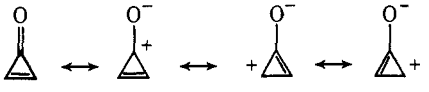
+C=O bond leaving the ring with the diamagnetic $4n + 2$ configuration of electrons. Thus, on first analysis, cyclopropenone should have a more negative $\Delta\chi$ (increased diamagnetism) than cyclopropene, a prediction which is in contrast with the observation. Two factors may be contributing to the lack of large diamagnetism in cyclopropenone. First of all, even in the completely delocalized cyclopropenyl cation, to which cyclopropenone is related, the diamagnetic ring current effects are small. As has been pointed out[19] in connection with the nmr spectra of cyclopropenyl cations, the delocalization of only two π electrons over such a small ring leads to ring-current deshielding effects only 25% of those in benzene.

The second factor is that cyclopropenone is not completely "delocalized;" *i.e.*, it is a hybrid of structures A–D which differ in energy and it is not simply a hybrid of B, C, and D mixed with equal weight.



A B C D

This is apparent from the geometry determined in the present study and from ^{13}C nmr signals (in $CDCl_3$) at -155.1 ppm (C_1) and -158.3 ppm (C_2 and C_3) relative to tetramethylsilane; cyclopropenyl cation has its ^{13}C nmr signal at -174 ppm *vs.* tetramethylsilane.[20] Thus, cyclopropenone cannot be considered to be a cyclopropenyl cation almost unperturbed by the oxide substituent. In fact, our earlier work would suggest that the carbonyl group would act to suppress the diamagnetic anisotropy which could be present in the noncarbonyl substituted parent molecule. Discussion of the delocalization in terms of the above unequal contributions due to the presence of the carbonyl is a situation which has apparently not been treated in detail theoretically, although it is clear that if structure B is lower in energy than structures C and D, the result will be a decreased ring current compared with that in unperturbed cyclopropenyl cation.

It is interesting that by the magnetic criterion "aromaticity" cannot be detected, although aromaticity in cyclopropenone is suggested by its other chemical and physical properties. This again raises the question of the correlation between the different criteria of aromatic character and issues a caution that statements about "aromaticity" should be made only with respect to well-defined criteria and models.

Acknowledgment. We wish to thank J. Pochan, H. Andrist, and G. Ryan for help in the early stages of this work. The support of the National Science Foundation is gratefully acknowledged.

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Microwave Spectrum and Conformation of Formimide

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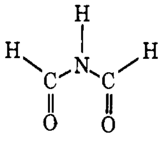
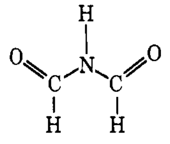
Abstract: The microwave spectrum of formimide and *N*-deuterioformimide has been investigated. Vibrational satellite structure and rotational constants strongly support an asymmetric cis–trans planar structure in the gas phase. An approximate treatment of the observed quadrupole coupling constants gives a C–N double bond character of 66%. A reinterpretation of the infrared spectrum of molten formimide shows that the cis–trans conformer is also preferred in the liquid phase. A cis–trans conformation is consistent with a bond dipole model and with the structures of similar compounds.

Formimide (diformamide, $HN(CHO)_2$) is one of the simplest molecules with an amide bond, a key determinant of protein conformation. The microwave spectrum of formimide was investigated to determine the gas phase conformational properties of this bond. All detailed structural studies to date on amides have shown the bond to be planar (solid state studies)[1-3] or very nearly planar (gas phase studies)[4-6] so formimide can be expected to be approximately planar. Three planar conformers (I–III) are possible in the keto form.



I



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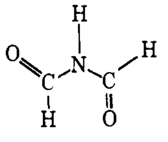

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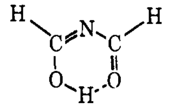

IV

Six rotameric forms of the enol tautomer are possible. Based on published studies of keto–enol isomerism,[7]

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Table I. Fit of Observed Quadrupole Splittings (MHz)

Transition		HN(CHO)$_2$		DN(CHO)$_2$	
J'–J	F'–F	Obsd[a]	$\Delta\nu$[b]	Obsd[a]	$\Delta\nu$[b]
$2_{1,2}$–$1_{0,1}$	3–2	29457.66	0.01	27249.05	−0.03
	2–1	29458.20		27249.60	
$3_{1,3}$–$2_{0,2}$	4–3 2–1	34584.14	0.01	32282.78	0.00
	3–2	34584.86		32283.53	
$4_{1,4}$–$3_{0,3}$	5–4 3–2	39532.86	−0.04	37124.97	0.09
	4–3	39533.60		37125.77	
$8_{0,8}$–$7_{1,7}$	9–8 7–6	31061.07	0.01	32933.29	0.03
	8–7	31060.45		32932.70	
$9_{0,9}$–$8_{1,8}$	10–9 8–7	37696.20	0.01	32489.22	0.06
	9–8	37695.63		32488.72	
$9_{1,8}$–$9_{0,9}$	10–10 8–8	28427.29	0.00		
	9–9	28426.06			
$10_{1,9}$–$10_{0,10}$	11–11 9–9	30932.88	−0.02	30398.02	0.02
	10–10	30931.58		30396.70	
$11_{1,10}$–$11_{0,11}$	12–12 10–10	33803.08	0.01	33667.90	−0.02
	11–11	33801.76		33666.50	
$12_{1,11}$–$12_{0,12}$	13–13 11–11	37052.55	0.00	37360.03	−0.02
	12–12	37051.17		37358.58	
$12_{1,11}$–$11_{2,10}$	13–12 11–10			32650.10	0.03
	12–11			32649.36	
$13_{1,12}$–$12_{2,11}$	14–13 12–11	33751.62	−0.03		
	13–12	33750.84			
$19_{2,17}$–$18_{3,16}$	20–19 18–17	32910.99	0.00		
	19–18	32910.31			
		$\chi_{aa} = 1.88 \pm 0.11$ $\chi_{bb} = 1.53 \pm 0.07$ $\chi_{cc} = -3.41 \pm 0.07$		$\chi_{aa} = 1.65 \pm 0.28$ $\chi_{bb} = 1.69 \pm 0.18$ $\chi_{cc} = -3.34 \pm 0.18$	

χ_{cc} (mean) = −3.39

[a] Reproducible to ±0.05 MHz. [b] $\Delta\nu$ = error in fit of splitting, obsd − calcd.

the internal hydrogen bonded form (IV) is the most likely enol conformer and was used for the initial prediction. The symmetric internal hydrogen bond in structure IV is of interest. Only two molecules with this feature, 6-hydroxy-2-formylfulvene[8] and malonaldehyde,[9] have been studied by microwave spectroscopy. Structures I and II have C_2 symmetry, and IV would be expected to have effective C_2 symmetry due to tunnelling of the hydrogen bonded proton. In these cases the dipole moment would lie along the C_2 (B) axis, yielding a b-type spectrum. Structure III would display both a- and b-type spectra.

Experimental Section

Formimide was prepared according to the method of Allenstein by careful hydrolysis of *N*-dichloromethylformamidinium chloride (DFC) in a K_2CO_3 ether slurry containing a trace of water.[10] DFC was prepared by reaction of anhydrous HCl with HCN dissolved in anhydrous ether.[11] The formamide was recrystallized from ether and was stored in a desiccator over Ascarite. The most likely impurities are formic acid and formamide, the hydrolysis products. Formimide has a room temperature vapor pressure of *ca.* 70 μ. To minimize volatile impurity lines, the sample was introduced into the spectrometer by completely vaporizing small (*ca.* 1 mg) portions.

N-Deuterioformimide was prepared by the exchange of formimide dissolved in D_2O followed by distillation of the excess D_2O and *N*-dideuterioformamide formed by partial hydrolysis of the product. Before making measurements on the deuterated species, the sample cell was preseasoned with D_2O.

R-band measurements were made on a Hewlett-Packard 8460A MRR spectrometer which has been modified to allow microwave–microwave double resonance (mdr) experiments. K, P, and K_u band measurements were made on a conventional Stark modulated spectrometer. Microwave radiofrequency double resonance (mrfdr) experiments were made using the method of Wodarczyk and Wilson.[12]

Assignment

At room temperature the observed spectrum is very rich with lines roughly every 5 MHz. Spectra of formamide and formic acid were used to sort out lines due to these impurities. Rapid scans made at several voltages for the purpose of pattern recognition were not useful in the assignment. The scans did establish that a significant proportion of the lines were fully modulated at low electric fields, ≤100 V/cm. This fact supports structure III, a near prolate top (κ = −0.95) with dipole connected nearly degenerate K doublets. A spectrum based on that structure pre-

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(8) H. Pickett, to be published.

(9) W. Rowe, to be published.

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(11) E. Allenstein, A. Schmidt, and V. Beyl, *ibid.*, **99**, 431 (1966).

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

Table II. Centrifugal Distortion Fit of Observed Frequencies (MHz)

	$HN(CHO)_2$		$DN(CHO)_2$	
Transition	Obsd[a]	$\Delta\nu$[b]	Obsd[a]	$\Delta\nu$[b]
$2_{0,2}-1_{0,1}$	11365.82[d]	0.09		
$2_{1,2}-1_{0,1}$	29457.81	−0.00	27249.19	0.01
$3_{0,3}-2_{0,2}$	17034.18[d]	−0.29		
$3_{1,3}-2_{1,2}$	16492.11[d]	0.17		
$3_{1,2}-2_{1,1}$	17614.70[d]	−0.09		
$3_{2,2}-2_{2,1}$	17058.45[c]	1.20		
$3_{2,1}-2_{2,0}$	17080.08[d]	−0.32		
$3_{1,3}-2_{0,2}$	34584.36	−0.01	32283.01	0.00
$4_{0,4}-3_{0,3}$	22686.61[d,f]	0.28		
$4_{1,4}-3_{1,3}$	21983.30[d]	0.12		
$4_{1,3}-3_{1,2}$	23479.55[d]	−0.04		
$4_{2,3}-3_{2,2}$	22739.02[c,f]	0.49		
$4_{2,2}-3_{2,1}$	22794.54[d]	−0.22		
$4_{1,4}-3_{0,3}$	39533.09	0.01	37125.24	0.01
$5_{0,5}-4_{0,4}$	28315.81[f]	−0.02	28064.93	0.01
$5_{1,4}-4_{1,4}$	27468.67	0.01	27162.76	0.00
$5_{1,4}-4_{1,3}$	29338.38	−0.02		
$5_{2,3}-4_{2,2}$	28528.17	−0.04	28348.32	−0.03
$5_{2,4}-4_{2,3}$	28145.96[f]	−0.03	28198.44	0.02
$5_{3,3}-4_{3,2}$	28447.95[e]	0.10	28240.75[e]	0.09
$5_{3,2}-4_{3,1}$	28448.80[e]	−0.16	33902.46[e]	−0.04
$5_{4,2}-4_{4,1}$ $5_{4,1}-4_{4,0}$	28442.27	−0.05	28233.04	−0.04
$6_{0,6}-5_{0,5}$	33917.80	0.00	33596.73	0.00
$6_{1,5}-5_{1,4}$	35189.51	−0.20	35019.05	0.03
$6_{1,6}-5_{1,5}$	32947.54	−0.01	32575.78	0.02
$6_{2,5}-5_{2,4}$	34088.70	0.04	33824.14	0.04
$6_{2,4}-5_{2,3}$	34284.30	0.00	34084.95	−0.04
$6_{3,4}-5_{3,3}$	34144.22[e]	0.08	33897.69[e]	0.06
$6_{3,3}-5_{3,2}$	34147.00[e]	−0.10	33902.46[e]	−0.04
$6_{4,3}-5_{4,2}$ $6_{4,2}-5_{4,1}$	34134.07[c]	−0.62	33885.14	0.10
$6_{5,2}-5_{5,1}$ $6_{5,1}-5_{5,0}$	34130.79	−0.02	33879.23	−0.05
$7_{0,7}-6_{0,6}$	39487.57	−0.02	39086.65	0.02
$7_{1,7}-6_{1,6}$	38418.80	0.00	37978.88	0.03
$7_{2,6}-6_{2,5}$	39755.60	0.00	39442.01	−0.14
$7_{2,5}-6_{2,4}$			39855.72	−0.06
$7_{3,5}-6_{3,4}$	39843.69[e]	0.05	39558.72[e]	0.05
$7_{3,4}-6_{3,3}$	39850.30[e]	0.00	39569.60[e]	0.00
$7_{4,4}-6_{4,3}$ $7_{4,3}-6_{4,2}$	39829.19	−0.01 −0.06	39539.86	0.05 −0.07
$7_{5,3}-6_{5,2}$ $7_{5,2}-6_{5,1}$	39822.56	0.01	39530.41	0.09
$7_{6,2}-6_{6,1}$ $7_{6,1}-6_{6,0}$	39820.04	0.03	39526.13	−0.03
$8_{0,8}-7_{1,7}$	31060.86	−0.01	32933.10	0.01
$9_{0,9}-8_{1,8}$	37696.01	0.02	39489.06	0.01
$9_{1,8}-9_{0,9}$	28426.88	0.02		
$10_{1,9}-10_{0,10}$	30932.44	0.01	30397.58	0.00
$11_{1,10}-11_{0,11}$	33802.64	−0.01	33667.43	0.00
$11_{2,9}-10_{3,8}$	−27796.38	0.01		
$12_{1,11}-12_{0,12}$	37052.09	−0.01	37359.54	0.00
$13_{1,12}-12_{2,11}$	33751.36	0.00		
$16_{3,13}-15_{4,12}$	−37546.16	−0.00		
$17_{3,14}-16_{4,13}$	−31236.02	0.00		

[a] Observed frequency or hypothetical center of quadrupole fine structure if resolved, reproducible to ±0.05 MHz except where otherwise noted. [b] $\Delta\nu$ = obsd − calcd. [c] Obvious overlap, transition not included in fit. [d] Uncertainty of ±0.2 MHz. [e] Assignment confirmed by mrfdr. [f] Assignment confirmed by mdr.

Table III. Molecular Parameters

	$HN(CHO)_2$	$DN(CHO)_2$
A	21490.671 ± 0.018	19396.690 ± 0.030
B	3029.943 ± 0.002	3025.547 ± 0.004
C	2655.748 ± 0.002	2617.488 ± 0.004
τ_{aaaa}	−0.519176	Not determined
τ_{bbbb}	−0.00437662	−0.00362099
τ_{cccc}	−0.00200539	−0.00147052
τ_{bbaa}	0.0297826	0.0204654
τ_{ccaa}	0.0149522	0.0153173
τ_{bbcc}	−0.00290754	−0.00233744
τ_{baba}	−0.00381457	−0.00166630
τ_{bcbc}	-6.95×10^{-6}	-8.75×10^{-4}
I_a	23.51606 ± 0.00002	26.05475 ± 0.00004
I_b	166.79389 ± 0.00011	167.03625 ± 0.00025
I_c	190.29517 ± 0.00015	193.07674 ± 0.00026
Δ	−0.01480 ± 0.00018	−0.01426 ± 0.00030

dicted many K doublets in the range of mrfdr capability (4–60 MHz) but only one transition pair, 6_3–5_3, whose upper and lower states could both be pumped by rf power. All fast moving lines in the region predicted were examined by mrfdr, and the desired pair was located within 100 MHz of the predicted frequency. The assignment was confirmed by finding the 7_3–6_3 and 5_3–4_3 mrfdr pairs near predicted values using the appropriate 6_3–5_3 pump frequencies.

Using rotational constants based on these transitions and the J^2–K^2 R branch relative intensity rule, the other $K_{-1} > 3$ R band a-type transitions were easily located. The process of rotational constant refinement and line search led to assignment of all a-type R branch transitions in the region 8–40 GHz except for the $K_{-1} = 1$ and the very weak transitions. The tentative assignment was supported by observing mdr with the following pump-signal pairs: 4_{04}–3_{03}, 5_{05}–4_{04} and 4_{23}–3_{22}, 5_{24}–4_{23}.

Attempts to locate the $K_{-1} = 1$ transitions, which are sensitive to $B - C$, a quantity poorly determined by the other transitions, using rough predictions based on a rigid rotor fit of the assigned $K_{-1} = 1$ lines, were fruitless. Inclusion of centrifugal distortion through P^4, however, gave better predictions which allowed the $K_{-1} = 1$ transitions to be located with ease. Inclusion of the $K_{-1} = 1$ transitions into the centrifugal distortion fit gave a reliable b-type spectrum prediction which quickly led to the assignment of 13 b-type lines. Most of the b-type lines were split by the effect of the N^{14} quadrupole. A quantitative study of the effect was useful in confirming the assignment.

An excellent estimate of the rotational constants of *N*-deuterioformimide was made by adding the difference in rotational constants based on a model structure (*vide infra*) between normal and deuterated species to the experimentally determined values for the normal isotopic species. Use of these estimated constants and centrifugal distortion constants for the normal species gave sufficiently accurate predictions that the N-deuterated species was quickly assigned. The fit of the quadrupole splitting and of assigned transitions and the derived parameters are presented in Tables I, II, and III. Deviations can be explained by overlaps with other lines in the exceedingly rich spectrum or (for low *J*-type transitions) by experimental uncertainty in measuring weak quadrupole broadened lines.

The attempt to determine the dipole moment components was thwarted by overlapping lines, unresolved Stark effect, and weakness of useful transitions. Under these conditions, measurement of the rate of growth of lines with increasing Stark voltage was of semiquantitative quality and only demonstrated the presence of both a and b dipole components, a conclusion that was better supported by measurement of a- and b-type spectra. Comparison, however, of relative intensities of $K_{-1} = 1$ a-type to b-type lines gave a dipole moment ratio of $|\mu_b/\mu_a| = 1.44 \pm 0.06$. To minimize overlap problems, only b-type lines with a quadrupole splitting greater than 1 MHz were used.

Structure

In the absence of zero-point motion, the inertial defect, $\Delta = I_c - I_a - I_b$, is rigorously zero for a planar model. The small value of $\Delta = -0.01480 \pm 0.00018$ amu Å^2 for formimide strongly suggests planarity since vibration contributions to Δ can be as large as 0.2 amu Å^2.[13] However, if the amino proton is slightly out of plane, the negative contribution to Δ by nonplanarity can be masked by positive contributions from in-plane Coriolis coupled modes. Formamide ($\Delta = 0.0086$ amu Å^2) is an example of this cancellation.[6] Nonplanarity in formamide was revealed by study of the effect of isotopic substitution on Δ and the vibrational satellite pattern. From Kraitchman's equations,[14] the coordinates of the substituted atom in the principal axis system can be obtained from the changes in the moments of inertia upon isotopic substitution. Results of application of Kraitchman's equations are presented in Table IV. The out-of-plane coordinate is barely imaginary, strongly supporting planarity. By contrast, in formamide, application of Kraitchman's equation confirms the suspected nonplanarity of the amino protons.[6]

Table IV. Kraitchman Coordinates of Exchangeable Proton (Å)

$\|a\|$	0.4900 ± 0.0004
$\|b\|$	1.6008 ± 0.0010
$\|c\|$	Imaginary $c^2 = -0.00027 \pm 0.00018$ Å^2

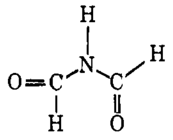
The vibrational satellite spectrum of formimide was studied as a test of planarity. For a normal vibration (NH out-of-plane deformation in a planar molecule) governed by the harmonic oscillator (single minimum) force law, the molecule in its various vibrational states will exhibit a series of closely spaced lines ($B_v = B_0 - \alpha_b v$) with intensities modulated by the Boltzmann factor. For an "abnormal" vibration (inversion motion in a slightly nonplanar molecule) governed by a strongly anharmonic double minimum potential, the spectrum normally observed consists of the ground state line and an excited state line of comparable intensity determined by the inversion splitting. If observable, the intensity of transitions of molecules in the next two energy states will be greatly reduced compared to those in the first two. A thorough search for vibrational satellites was made with an mrfdr (S/N = 10/1) study of the 7_3–6_3, 6_3–5_3, and 5_3–4_3 transitions in which the signal frequency was varied 1 GHz. A complex satellite pattern attributable to six vibration modes was observed. Lines due to three of the modes were sufficiently weak (<10%) compared to ground-state lines that only transitions in the first excited vibrational state were observable; semiquantitative relative intensity measurements gave a lower bound of 450 cm^{-1} for these modes. Lines due to the other modes were roughly one-third to one-half as intense as the ground state lines. However, for each of these modes, lines for the next vibrational state were located. The S/N ratio did not allow study of the molecule in higher vibrational states. Frequencies and semiquantitative relative intensities were consistent with a harmonic oscillator potential, supporting planarity. The relative positions of the vibrational satellites for $K \geq 3$ transitions are largely determined by the change in $B + C$ with vibrational quantum number, $(B + C)_v = (B + C)_0 - \Sigma\alpha_i v_i$. The values of α obtained are given in Table V. Both the low-frequency infrared spectrum and the relative intensity derived vibrational frequencies are poorly determined so it is not possible to assign the satellites to normal coordinates.

Table V. Vibrational Satellite Parameters

Mode	α, MHz	Vib freq, cm^{-1}
1	-7.45 ± 0.11	110 ± 80
2	-7.83 ± 0.10	110 ± 80
3	-10.24 ± 0.13	250 ± 80

Formimide is the first amide found to be planar in the gas phase. Although the inertial defect and vibrational satellite data strongly support planarity, they do not rule out a shallow double minimum potential in which the barrier is much less than the NH out-of-plane deformation frequency. However, definition of planarity in such a situation becomes a case of semantics.

The nitrogen quadrupole coupling constants, which are dependent on the population of the s, p_x, p_y, and p_z orbitals about the nitrogen nucleus, may be interpreted according to the treatment of Townes and Dailey.[15] As in the case of formamide, one may write several canonical forms for formimide (**1**–**3**). In a planar molecule, the C axis is parallel to the out-of-plane principal quadrupole axis, so χ_z equals χ_{cc} which in the Townes treatment is $[n - 1/3(a + b + c)]\chi_p$, where n is the population of the nitrogen lone pair and a, b, and c are the populations of the N-H, N-C (cis), and N-C (trans), respectively, and $\chi_p = -10$ MHz, the field gradient for a single p electron. χ_z in forms **2** and **3** is zero, since (assuming perfect covalency) the electron distribution about the nitrogen is symmetric. Similarly, χ_z for form **1** is χ_p or -10 MHz. Since the observed value is -3.39 MHz, the weight of forms **2** and **3** (double bond character) is 66% which is very close to the similarly obtained value for formamide.[16] Inequality of the in-plane components of the field gradient with respect to any two in-



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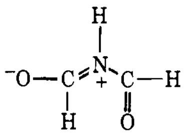

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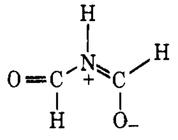

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plane perpendicular axes is a measure of the differences in ionicity of the N–H and C–N bonds. The difference between χ_{aa} and χ_{bb} suggests that the C–N bond is slightly more ionic than the N–H bond, in agreement with reasonable electronegativity differences.[17] The ionicity of the bonds has only a small effect on the estimate of double bond character and has been neglected since a more sophisticated analysis of the entire quadrupole problem would be necessary if this effect were to be considered.

Only structure III (cis–trans) is consistent with the observed a- and b-type spectra and is further supported by the close agreement of observed rotational constants with those based on model calculations (Table VI). The success of the model in predicting the shifts upon deuteration (ΔB −2.49 pred, −4.39 obsd; ΔC −40.26 pred, −38.26 obsd; $\Delta(B + C)$ −42.75 obsd, −42.65 obsd, shifts are in MHz) rules out any enol structure that could have a- and b-type spectra. This is further reflected by the excellent agreement of measured and predicted coordinates of the imino proton. A simple bond moment calculation[18] of dipole moments based on structure III gives $|\mu_a| = 2.20$ D, $|\mu_b| = 2.91$ D, or $|\mu_b/\mu_a| = 1.32$, whereas the measured ratio is 1.44 ± 0.06. A dipole–dipole interaction model also favors structure III where the C=O dipoles are most nearly antiparallel while still preserving planarity. Given the richness of the spectrum, the presence of other rotamers cannot be ruled out; although the following reasoning suggests that if several conformers are present, the cis–trans isomer is the most abundant. Most of the assigned b-type transitions are the strongest in the spectrum. With their C=O dipoles parallel, the other possible conformers would have the largest dipole moments, and, if they were present in a significant amount, their spectrum would be expected to dwarf the cis–trans spectrum. Furthermore, the transitions for the other conformers would be predicted to be slowly modulated whereas the vast majority of observed lines exhibit fast modulation.

Table VI. Molecular Parameters Calculated from Model Structures

Structure	Rotational constants, MHz B	C	Principal axis coordinates of exchangeable proton, Å a	b
I (trans–trans)	5214	3463	0.000	1.075
II (cis–cis)	2410	2268	0.000	2.038
III (cis–trans)	3058	2642	0.364	1.688
IV (hydrogen-bonded)	5735	3648	0.240	1.228
Observed	3030	2656	0.490	1.601

All angles (except ∠COH = 108° in structure IV) are 120°. Assumed bond lengths (Å): C=O, 1.216; C—H, 1.114; C—N, 1.44; C=N, 1.30; N—H, 1.014; O—H, 1.00; C—O, 1.41.

Although this is the first structural study of formimide, infrared studies on imides including formimide and structural studies on similar systems agree with the conclusions of this work. Infrared studies on CCl_4–formimide solutions of varying concentration led to the conclusion that hydrogen bonding in formimide is inter- rather than intramolecular, ruling against structure IV.[10] The room-temperature nmr spectrum was observed to consist of two peaks with the intensity ratio 2:1, a result that is consistent with any of the keto conformers if rotation about the C–N bond is rapid on the nmr time scale.[10] Formic anhydride, isoelectronic with formimide, and formic–acetic anhydride have been found to be cis–trans in an electron diffraction study although acetic anhydride was found to be trans–trans.[19] Acetimide (diacetamide) has two known crystalline modifications; in the metastable form, the molecule is trans–trans, in the stable form, cis–trans.[20] Formimide sublimes to easily form well-defined crystals which is suggestive of the presence of only one conformer in the solid state. Unfortunately, the crystal structure of formimide has not been determined. In fact, a complete solid state structure is not available for any of the amides thus far studied in the gas phase.

Table VII. Assignment of Infrared Spectrum of Formimide

	$HN(CHO)_2$	Freq, cm^{-1}	$DN(CDO)_2$
3255 s	NH str	2415 s	ND str
3100 sh	NH str	2325 sh	ND str
2910 s	CH str	2202 s	CD str
2775 sh	CH str	2070 sh	CD str
1679 s	CO str	1650 s	CO str
1740 m, sh	CO str	1714, 1742 sh	CO str
1466 s	Imide II	1322 s	Imide II′
1253 s	Imide III	1228 m	Imide III′
1178 s	Imide III	967 s	Imide III′
1337 m	δ CH	1038 m	δ CD
785 m	NH out-of-plane deformation?	589 m	ND out-of-plane deformation?

Uno, Machida, and coworkers have published an exhaustive study of the infrared spectra and normal vibrations of conformers of imides.[20,21] The study established that the cis–trans conformer is preferred in solution for all acyclic imides studied. The study also implicated the following infrared bands as characteristic of cis–trans imides (the corresponding acetimide frequencies are given in cm^{-1}).

Imide I bands, C=O stretching vibration with a small shift upon deuteration, reduced symmetry of the cis–trans configuration results in two infrared active modes (1736 m, 1701 vs).

Imide II and imide III bands, coupling between N–H in-plane deformation and C–N stretching modes, only present in trans amides (1506 s, 1310 s, 1223 s).

Imide II′ bands, C–N stretching vibration when coupling is broken by deuteration of amino proton (1360 s, 1290 sh).

Imide III′ band, N–D in-plane deformation, uncoupled with C–N stretch (1111 m).

The infrared spectrum of molten formimide and and perdeuterioformimide was reported by Allenstein[10] but was not interpreted in the light of the work of

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Uno and Machida on imide conformers. A reanalysis of the 3500–500-cm^{-1} spectrum (Table VII) is completely consistent with formimide being cis-trans in the liquid state, in agreement with the gas-phase microwave data.

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Position-Dependent Deuterium Effects on Radiationless Transitions in Anthracene[1]

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Abstract: The triplet lifetimes of several specifically deuterated anthracenes are measured in glassy solution at 77°K by monitoring the decay of triplet–triplet absorption after flash excitation. The derivatives studied comprise the *9,10-*d_2, *1,4-*d_2, *2,3-*d_2, *1,4,5,8-*d_4, *2,3,6,7-*d_4, *1,2,3,4-*d_4, and d_{10} compounds. Their triplet lifetimes show a significant dependence on the position of substitution. This dependence is interpreted theoretically, and the ratio of triplet deactivation rates for isomers containing the same number of deuterium substituents is calculated and compared to the experimental lifetime ratios. It is pointed out how this comparison might be used to further elucidate the theoretical interpretation of radiationless transitions.

The observation of a deuterium effect on the triplet state lifetimes of aromatic hydrocarbons has provided an important stimulus for the development of theories of radiationless processes.[2,3] The first effects were observed by Hutchison and Mangum[4] for naphthalene and by Wright, Frosch, and Robinson[5] for benzene. In each case a large increase of the triplet state lifetime was observed (2.1 to 16.9 sec for naphthalene and 16 to 26 sec for benzene). These results were explained by the Robinson and Frosch theory of radiationless transitions[6] in terms of the Franck–Condon factor associated with the rate k of a radiationless transition according to the simple Golden Rule formula of time-dependent perturbation theory.

$$k = (2\pi/\hbar)\rho JF(\mathrm{E}) \qquad (1)$$

Here ρ is the density of final vibrationally excited states and J is an electronic integral coupling the two states. The Franck–Condon factor F(E) is the well-known sum of products of vibrational overlap integrals. Deuterating aromatic hydrocarbons increases their triplet lifetimes due to an increase in Franck–Condon factors. This can be understood on the basis of the decreased overlap of the lower frequency CD modes relative to CH modes for the same energy gap. This effect is now well established experimentally[7] and the involvement of Franck–Condon factors has received extensive theoretical verification from the calculations of Siebrand.[7,8]

More recently a different type of deuterium effect on triplet lifetimes was observed by Hirota and Hutchison[9] and by Watts and Strickler[10] for naphthalene and by Simpson, *et al.*, for biphenyl.[11] In both molecules the triplet lifetime showed a dependence not only on the number of deuterium substituents but also on the position of substitution. In the naphthalene experiments, the authors compared the triplet lifetimes of derivatives having numerically the same but positionally different deuterium substituents. If the deuterium effect was due solely to an effect on the Franck–Condon factor associated with the vibrational modes, which have an equal *a priori* probability for accepting the electronic energy, then two such isomers would show essentially the same triplet decay rate. However, in the extensive series of naphthalene isomers investigated by Watts, *et al.*,[10] the differences were substantial and consistently demonstrated that deuterium substitution in an α position had a greater lifetime increasing effect than deuterium substitution in a β position. The possibility that the observed effect is due to an effect on the radiative decay probability is remote because of the minor contribution of this channel to triplet deactivation.[12]

The roughly additive nature of the effect observed by Watts, *et al.*, implies that it must be local in character. An explanation of the results based on this observation has been given by Henry and Siebrand.[13,14] Starting

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