

and H-atom transfer, occur to a significant extent, it will be possible to directly measure the extent to which the reaction proceeds by each of the two oxidation mechanisms.

**Rate Constants of R + NO<sub>2</sub> Reactions.** The two R + NO<sub>2</sub> reactions investigated in this study as well as the two which were studied earlier proceed extremely rapidly. The rate constants for the reactions of the three hydrogen-containing radicals (CH<sub>3</sub>, C<sub>3</sub>H<sub>5</sub>, and CH<sub>3</sub>CO) with NO<sub>2</sub> at ambient temperature are between 2.5 and 4 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This corresponds to a thermally averaged cross section at 300 K of between 3 and 7 Å<sup>2</sup>. None of these reactions could, therefore, have a significant barrier to reaction (*E<sub>a</sub>* must be less than 1 kcal/mol).

The reaction of the perhalogenated radical with NO<sub>2</sub> is distinctly slower (by a factor of 3) than the other three reactions studied. Halogen substitution is known to reduce the reactivity of hydrocarbon free radicals. For example, the CF<sub>3</sub> + NO<sub>2</sub> rate constant at 300 K is a factor of 10 less than that of the CH<sub>3</sub> + NO<sub>2</sub> reaction.<sup>4</sup>

There have been no prior measurements of the rate constants of reaction 4 or 5.<sup>6,2</sup>

The modeling of the kinetics of both the thermal and the photochemical nitration of hydrocarbons requires quantitative information on R + NO<sub>2</sub> reactions.<sup>61,63,64</sup> The importance of the direct O-atom transfer route has heretofore been either underestimated or not taken into account in a quantitative manner owing to a prior lack of mechanistic and kinetic information on this general type of reaction. The results of this study provide new quantitative information for obtaining a better understanding of the oxidation of hydrocarbons by NO<sub>2</sub>.

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(62) An indirect determination of  $k(\text{CH}_3\text{CO} + \text{NO}_2)/k(\text{CH}_3\text{CO} + \text{NO})$  has been reported (see ref 38).

(63) Ballod, A. P.; Shtern, V. Ya. *Usp. Khim.* **1976**, *45*, 1428-1460.

(64) Umsted, M. E.; Fleming, J. W.; Lin, M. C. *IEEE J. Quantum Electron.* **1980**, *QE-16*, 1227-1229.

## Bifurcated Hydrogen Bond and Large Amplitude Vibrations in Glycine Methyl Ester

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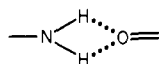
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**Abstract:** The rotational spectrum of glycine methyl ester has been studied in order to investigate the nature of its hydrogen bond and its large amplitude motions. The moments of inertia of the normal, NHD, and ND<sub>2</sub> isotopic species indicate that the molecule has a plane of symmetry which contains all the heavy atoms and an internal bifurcated hydrogen bond in which the amino group chelates the carbonyl oxygen. From an analysis of the A-E splittings in the ground vibrational state, the methyl barrier to internal rotation has been determined to be  $V_3 = 1177 \pm 30$  cal/mol. The rotational spectra of some vibrational satellites have been also assigned.

### 1. Introduction

The study of internal hydrogen bonding by microwave spectroscopy (MWS) has supplied information for small systems as small as the isolated molecules in the gas phase (see, for example, ref 1-8 and references therein). However, few molecules with a N—H...O internal hydrogen bond, the most common kind in biological systems, have been investigated in this way. 2-Methoxyethylamine,<sup>1</sup> where only the conformation stabilized by the internal hydrogen bond has been detected, was the first one studied.

The more stable conformation of glycine (GLY), the smallest amino acid, presents an internal bifurcated hydrogen bond:<sup>2</sup>



but two previous studies with MWS detected a conformer displaying a hydrogen bond of the type O—H...N.<sup>3,4</sup> This kind of hydrogen bond appears to be preferred with respect to the N—

H...O one in 2-aminoethanol,<sup>5</sup> alaninol and 1-amino-2-propanol,<sup>6</sup> 2-methylaminoethanol,<sup>7</sup> and 3-aminopropanol.<sup>8</sup>

Some time ago, when we were aware only of the results of ref 3 and 4, we decided to study the methyl ester of glycine (GME), where the methyl group replacing the hydroxyl hydrogen inhibits the formation of the O—H...N hydrogen bond, in order to obtain a molecular system with a N—H...O internal hydrogen bond. After we had obtained a great deal of information on GME, a second paper by Suenram and Lovas on GLY appeared.<sup>2</sup> They reported the microwave spectrum of the conformation with the internal bifurcated hydrogen bond and stated this second conformer to be about 0.5 kcal mol<sup>-1</sup> more stable than the conformer reported in ref 3 and 4. Nevertheless, we completed our study on GME, which is (with respect to the hydrogen bonding) a more simple system. Furthermore, the study of the large amplitude internal motions like those of the methyl group and the two heavy atom skeletal torsions is of interest in order to obtain information about the corresponding potential surfaces and the possible tor-

(5) Penn, R. E.; Curl, R. F., Jr. *J. Chem. Phys.* **1971**, *55*, 651-658.

(6) Ellingsen, B. H.; Marstokk, K. M.; Møllendal, H. *J. Mol. Struct.* **1978**, *48*, 9-23. Marstokk, K. M.; Møllendal, H. *Ibid.* **1976**, *35*, 57-66.

(7) Penn, R. E.; Buxton, L. W. *J. Mol. Spectrosc.* **1975**, *56*, 229-238.

(8) McMahan, M. A.; Sharma, S. D.; Curl, R. F., Jr. *J. Mol. Spectrosc.* **1979**, *75*, 220-233.

(1) Caminati, W.; Wilson, E. B. *J. Mol. Spectrosc.* **1980**, *81*, 356-372.

(2) Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* **1980**, *102*, 7180-7184.

(3) Brown, R. D.; Godfrey, P. D.; Storey, J. W. V.; Bassez, M. P. *J. Chem. Soc., Chem. Commun.* **1978**, 547-548.

(4) Suenram, R. D.; Lovas, F. J. *J. Mol. Spectrosc.* **1978**, *72*, 372-382.

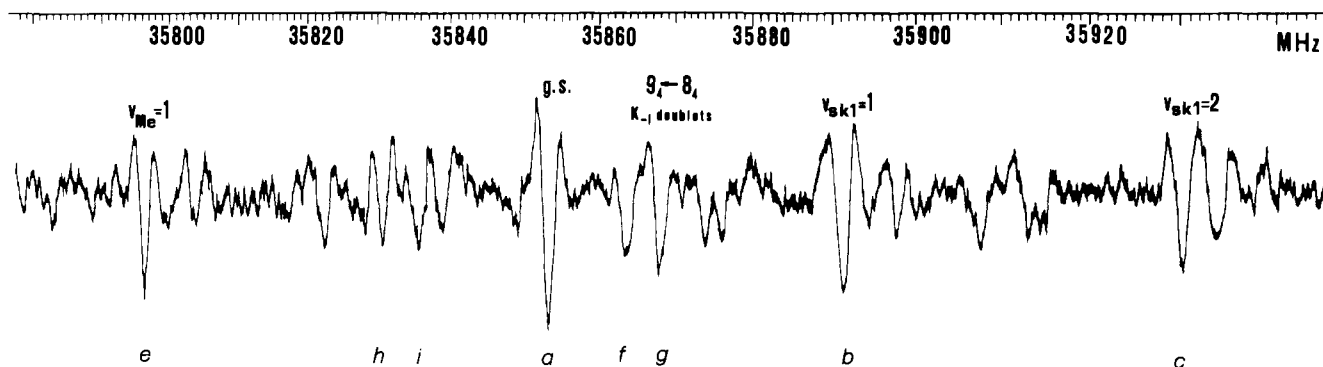


Figure 1. Recording of the  $9_{4,6} \leftarrow 8_{4,5}$  and  $9_{4,5} \leftarrow 8_{4,4}$  K doublet of glycine methyl ester showing the various vibrational satellites. The spectrum was obtained by the radio-frequency microwave double resonance technique.

Table I. Rotational Constants (MHz), Centrifugal Distortion Constants (kHz), Inertial Defects ( $\mu\text{A}^2$ ), Number of Transitions and Standard Deviations (MHz) of the Fits, and Vibrational Energies ( $\text{cm}^{-1}$ ) for "A" Sublevels of GME

	a (ground state)	b ( $V_{SK1}=1$ )	c ( $V_{SK1}=2$ )	d ( $V_{SK1}=3$ )	e ( $V_{Me}=1$ )	f	g	h	i
A	9691.01 (6) <sup>a</sup>	9627.8 (8)	9559.5 (8)	9489.1 (6)	9600.8 (8)				
B	2153.147 (4)	2153.86 (1)	2154.51 (2)	2155.25 (1)	2149.20 (1)	3973.3 (2) <sup>b</sup>	3973.8 (2) <sup>b</sup>	3969.6 (2) <sup>b</sup>	3970.1 (2) <sup>b</sup>
C	1819.002 (1)	1822.68 (1)	1826.39 (2)	1830.21 (1)	1816.56 (1)				
$\Delta_J$	0.17 (3)	0.41 (8)	0.20 (9)	0.07 (5)	0.16 (7)				
$\Delta_{JK}$	1.17 (4)	0.5 (2)	0.5 (3)	0.6 (3)	0.3 (1)				
$\Delta_K$	8 (5)								
$\delta_J$	0.026 (1)								
$\delta_K$	0.10								
$\Delta_c$	9.032	9.857	10.724	11.615	9.580				
n	50	18	17	14	21				
$\sigma$	0.08	0.09	0.10	0.07	0.10				
$E_v$	0	$53 \pm 15$	$128 \pm 20$	$160 \pm 30$	$97 \pm 30$	$165 \pm 40$	$140 \pm 40$	$175 \pm 40$	$195 \pm 40$

<sup>a</sup> Standard errors. <sup>b</sup> (B + C).

sion-torsion interactions. For example, in methyl fluorothioformate the sequence of the A-E levels was reversed in the first excited state of the skeletal torsion with respect to the ground state, owing to an interaction with the methyl torsion.<sup>9</sup>

## 2. Experimental Section

GME was liberated from a suspension of its hydrochloride (98% pure, supplied by Aldrich Chemical Co.) in dry ether by flowing a stream of dried ammonia at 0 °C.<sup>10</sup> After separation of the ammonium chloride the solution of the free ester in ether was submitted to a trap-to-trap distillation. At room temperature the compound polycondenses in few hours, therefore, the sample was stored in a -78 °C bath.

GME-NHD was prepared directly in the microwave absorption cell by exchange with D<sub>2</sub>O which had previously been introduced into the cell.

GME-ND<sub>2</sub> was obtained by shaking the normal compound with an excess of D<sub>2</sub>O; then the mixture was subjected to a rapid trap-to-trap distillation to separate the ester and water mixture.

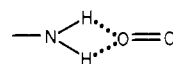
Microwave spectra were observed using a Hewlett-Packard 8400C spectrometer by flowing the gas through the absorption cell. Spectra were recorded both at room temperature and at ~260 K. Frequency measurements are believed to be more accurate than 0.1 MHz, except for the weaker lines of some of the excited states where an accuracy of 0.2 MHz is more appropriate.

A number of radio-frequency microwave double resonance experiments of the type described by Wodarczyk and Wilson<sup>11</sup> were made in connection with the assignment of the spectra. Relative intensity measurements were made using the method of Esbitt and Wilson.<sup>12</sup>

## 3. Results and Discussions

**3.1. Analysis of Spectra.** Model calculations based on the structure of GLY,<sup>13</sup> assuming the O-CH<sub>3</sub> distance as in methyl formate<sup>14</sup> and a regular methyl group, were performed for several

possible conformers of GME. Fast-scan spectra showed a weak series of  $\mu_a$  R-branch bands and gave  $B + C = 3986 \pm 3$  MHz. This value was close to that calculated for the conformer with a



internal hydrogen bond and with the methyl group cis with respect to the carbonyl group ( $(B + C)_{\text{calcd}} \approx 3980$  MHz).

Radio-frequency microwave double resonance experiments were performed in order to search for the  $\mu_a$  R-branch lines with  $K_{-1} = 4$ , for which the "K" doublet separations were calculated to be in the range 3-120 MHz for  $J = 8-10$ . Figure 1 shows the pattern for the  $9_{4,6} \leftarrow 8_{4,5}$  and  $9_{4,5} \leftarrow 8_{4,4}$  transitions obtained by "pumping" at the  $9_{4,6} \leftarrow 9_{4,5}$  calculated frequency.

For state a, the ground state, several other "a" "R" lines were measured with the usual Stark modulation. Furthermore, many  $\mu_b$ -type Q-branch lines with  $J$  ranging from 14 to 24 and  $K_{-1} = 2 \leftarrow 1$  and  $3 \leftarrow 2$  were found to be doublets split from a few to tens of MHz. The components of these doublets have the same intensity and they can be attributed to the "A" and "E" sublevels due to the internal rotation of the methyl group. A-E splittings were then observed for some  $\mu_b$ -type R-branch lines and for the  $K_{-1} = 3$   $\mu_a$ -type R-branch lines.

For states b, c, d, and e only "A" component lines of  $\mu_a$ -type R-branch lines were assigned. (The satellite labeled d does not appear in Figure 1.)

To fit the "A" component lines, a semirigid model<sup>15</sup> (I<sup>r</sup> representation) was used, varying all the five centrifugal distortion parameters for the state a, whereas only  $\Delta_J$  and  $\Delta_{JK}$  have been allowed to vary for states b-e. For the weaker satellites f-i only the lines observed with the double resonance technique have been detected.

(9) Caminati, W.; Meyer, R. *J. Mol. Spectrosc.* **1981**, *90*, 197-214.  
 (10) Frankel, M.; Katchalski, E. *J. Am. Chem. Soc.* **1942**, *64*, 2266.  
 (11) Wodarczyk, F. J.; Wilson, E. B. *J. Mol. Spectrosc.* **1971**, *37*, 445-463.  
 (12) Esbitt, A. S.; Wilson, E. B., Jr. *Rev. Sci. Instrum.* **1963**, *34*, 901-907.  
 (13) Schäfer, L.; Sellers, H. L.; Lovas, F. J.; Suenram, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 6566-6568.

(14) Curl, R. F., Jr. *J. Chem. Phys.* **1959**, *30*, 1529-1536.  
 (15) Watson, J. K. G. *J. Chem. Phys.* **1967**, *46*, 1935-1949.

Table II. Rotational Constants and Internal Rotation Parameters from a PAM Analysis of the Ground State of GME

$A_r$ /MHz	9689.43 (3) <sup>a</sup>	$\theta$ /deg	24 (1)
$B_r$ /MHz	2153.183 (3)	$s$	32.8 (1)
$C_r$ /MHz	1818.955 (3)	$I_\alpha/10^4 m_u \text{pm}^2$	3.198 <sup>b</sup>
$\Delta_c/10^4 m_u \text{pm}^2$	9.029	$V_3/\text{cal mol}^{-1}$	1177 (30)
$\sigma_{AE}^c$ /MHz	0.36	$n^d$	89

<sup>a</sup> Standard error. <sup>b</sup> Fixed (see text). <sup>c</sup> Standard deviation of the fit. <sup>d</sup> Number of transitions used in the fit.

Table III. Methyl Barrier to Internal Rotation for Substituted Methyl Formates

molecule	formula	$V/\text{cal mol}^{-1}$
methyl formate <sup>14</sup>	HCOOCH <sub>3</sub>	1190 ± 40
methyl fluoroformate <sup>21</sup>	FCOOCH <sub>3</sub>	1077 ± 30
methyl cyanoformate <sup>21</sup>	CNCOOCH <sub>3</sub>	1172 ± 30
methyl acetate <sup>21</sup>	CH <sub>3</sub> COOCH <sub>3</sub>	1215 ± 30
<i>cis</i> -methyl acrylate <sup>21</sup>	CH <sub>2</sub> =CHCOOCH <sub>3</sub>	1220 ± 30
methyl propiolate <sup>21</sup>	HC≡CCOOCH <sub>3</sub>	1266 ± 30
methyl chloroformate <sup>22</sup>	ClCOOCH <sub>3</sub>	1250 ± 30
methyl glycolate <sup>30</sup>	HOCH <sub>2</sub> COOCH <sub>3</sub>	1131 ± 30
glycine methyl ester	H <sub>2</sub> NCH <sub>2</sub> COOCH <sub>3</sub>	1177 ± 30

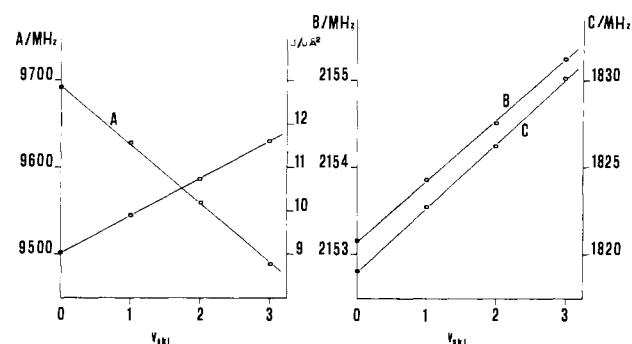


Figure 2. Variation of (a) the rotational constant  $A$  and inertial defect  $\Delta_c$ , and (b) the rotational constants  $B$  and  $C$  with vibrational quantum number for excited states of the torsional vibration around the C-C bond in glycine methyl ester.

Rotational constants, centrifugal distortion constants, inertial defects  $\Delta_c (=I_a + I_b - I_c)$ , and vibrational energies from intensity measurements are reported in Table I. The list of measured transitions is given as supplementary material.

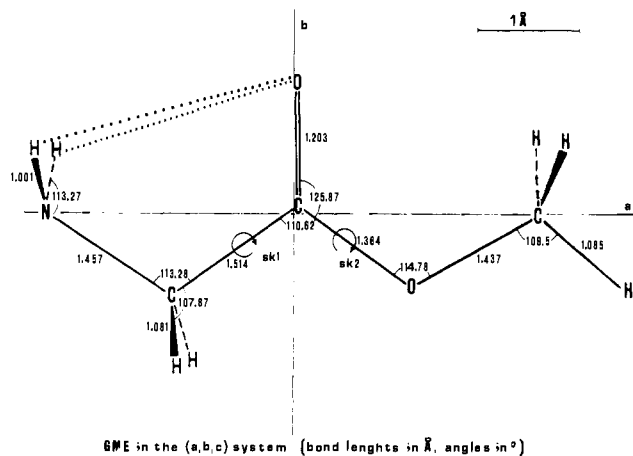
**3.2. Methyl Barrier to Internal Rotation from the Ground State A-E Splittings.** The  $\Delta_c$  value for the "A" sublevel of the ground state (state *a*) is very close to that expected for a rigid molecule with six hydrogen atoms (two methylic, two methylenic, and two amino) out of the plane containing the heavy atoms, indicating that the methyl barrier to internal rotation is greater than 0.5 kcal/mol.

The Herschbach principal axis method (PAM) model<sup>16</sup> was used to obtain the internal rotation parameters from the A-E splittings of the ground-state lines. Perturbation coefficients  $W_{\nu\sigma}^{(n)}$  up to  $n = 4$  and Stelman's denominator corrections ( $n = d$ )<sup>17</sup> have been introduced in the Hamiltonian. The rotational transition frequencies have been corrected for centrifugal distortion effects calculated with the centrifugal distortion constants reported in Table I for the "A" state. The contributions to the centrifugal distortion constants, due to the internal rotation,<sup>16</sup> have been calculated to be negligible. In Table II the results of the PAM analysis are shown.  $A_r$ ,  $B_r$ , and  $C_r$  are the rigid rotational constants,  $\theta$  is the angle between the "a" axis and the internal rotation axis,  $s$  is the dimensionless reduced barrier, and  $I_\alpha$  is the moment of inertia of the top, which has been fixed to the value found for thiolactic acid.<sup>18</sup>

(16) Herschbach, D. R. *J. Chem. Phys.* **1959**, *31*, 91-108.

(17) Stelman, D. *J. Chem. Phys.* **1964**, *41*, 2111-2115.

(18) Naito, T.; Phashi, O.; Yamaguchi, I. *J. Mol. Spectrosc.* **1977**, *68*, 32-40.



GME in the (a,b,c) system (bond lengths in Å, angles in °)

Figure 3. Structure assumed for glycine methyl ester; the principal axis system is shown. (Bond lengths in Å, angles in deg.)

Table IV. Vibration Rotation Interaction Constants (MHz) and Force Constant ( $\text{cm}^{-1} \text{deg}^{-2}$ ) of the C-C Skeletal Torsion (SK1)

$A_0 = 9721.7$ (11) <sup>a</sup>	$\alpha^A = 60.2$ (14)	$\beta^A = -1.8$ (3)
$B_0 = 2152.82$ (6)	$\alpha^B = -0.67$ (7)	$\beta^B = 0.008$ (17)
$C_0 = 1817.20$ (3)	$\alpha^C = -3.59$ (4)	$\beta^C = 0.036$ (9)
$k = 2.63-5.34$		

<sup>a</sup> Standard errors in parentheses.

Table V. Rotational Constants (MHz), Centrifugal Distortion Constants (kHz),  $\Delta_c$  ( $\mu\text{A}^2$ ), and Vibrational Energies  $E_v$  ( $\text{cm}^{-1}$ ) for "A" sublevels of GME-Deuterated Species

	GME-ND <sub>2</sub>		GME-NHD
	ground state	$V_{SK1} = 1$	ground state
$A$	9327.0 (9) <sup>a</sup>	9271.4 (8)	9507 (1)
$B$	2035.40 (2)	2036.31 (1)	2092.12 (2)
$C$	1737.86 (2)	1741.11 (1)	1776.81 (2)
$\Delta_J$	0.24 (8)	0.17 (7)	0.08 (12)
$\Delta_{JK}$	0.9 (1)	0.8 (3)	1.2 (3)
$\Delta_c$	11.673	12.430	10.291
$n^b$	21	18	16
$\sigma^c$	0.12	0.10	0.14
$E_v$	0	55	0

<sup>a</sup> Standard errors in parentheses. <sup>b</sup> Number of lines used in the fit. <sup>c</sup> Standard deviations of the fits.

The value of the methyl barrier to internal rotation is close to that of methyl glycolate<sup>30</sup> and to those of several substituted methyl formates,<sup>14,21,22</sup> a series to which methyl glycolate and GME belong. A comparative scheme is given in Table III.

**3.3. Excited States. (a) C-C Skeletal Torsion.** The nearly equal spacing and exponential decrease in intensity of the rotational transitions in going from the ground to the *b*, *c*, and *d* vibrational satellites indicate that they belong to successive states of a near-harmonic vibration. The variation of the rotational constants and of the inertial defect with the vibrational quantum number, shown in Figure 2, suggests that the vibration is an "out-of-plane" motion. Relative intensity measurements (see Table I) give an energy separation between the ground and the first excited state of  $53 \pm 15 \text{ cm}^{-1}$ , while a fitting of the three measured vibrational energies to a harmonic approximation gives a harmonic frequency  $\nu_{SK1}^0 = 57 \pm 10 \text{ cm}^{-1}$ . As shown in Figure 3, GME allows two low-energy skeletal torsions, labeled SK1 (torsion around the C-C bond) and SK2 (torsion around the C-O bond), respectively. As for GLY, a vibrational satellite at  $65 \text{ cm}^{-1}$  has been assigned to the C-C skeletal torsion,<sup>8</sup> while the C-O skeletal torsion frequency in similar compounds has been found to be in the range 170-190  $\text{cm}^{-1}$ ,<sup>19</sup> we believe this motion to be the C-C skeletal torsion, labeled SK1 in Figure 3. The vibration-rotation constants and

(19) Williams, G.; Owen, N. L. *Trans. Faraday Soc.* **1971**, *67*, 950-960.

Table VI.  $r_s$  Coordinates for the Amine Hydrogens<sup>a</sup>

parent subst	GME-NH <sub>2</sub> GME-NHD		GME-ND <sub>2</sub> GME-NHD		GME-NHD GME-NH <sub>2</sub>		GME-NHD GME-ND <sub>2</sub>		GME-NH <sub>2</sub> GME-ND <sub>2</sub>	
	$r_s$	model	$r_s$	model	$r_s$	model	$r_s$	model	$r_s$	model
a	2.494	2.553	2.442	2.505	2.478	2.536	2.463	2.521	2.494	2.553
b	0.624	0.572	0.569	0.522	0.605	0.554	0.585	0.536	0.611	0.572
c	0.809	0.821	0.810	0.821	0.772	0.784	0.847	0.859	0.815	0.821
$r_{H \cdots H}$	1.618		1.620		1.619				1.630	

<sup>a</sup> The experimental uncertainties are always very close to 1, 4, and 3 mA respectively for |a|, |b|, |c|.

the rotational constants free from the effects of this vibrational mode are obtained using formulas of the type  $A_v = A_0 - \alpha^A(v + 1/2) + \beta^A(v + 1/2)^2$ , and they are reported in Table IV together with the force constant for the torsion as calculated in the harmonic approximation.

(b) **First Excited State of the Methyl Torsion ( $v_{Me} = 1$ ).** State *c* shows the same trend in intensity and change in rotational constants relative to the ground state as that found for the first excited methyl torsional state and ground state of methyl glycolate,<sup>20</sup> a molecule inertially and conformationally similar to GME. Consequently state *c* is assigned to  $v_{Me} = 1$ . The variation of the rotational constants with respect to the ground state corresponds to the effect due to internal rotation, that is

$$A_{v,\sigma} = A_r + F\rho_a^2 W_{v,\sigma}^{(2)}, \text{ etc.}$$

where  $\rho_a = \lambda_a(I_a/I_a)$  and  $W_{v,\sigma}^{(2)}$  is the second-order perturbation coefficient<sup>16</sup> for the appropriate value of the reduced barrier *s*.

(c) **Other Vibrational Satellites.** For the states *f*, *g*, *h*, and *i* only two transitions have been measured by using the *rfmwdr* technique. All have similar values of vibrational energy ( $E_v = 140\text{--}195 \text{ cm}^{-1}$ ; see Table I). One of the two satellites at lower frequency (*h* and *i*) should belong to the C—O skeletal torsion (SK2 of Figure 3) while the other one is probably the combination state ( $v_{Me} = 1, v_{SK1} = 1$ ).

The two remaining vibrational satellites at higher frequency (*f* and *g*) could belong to the  $v_{Me} = 2$  state (the  $W_{2,A}^{(2)}$  coefficient has an opposite sign with respect to the  $W_{1,A}^{(2)}$  one) and to the lowest in-plane vibration of the heavy atoms, but the large uncertainty on the vibrational energy and the lack of data about the inertial defects leave some doubts about these assignments.

**3.4. Deuterated Species.** For the deuterated isotopic species GME-ND<sub>2</sub>, rotational transitions in the ground state and in the first excited state of the C—C skeletal torsion have been measured. For the GME-NHD species only rotational transitions for the ground state have been measured. For both isotopic species only  $\mu_a$ -type R-branch lines were measured as these rotational constants sufficiently precise to obtain structural information. The experimental frequencies are given as supplementary material. Rotational constants, centrifugal distortion constants, and inertial defects are given in Table V.

**3.5. Conformation, Structure, and Dipole Moment.** The values of the rotational constants of the three isotopic species and the  $r_s$  coordinates of the amino hydrogens (see Table VI) agree with a conformation with a plane of symmetry containing all the heavy atoms, with a bifurcated hydrogen bond, and with the methyl group syn with respect to the carbonyl group, as is shown in Figure 3. This is the most stable configuration for all the substituted methyl formates investigated by MWS.<sup>14,20–22</sup> We do not have data about the equilibrium configuration of the methyl group, as we did not study the CH<sub>2</sub>D species. However, in the figure the CH<sub>3</sub> group is drawn as in methyl formate, where the CH<sub>2</sub>D species have been studied. In fact, as the  $V_3$  values are similar, the equilibrium configuration should be the same. An unsuccessful search has been made for the conformer with the methyl group anti to the carbonyl group looking for “a” “K<sub>-1</sub>” doublets by using

Table VII. Stark Coefficients (Hz V<sup>-2</sup> cm<sup>2</sup> D<sup>-2</sup>) and Stark Effect for Some Transitions of GME and Dipole Moment (*D*)

transition <sup>a</sup>	$\Delta A^a$	$\Delta B^a$	$\Delta A^b$	$\Delta B^b$	$\Delta\nu/E^2$ (Hz V <sup>-2</sup> cm <sup>2</sup> )	
					obsd	calcd
9 <sub>0,9</sub> ← 8 <sub>0,8</sub>	-0.630	0.010	-0.076	0.031	-1.45	-1.48
9 <sub>1,9</sub> ← 8 <sub>1,8</sub>	-0.044	0.005	-3.581	0.070	-2.01	-1.97
9 <sub>1,8</sub> ← 8 <sub>1,7</sub>	-0.041	0.001	-0.165	-0.014	-0.24	-0.26
$\mu_a = 1.6$ (2)		$\mu_b = 0.8$ (1)		$\mu_{tot} = 1.8$ (2)		

<sup>a</sup> The value of *M* is not indicated as various Stark lobes superimpose (see text).

the radio-frequency microwave resonance. As  $\mu_a$  should change little in going from the syn to the anti conformation, and as we have been able to detect vibrational satellites up to 200 cm<sup>-1</sup> high in energy, the anti conformation must be at least 0.5 kcal/mol less stable than the observed one.

Structural parameters of GLY obtained by an “ab initio” calculation,<sup>13</sup> together with O=C—O and C—O—C(CH<sub>3</sub>) angles and OC(CH<sub>3</sub>) distance taken from methyl formate,<sup>14</sup> reproduce satisfactorily the experimental rotational constants of GME (within 0.1% *B* and *C* and 0.3% *A*). Owing to the lack of experimental data, no further adjustments were made on this structure, which is shown in Figure 3. The substitution coordinates of the amino hydrogen atoms, obtained using the methods of Kraitchman<sup>23</sup> and Chutjian<sup>24</sup> are reported in Table VI. The agreement among the  $r_s$  H...H distances of the amino group obtained from different combinations of the isotopic species indicate that the Ubbelohde effect,<sup>25</sup> that is, the shrinkage upon deuteration of the distance between the heavy atoms involved in the hydrogen bond, in this molecule is smaller than in other cases (see, for example, ref 1 and 26).

No effects due to the <sup>14</sup>N quadrupole coupling have been observed.

A precise determination of the dipole moment was not possible as the spectrum was too weak to detect single Stark lobes. The 9<sub>09</sub> ← 8<sub>08</sub>, 9<sub>19</sub> ← 8<sub>18</sub>, and 9<sub>18</sub> ← 8<sub>17</sub> transitions show a single strong Stark lobe due to the piling up of several single components. This agrees with the small values of the  $\Delta B$  coefficients calculated for the usual second-order Stark effect.<sup>27</sup>

$$\Delta\nu/E^2 = (\Delta A^a + \Delta B^a M^2)\mu_a^2 + (\Delta A^b + \Delta B^b M^2)\mu_b^2$$

These coefficients and the estimated dipole moment components are given in Table VII.

The cell was calibrated with  $|M| = 0, 2, J = 3 \leftarrow 2$  Stark lobe displacements of OCS ( $\mu = 0.7152^{28}$ ).

**3.6. Bifurcated Hydrogen Bond.** In contrast with the result of some IR investigations in dilute solution (see, for example, ref 29), this work is further evidence, after those of ref 1 and 2, that in molecules with a possible N—H...O hydrogen-bonded con-

(23) Kraitchman, K. *Am. J. Phys.* **1953**, *21*, 17–24.

(24) Chutjian, A. *J. Mol. Spectrosc.* **1964**, *14*, 361–370.

(25) Ubbelohde, A. R.; Gallagher, K. J. *Acta Crystallogr.* **1955**, *8*, 71–83.

(26) Penn, R. E.; Olsen, R. J. *J. Mol. Spectrosc.* **1976**, *62*, 423–428.

(27) Golden, S.; Wilson, E. B., Jr. *J. Chem. Phys.* **1948**, *16*, 669.

(28) Muentler, J. *J. Chem. Phys.* **1968**, *48*, 4544–4547.

(29) Buckley, P.; Brochu, M. *Can. J. Chem.* **1972**, *50*, 1149–1156.

(30) Caminati, W.; Cervellati, R. *J. Mol. Struct.* **1982**, *81*, 143–145.

(20) Caminati, W.; Cervellati, R., to be submitted for publication.

(21) Williams, G.; Owen, N. L.; Sheridan, J. *Trans. Faraday Soc.* **1971**, *67*, 922–949.

(22) Lister, D. G.; Owen, N. L. *Trans. Faraday Soc.* **1973**, *69*, 1036–1042.

formation, H-bonding appears to be an important factor in determining the conformation in the isolated molecule in the gas phase. However, even if N—H...O is a strong kind of hydrogen bond, it appears to be not as strong as O—H...N (see ref 2 and 5-8 and the Introduction). The experimental evidence that the conformer of GLY with a bifurcated hydrogen bond (double N—H...O hydrogen bond) is about 0.5 kcal/mol more stable than the conformer with the O—H...N internal hydrogen bond<sup>2</sup> suggests that the bond energy of N—H...O is slightly more than half that of the O—H...N bond, at least in molecular systems where the hydrogen bond belongs to a five-membered ring including a sp<sup>2</sup> carbon.

The C=O group appears to be in the middle of the amine group, because otherwise it could there be (i) a double minimum

with tunnelling, which would originate two O<sup>+</sup> and O<sup>-</sup> levels close in energy, or (ii) a deeper double minimum which would cause two different NHD species, but we did not observe either of the two effects.

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**Supplementary Material Available:** A listing of the experimental transitions frequencies is available (3 pages). Ordering information is given on any current masthead page.

## A Study of the Unimolecular Decomposition of the (C<sub>2</sub>H<sub>2</sub>)<sub>3</sub><sup>+</sup> Complex

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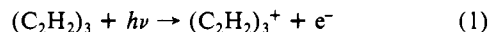
Contribution from Ames Laboratory,<sup>†</sup> U.S. Department of Energy, and Department of Chemistry, Iowa State University, Ames, Iowa 50011. Received October 16, 1981.

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**Abstract:** The C<sub>6</sub>H<sub>5</sub><sup>+</sup>, C<sub>6</sub>H<sub>4</sub><sup>+</sup>, C<sub>4</sub>H<sub>4</sub><sup>+</sup>, C<sub>4</sub>H<sub>3</sub><sup>+</sup>, C<sub>4</sub>H<sub>2</sub><sup>+</sup>, and C<sub>3</sub>H<sub>3</sub><sup>+</sup> ions were identified as the primary fragment ions from the unimolecular decomposition of (C<sub>2</sub>H<sub>2</sub>)<sub>3</sub><sup>+</sup> in the total energy range 17.10–26.10 eV (neutral (C<sub>2</sub>H<sub>2</sub>)<sub>3</sub> heat of formation plus excitation energy). The appearance energies (AE) for C<sub>6</sub>H<sub>5</sub><sup>+</sup>, C<sub>6</sub>H<sub>4</sub><sup>+</sup>, C<sub>4</sub>H<sub>4</sub><sup>+</sup>, and C<sub>3</sub>H<sub>3</sub><sup>+</sup> were found to be identical and have the value of 10.10 ± 0.04 eV (1228 ± 5 Å). The ionization energy (IE) of (C<sub>2</sub>H<sub>2</sub>)<sub>3</sub> was determined to be 9.83 ± 0.04 eV (1261 ± 5 Å). The measured AE's for the formation of C<sub>4</sub>H<sub>3</sub><sup>+</sup> and C<sub>4</sub>H<sub>2</sub><sup>+</sup> from (C<sub>2</sub>H<sub>2</sub>)<sub>3</sub> in the total energy scale were found to be in agreement with those determined for C<sub>4</sub>H<sub>3</sub><sup>+</sup> and C<sub>4</sub>H<sub>2</sub><sup>+</sup> from 2,4-hexadiyne, 1,5-hexadiyne, and benzene. This, together with the favorable comparison observed between the relative intensities of the C<sub>6</sub>H<sub>5</sub><sup>+</sup>, C<sub>6</sub>H<sub>4</sub><sup>+</sup>, and C<sub>3</sub>H<sub>3</sub><sup>+</sup> ions from (C<sub>2</sub>H<sub>2</sub>)<sub>3</sub> measured in this work and those reported previously from the benzene, 2,4-hexadiyne, and 1,3-hexadiyne molecular ions in the total energy range 16.87–17.37 eV, strongly supports the conclusion that the (C<sub>2</sub>H<sub>2</sub>)<sub>3</sub><sup>+</sup> ions rearrange to some common precursors as do other stable C<sub>6</sub>H<sub>6</sub><sup>+</sup> isomers prior to dissociation. The difference (0.26 ± 0.06 eV) of the AE's for C<sub>6</sub>H<sub>5</sub><sup>+</sup>, C<sub>6</sub>H<sub>4</sub><sup>+</sup>, C<sub>4</sub>H<sub>4</sub><sup>+</sup>, and C<sub>3</sub>H<sub>3</sub><sup>+</sup> and the IE of (C<sub>2</sub>H<sub>2</sub>)<sub>3</sub> is interpreted as the potential energy barrier for the rearrangement of (C<sub>2</sub>H<sub>2</sub>)<sub>3</sub><sup>+</sup> to other stable C<sub>6</sub>H<sub>6</sub><sup>+</sup> isomers.

The mechanism for the unimolecular decomposition of the benzene ion has been the subject of many experimental<sup>1-9</sup> and theoretical<sup>7,10,11</sup> investigations during the last decade. The major fragment ions resulting from the unimolecular decomposition of the excited benzene molecular ions with excitation energies below 20 eV are C<sub>6</sub>H<sub>5</sub><sup>+</sup>, C<sub>6</sub>H<sub>4</sub><sup>+</sup>, C<sub>4</sub>H<sub>4</sub><sup>+</sup>, and C<sub>3</sub>H<sub>3</sub><sup>+</sup>. The same product ions are observed from C<sub>6</sub>H<sub>6</sub><sup>+</sup> formed by photoionization of some stable isomers of C<sub>6</sub>H<sub>6</sub> such as 1,5-hexadiyne,<sup>8,12</sup> 2,4-hexadiyne,<sup>8,12-14</sup> and 1,3-hexadiyne.<sup>12,14</sup> The fact that, within experimental errors, the benzene, 1,5-hexadiyne, and 2,4-hexadiyne molecular ions dissociate to the four product ions with identical branching ratios in the total energy range ~15.0–15.5 eV (neutral C<sub>6</sub>H<sub>6</sub> heat of formation plus excitation energy) indicates that all these isomers of C<sub>6</sub>H<sub>6</sub><sup>+</sup> rearrange to a common precursor ion prior to fragmentation. The experimental and calculated unimolecular fragmentation rates for C<sub>6</sub>H<sub>6</sub><sup>+</sup> are consistent with the interpretation that this common precursor has the benzene molecular ion structure.<sup>8</sup> Above this energy range, there is evidence that newly accessible processes involve some intermediate complexes other than the common precursor ions.<sup>8,13,14</sup> The kinetic energy release data of Keough et al.<sup>15</sup> suggest that the reactive form of the benzene molecular ion at higher excitation energies has an acyclic structure.

In this paper, we report the results of a study of the unimolecular decomposition of acetylene trimer ions which are synthesized by the direct photoionization of van der Waals trimers of acetylene.



- (1) B. Andlauer and Ch. Ottinger, *J. Chem. Phys.*, **55**, 1471 (1971); B. Andlauer and Ch. Ottinger, *Z. Naturforsch., A*, **27A**, 293 (1972).
- (2) J. H. D. Eland and H. Schulte, *J. Chem. Phys.*, **62**, 3835 (1975).
- (3) J. H. D. Eland, R. Frey, H. Schulte, and B. Brehm, *Int. J. Mass Spectrom. Ion Phys.*, **21**, 209 (1976).
- (4) J. H. Beynon, R. M. Caprioli, W. O. Perry, and W. E. Baitinger, *J. Am. Chem. Soc.*, **94**, 6828 (1972).
- (5) W. A. Chupka in "Chemical Spectroscopy and Photochemistry in the Vacuum-Ultraviolet", C. Sandorfy, P. J. Ausloos, and M. B. Robin, Eds., Reidel, Dordrecht, 1974, p 433.
- (6) W. A. Chupka, J. Berkowitz, and S. I. Miller, paper presented at American Society for Mass Spectrometry, 20th Annual Conference on Mass Spectrometry and Allied Topics, Dallas, Texas, June 1972.
- (7) H. M. Rosenstock, J. T. Larkins, and J. A. Walker, *Int. J. Mass Spectrom. Ion Phys.*, **11**, 309 (1973).
- (8) T. Baer, G. D. Willett, D. Smith, and J. S. Phillips, *J. Chem. Phys.*, **70**, 4076 (1979).
- (9) B. O. Jonsson and E. Lindholm, *Ark. Fys.*, **39**, 65 (1969).
- (10) C. E. Klots, *Z. Naturforsch., A*, **27A**, 553 (1972).
- (11) M. L. Vestal in "Fundamental Processes in Radiation Chemistry", P. Ausloos, Ed., Wiley, New York, 1968, p 59.
- (12) H. M. Rosenstock, K. E. McCulloh, and F. P. Lossing, *Int. J. Mass Spectrom. Ion Phys.*, **25**, 327 (1977).
- (13) J. Dannacher, *Chem. Phys.*, **29**, 339 (1978).
- (14) J. Dannacher, *Adv. Mass Spectrom.*, **8A**, 37 (1979).
- (15) T. Keough, T. Ast, J. H. Beynon, and R. G. Cooks, *Org. Mass Spectrom.*, **7**, 245 (1973).

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