,3} -12 _{1,2}	27,698.55 (-0.01) ^a	27,719.20 (0.07) ^a	27,353.60 (0.03) ^a
13 _{1,12} -12 _{1,11}	29,757.90 (-0.08)	29,776.30 (-0.15)	29,387.40 (-0.06)
13 _{2,12} -12 _{2,11}	29,756.65 (-0.07)	29,775.15 (-0.08)	29,386.00 (-0.15)
13 _{8,6} -12 _{8,5}	35,720.00 (-0.37) ^{b,e}		
13 _{8,5} -12 _{8,4}	35,737.15 (-0.52) ^{b,e}		
14 _{4,11} -13 _{4,10}	22,059.70 (0.06)		
14 _{8,11} -13 _{8,10}	21,921.60 (-0.06)		
14 _{1,14} -13 _{1,13}	29,750.10 (-0.05) ^a	29,772.30 (-0.08) ^a	29,379.60 (0.0) ^a
14 _{1,13} -13 _{1,12}			31,411.50 (-0.07) ^a
14 _{8,7} -13 _{8,6}	38,646.83 (-0.47) ^{b,e}		
14 _{8,6} -13 _{8,5}	38,702.31 (-0.53) ^{b,e}		
14 _{9,6} -13 _{9,5}			37,855.30 (0.25) ^f
14 _{9,5} -13 _{9,4}			37,857.90 (-0.49) ^f
15 _{1,5} -14 _{1,4}			31,405.90 (0.24) ^a

^a Observed - calculated using constants of Table II; errors in experimental frequencies estimated at ~ 0.1 MHz. ^b Not used in fit. ^c RFMDR, 7-MHz pump. ^d RFMDR, 30-MHz pump. ^e RFMDR, 23-MHz pump. ^f RFMDR, 4.3-MHz pump. ^g Intensity weighted average.

in which the primes denote the values for the upper level of the transition. Substitution of $J' = J_0 - n$ and $K'_{+1} = J_0 - 2n$ yields

$$\nu = C(2J_0 + 1) + (A + B - 4C)(n + 1/2) \quad (2)$$

The reason for this rearrangement comes from the fact that $A + B - 4C$ is zero for oblate planar symmetric-top molecules and is often a small number for planar, or near planar, asymmetric-top molecules since in planar molecules $I_a + I_b = I_c$. Therefore, we should expect these low K_{-1} transitions to cluster at frequencies which are odd multiples of the C rotational constant. The transitions can be further identified from the Stark effect since it will not be strong for these transitions unless there is a permanent dipole moment component along the c axis coupling the near oblate degeneracies, a possibility which is excluded for a planar molecule.

From the broad-banded spectrum of HFF we were able to find a series of strong lines with a weak Stark effect which were spaced equally at close to twice the expected value of C . Subsequent

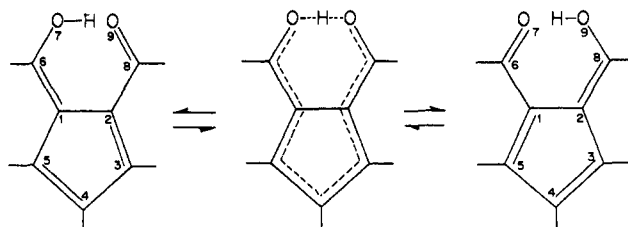


Figure 1. 6-Hydroxy-2-formylfulvene.

microwave-microwave double resonance studies^g of lines in this series at 25647.0 and 27698.55 MHz showed that indeed the tran-

(5) R. C. Woods III, A. M. Ronn, and E. B. Wilson, *Rev. Sci. Instrum.*, **37**, 927 (1966).

Table II. Rotational Constants

	HFF-gnd	HFF-exctd	d-HFF-gnd
<i>A</i>	2816.401 ± 0.02, ^a MHz	2812.340 ± 0.06	2786.574 ± 0.1
<i>B</i>	1613.434 ± 0.003	1614.719 ± 0.007	1591.607 ± 0.01
<i>C</i>	1025.852 ± 0.003	1026.681 ± 0.004	1013.075 ± 0.003
<i>κ</i>	-0.34368		
<i>I_a</i>	179.440, amu Å ²	179.699	181.361
<i>I_b</i>	313.230	312.981	317.526
<i>I_c - I_a - I_b</i>	-0.030	-0.438	-0.033

^a Random errors—95% confidence limits.

sitions shared a common energy level and were consistent with an assignment to the 12₁₂-11₁₁ and 13₁₃-12₁₂ transitions, respectively. As might be expected from eq 2, these transitions are sensitive to *C* and to the degree of planarity but are not very sensitive to the width to length ratio of the molecule. An isolated strong transition at 27,024.5 MHz was reasonably assigned to only two possibilities both of which were sensitive to this ratio. Only when it was assigned as the 10_{4,7}-9_{4,6} transition, did other lines of higher *K*₋₁ appear near where predicted. The identity of seven of these lines was confirmed with radio frequency-microwave double resonance.⁶

There are apparently several sets of rotational spectra associated with thermally populated excited vibrational states. Only one such set had sufficient intensity to be completely assigned. From relative intensity measurements, this vibrational state is 150 ± 20 cm⁻¹ above ground state. The assignment of this vibrational-state spectrum and also the spectrum of the deuterated species proceeded essentially the same as for the parent ground-state molecule. The observed transitions are listed in Table I and the rotational constants obtained from a rigid rotor fit are listed in Table II. The fit is quite good, and all deviations which are significant relative to an experimental error of 0.1 MHz have a behavior characteristic of centrifugal distortion. Since no deviation is greater than 1 MHz, no fit including centrifugal distortion was attempted.

Nuclear Spin Statistics. If the stable molecular conformation is the symmetric form, the molecule will have *C*_{2v} symmetry and the requirements of exchange symmetry on the total wave function must be considered. A rotation of 180° about the symmetry axis exchanges two pairs of equivalent protons as well as a pair of oxygen atoms and three pairs of carbon atoms. The total wave function must, therefore, be symmetric with respect to the twofold rotation.⁷ Each pair of protons will have three symmetric nuclear spin functions and one antisymmetric nuclear spin function for a total of 3 × 3 + 1 × 1 = 10 symmetric nuclear spin functions and 3 × 1 + 1 × 3 = 6 antisymmetric nuclear spin functions. The symmetric rotational states will be those with an even value of *K*₋₁ since for HFF the *C*₂ axis will be coincident with the *a* axis.⁴ Vibrational states with *B*₁ or *B*₂ symmetry are by definition antisymmetric, while states with *A*₁ (including the ground state) or *A*₂ symmetry are symmetric. Therefore, transitions from odd rotational states in the ground vibrational state will have an intensity which is 6/10 as strong as expected relative to even rotational states. In contrast, transitions from odd rotational states in excited vibrational states of odd symmetry will be 10/6 stronger than expected on the basis of the even states.

If the stable conformation is asymmetric, the potential will have two equivalent minima. If the barrier in the potential between the two equivalent minimum energy forms is high, the ground vibrational state will be nearly degenerate with a state of *B*₁ symmetry, the two forming an "inversion" pair. Both the vibrationally averaged rotational constants and the populations will be nearly identical for the two vibrational states, the rotational transitions for the two states will superimpose, and the resultant spectrum will show no evidence of nuclear spin statistics. For intermediate barriers, the inversion splitting is larger, leading to a difference in population between the states. In addition, the effective rotational constants will be slightly different.

The observed spectrum of HFF for the parent and deuterated species agrees with the 6/10 ratio of odd/even expected for a symmetric structure within an estimated error of 10%. Pairs of transitions of low *K*₋₁ which would be degenerate in the oblate limit form good tests of this ratio, because they are close together and

have the same intensities and Stark modulation characteristics. Because of uncertainties associated with interferences with nearby lines, the ratio observed experimentally could be as high as 0.7. A vibrationally excited state of *B*₁ or *B*₂ symmetry which has a rotational spectrum unresolved from the ground state causes the ratio of intensities to deviate from 6/10 in the direction of unity. Therefore, these experimental data put a lower limit of 150 cm⁻¹ on the energy of an excited vibrational state of *B*₁ or *B*₂ symmetry, provided it has the same rotational constants as the ground state.

The assigned excited vibrational state also has the intensity ratio expected of an *A*₁ or *A*₂ vibrational state. Its intensity relative to the ground state puts the vibrational energy at 150 ± 20 cm⁻¹. In the deuterated species, a vibrationally excited-state spectrum similar in position and intensity is observed. In the parent compound we have searched near the 13₁₃-12₁₂ for unassigned strong lines and have found none which are greater than half the intensity of this line. These observations put a less qualified lower limit of 150 cm⁻¹ on the energy of an excited vibrational state.

Structure. From the sum *I_c - I_a - I_b* in Table II, we may immediately conclude that HFF is planar. The residual mass-weighted mean square out-of-plane displacement of 0.015 amu Å² is most likely the result of vibrational motion. Nonetheless, the six moments of inertia obtained from the spectra of the parent and deuterated species provide too little data to completely determine the structure of HFF. The data can be used to determine, nonetheless, whether an assumed structure is consistent. For the geometry of an asymmetric form, we used the bond angles and bond lengths determined by electron diffraction for 6,6-dimethylfulvene.⁸ In addition, parameters for the carbonyl group and the hydroxyl group were taken from formic acid.⁹ Finally, the angle of the formyl group relative to the ring was adjusted so that the O-O distance was 2.44 Å (or 2.64 Å) and the OHO angle was assumed to be 180°. From Table III it will be noted that the angle of the formyl group is not far from the angle the corresponding CH bond makes with the ring in dimethylfulvene (119°). Also the assumption of OHO linearity leads to reasonable values for the HOC angle. For the symmetric form, we averaged the equivalent bond angles and distances from the asymmetric form. In this case, the angles that both side groups made with the five-membered ring were varied so as to obtain the required O-O distances. Comparison of the calculated moments of inertia in Table III with the experimental moments in Table II shows that best agreement is with a symmetric structure with an O-O distance near 2.5 Å. However, an asymmetric structure with a similar O-O distance should not be excluded on these grounds alone.

The deuterium isotope data should allow us to calculate the position of the substituted hydrogen using equations developed by Kraitchman.¹⁰ The hydrogen coordinates determined this way are 2.055 and 1.408 Å for the components along the *a* and *b* axes, respectively. The value of 2.055 Å is in good agreement with that expected for the asymmetric form (1.972 Å) or the symmetric form (1.998 Å). The *b* coordinate is the distance from the *C*₂ axis for the symmetric form and must be zero for this case. For the asymmetric form the calculated value is 0.372 Å, hardly the large value observed. The anomalously large value of 1.408 Å can be explained by examining the derivation of Kraitchman's equations. The moment of inertia about the *a* axis for a planar molecule is

$$(I_a)_H = \sum m_i (r_b)_i^2 \quad (3)$$

in which *m_i* is the mass of atom *i* and (*r_b*)_{*i*} is the *b* coordinate of the

(6) F. J. Wodarczyk and E. B. Wilson, *J. Mol. Spectrosc.*, **37**, 445 (1971).

(7) E. B. Wilson, *J. Chem. Phys.*, **3**, 276 (1935).

(8) J. F. Chiang and S. H. Bauer, *J. Amer. Chem. Soc.*, **92**, 261 (1970).

(9) R. G. Lerner, B. P. Dailey, and J. P. Friend, *J. Chem. Phys.*, **26**, 680 (1957).

(10) J. Kraitchman, *Amer. J. Phys.*, **21**, 17 (1953).

Table III. Assumed Structures and Calculated Moments of Inertia

	Asymmetric	Symmetric
O ₇ O ₉	2.440 (2.640), Å	2.440 (2.640), Å
C ₁ C ₂	1.476	1.476
C ₂ C ₃	1.340	1.408
C ₁ C ₅	1.476	1.408
C ₃ C ₄	1.462	1.401
C ₅ C ₄	1.340	1.401
C ₆ C ₁	1.347	1.412
C ₅ C ₂	1.476	1.412
O ₇ C ₆	1.312	1.278
O ₉ C ₈	1.244	1.278
HO ₇	0.950	1.220 (1.320)
HC	1.10	1.10
C ₂ C ₁ C ₅	105.56°	106.72°
C ₁ C ₂ C ₃	107.88	106.72
C ₂ C ₃ C ₄	109.34	108.61
C ₁ C ₅ C ₄	107.88	108.61
C ₃ C ₄ C ₅	109.34	109.34
C ₆ C ₁ C ₅	127.22	125.25 (122.77)
C ₈ C ₂ C ₃	123.28(118.23)	125.25 (122.77)
O ₇ C ₆ C ₁	124.30	124.30
O ₉ C ₈ C ₂	124.30	124.30
HO ₇ C ₆	109.02 (107.23)	107.67 (105.19)
(I _a) _H	177.45 (189.62), amu Å ²	178.27 (190.54), amu Å ²
(I _b) _H	314.12 (309.44)	313.24 (308.60)
(I _a) _D	177.59 (189.86)	178.27 (190.54)
(I _b) _D	318.00 (313.23)	317.23 (312.54)

molecule in the center-of-mass, principal-axis system. Neglecting effects due to changes in the center of mass and principal axes, which are small for HFF, the moment of inertia for the deuterated species is

$$(I_a)_D = \sum m_i (r_b)_i^2 \quad (4)$$

If, upon deuteration, all r_b are constant and only the mass of the substituted atom changes, then eq 3 can be subtracted from eq 4 to yield the coordinate of the substituted atom. This is essentially the approach of Kraitchman. On the other hand, if the vibrationally averaged r_b for the two oxygen atoms were to change upon deuteration, the difference in the moments of inertia will reflect this change as well. By allowing only changes in r_b for the two oxygen atoms, we can get the calculated moments of inertia to agree almost precisely with the experimental values. With this adjustment, the O-O distance changes from 2.470 to 2.518 Å upon deuteration, and with such a change the value of r_b for the proton could be close to zero. This is not to say that the proton or the other heavy atoms do not change position upon deuteration as well, but the particular assumption used here provides an illustration of the small changes in coordinate required and does have some substantiation in the X-ray crystallographic data on hydrogen-bonded systems.¹¹ Since the anomaly is only in the r_b coordinate, the change upon deuteration should be primarily along the b direction, and some sort of change in O-O distance seems most reasonable. It should be noted in passing that the anomaly cannot be resolved by assuming that only the average hydrogen coordinate changes upon deuteration.

Discussion

The results presented in this paper touch on two related questions. The first is concerned with whether the heavy atoms are in a symmetric form at the minimum in the potential. The second is concerned with the nature of the hydrogen bond in this compound.

The microwave intensity data presented here puts a lower limit of 150 cm⁻¹ on any transition frequency from the ground vibrational state to an excited state of odd C₂ symmetry. If the reaction coordinate for tautomerization (which has odd C₂ symmetry) has a

(11) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, p 104.

symmetric double minimum potential, then this limit applies to the inversion splitting and a lower limit on the tautomerization rate can be placed at 2×10^{12} sec⁻¹. It is difficult to convert this limit to a limit on barrier height without exact knowledge of the nature of the reaction coordinate or the shape of the barrier. For a pure hydrogen OH stretching motion within a symmetric framework of heavy atoms, a barrier as high as 1500 cm⁻¹ above ground state cannot be ruled out.¹² On the other hand, if we take as the reaction coordinate, q , one which goes from a reasonable asymmetric structure ($q = \pm 1$) to a symmetric form ($q = 0$) which has bond angles and distances as close as possible to the asymmetric forms, then one can calculate¹³ a reduced mass for the coordinate of 2.1 amu Å². Using WKB formulas,¹⁴ and this mass with any reasonable barrier shape, it is difficult to see how the barrier could extend much above the ground vibrational level. Therefore, the microwave data suggest that structures with a symmetric heavy atom configuration have low energy. It is possible that more asymmetric structures could have lower energy, but if this is the case, the symmetric form barrier will be on the order of the vibrational zero-point energy. Unfortunately, such low barriers are difficult to determine without extensive vibrational data. The effective symmetry of the molecule is supported by nmr data,³ although the limits on rates imposed by nmr are of course much looser.

The hydrogen-bonding ring in this compound has the same number of atoms as the hydrogen maleate ion. A neutron-diffraction study of the latter has shown that the hydrogen atom is located centrally in the hydrogen bond with an OO distance of 2.44 Å.¹⁵ As discussed above, our assumptions about the structure of HFF require that the OO distance be close to that in the hydrogen maleate ion, and our intensity data are consistent with a symmetric hydrogen bond. At present, the only observed difference in hydrogen bonding between the two compounds appears in the infrared spectrum. The hydrogen maleate ion shows no change upon deuteration above 1600 cm⁻¹,¹⁶ while in HFF a broad band at 2850 cm⁻¹ disappears upon deuteration.³ If the band in the latter is assigned to an OH stretch, the correlations of Rundle¹⁷ (which should include this type of linear intramolecular hydrogen bond) would lead to an estimate for an OO bond length of 2.7 Å. It is most difficult to propose a reasonable structure of HFF which has an OO bond length of 2.7 Å and is at the same time in agreement with the observed moments of inertia. On the other hand, it is possible that the 2850-cm⁻¹ band is due to water, and the infrared measurements should be repeated with appropriate precautions. The OO bond distance should be checked by microwave studies of the ¹⁸O species or perhaps by diffraction techniques.

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(17) K. Nakamoto, M. Margoshes, and R. E. Rundle, *J. Amer. Chem. Soc.*, **77**, 6480 (1955).

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for making available the Hewlett-Packard 8400C microwave spectrometer used in some of the investigations.

Electronic Spectra of the Various Hydrogen-Bonded Species of Pyrazine in a Mixed Hydroxylic Solvent

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Abstract: The 77°K phosphorescence, phosphorescence excitation, and absorption spectra of pyrazine in ethanol with up to 0.2 mol fraction water are presented. The phosphorescence origin of pyrazine in pure ethanol lies at 26,290 cm^{-1} . For pyrazine in an ethanol-water solvent two additional phosphorescent systems with origins at 26,620 and 27,370 cm^{-1} appear. These are assigned as due to pyrazine hydrogen bonded with one and two water molecules, respectively. All three species are found to have lifetimes of less than 21 msec indicating lowest triplet states of $n\pi^*$ character for each. The excitation spectra of the three species are presented. These spectra indicate that upon going from one species to another the shifts in the singlet-singlet and singlet-triplet $n \rightarrow \pi^*$ transition energies are identical. The nature of the shifts upon going from one species to another is discussed. The phosphorescence quantum yield of the hydrated species is found to be less than that of the unhydrated species. Deuteration of the solvent has an enhancing effect on the phosphorescence quantum yield of the hydrated species but does not effect the yield of the unhydrated species.

Solvent shifts of the $n \rightarrow \pi^*$ transitions of azines and ketones have been investigated by many workers.¹⁻⁵ These transitions generally show a blue shift on changing from a hydrocarbon to a hydroxylic solvent. Brealey and Kasha have examined the change in the $n \rightarrow \pi^*$ absorption spectra of pyridazine and benzophenone in various hexane-ethanol solvent mixtures. Their studies clearly indicated that the blue shift upon addition of alcohol is due to the formation of a hydrogen-bonded complex of the alcohol with the azine or ketone. The blue shift results because the hydrogen bonding are stronger in the ground state than in the excited state. The role of the Franck-Condon principle on the blue shifts was later discussed by Pimentel⁶ and was shown by Krishna and Goodman to be important in the electronic spectra of pyrazine.⁴

In this paper we examine the electronic spectra of pyrazine in a mixed hydroxylic solvent of ethanol and water. We will show that three distinct hydrogen-bonded species exist in this solvent and will present their spectra. This system offers the unique opportunity of examining several hydrogen-bonded complexes of various strengths in the same solvent system. Pyrazine is chosen for study because it is a prototype molecule with well assigned lowest singlet and triplet excited states of B_{3u} ($n\pi^*$) character.^{3,7,8}

Experimental Section

Pyrazine (Aldrich Chemical Co.) was purified by repeated zone melting. Distilled water and absolute ethanol (U. S. Industrial

Chemical Co.) were used without further purification. "Superdry" ethanol was prepared by the method of Lund and Bjerrum.⁹ D_2O (Matheson Coleman and Bell) and CH_3CH_2OD (Stohler Isotope Chemical Co.) were used without further purification. All solutions were placed in quartz tubes and rapidly immersed in liquid nitrogen in optical quartz dewars. Degassing was found to have no effect on the spectra or lifetimes and was not employed in subsequent measurements. It was found that ethanol-water solutions with up to 10% water by volume will form perfect glasses if narrow quartz tubes of 3-4-mm inside diameter are used. The spectra were found to be independent of whether or not the glass cracked.

Excitation and emission spectra were taken on a Baird-Atomic Model SF-1 fluorescence spectrometer. Some emission spectra were also taken on a Jarrell-Ash 0.75-m Czerny-Turner spectrometer (Model 78-460) with exciting light from a 150-W Xenon lamp filtered with a $NiSO_4$ solution and a Corning 754 filter. An RCA 1P28 photomultiplier tube was used with this spectrometer. The absorption spectra were taken on a Cary 15 spectrometer with the samples placed in contact with liquid nitrogen in a quartz dewar.

Lifetimes were measured by using a variable-speed rotating cam to chop the exciting light and sending the decay signal into the Jarrell-Ash monochromator. The signal from the photo tube was displayed on a Textronix 5103 N storage oscilloscope.

Results

Phosphorescence Spectra. The 77°K phosphorescence spectrum of pyrazine in pure ethanol is shown in Figure 1A. The 0,0 band is the most intense band in the spectrum and lies at 26,290 cm^{-1} . We will call this subspectrum I in what follows. The phosphorescent lifetime is 20.5 msec and is consistent with the $^3B_{3u}$ ($n\pi^*$) assignment of the phosphorescent state.

The phosphorescence spectra of pyrazine in ethanol-water mixtures with mole fractions of water of 0.12, 0.17, and 0.22 are shown in Figures 1B-D, respectively. All of the spectra in this figure were excited with continuous radiation below 3300 Å so that all species get excited. We notice the appearance of two new bands to the blue of the origin of subspectrum I. One band is located at 26,620 cm^{-1} (origin of subspectrum II),

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