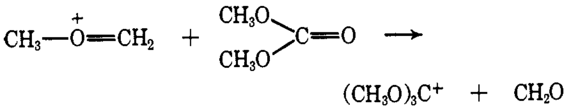
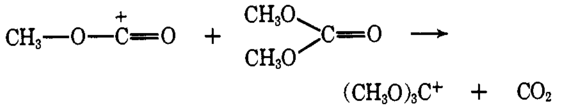


$$\mathrm{CH_3{-}\overset{+}{O}{=}CH_2} + \mathrm{(CH_3O)_2C{=}O} \longrightarrow \mathrm{(CH_3O)_3C^+} + \mathrm{CH_2O} \quad (22)$$



$$\mathrm{CH_3{-}O{-}\overset{+}{C}{=}O} + \mathrm{(CH_3O)_2C{=}O} \longrightarrow \mathrm{(CH_3O)_3C^+} + \mathrm{CO_2} \quad (23)$$

heat of formation of $C_2H_5O^+$ derived from the same source, where such data are available. *In each case where previously considered the structures identified are in agreement with postulated pathways of ion decomposition.*[38,39]

Conclusion

Distinguishing between ionic species having the same chemical constitution and mass but differing structures is both a difficult and interesting problem in mass spectrometry. It is apparent that specific reactivity of functional groups can be employed, in conjunction with the facility of ion cyclotron resonance spectroscopy for identifying ion–molecule reactions, to provide ion structural information. This constitutes a powerful addition to the methods involving thermochemical considerations,[10–15] metastable ion characteristics,[16,17] and collision-induced decompositions.[18] It is of interest to note that the present method can be employed to determine the structures of *products* of ion–molecule reactions. This application is currently under active scrutiny.

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[38] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967.

[39] Of particular interest are the results obtained for cyclic ethers whose fragmentation pathways have only recently been considered in detail by (a) R. Smakman and T. J. de Boer, *Org. Mass. Spectrosc.*, **1**, 403 (1968); (b) J. E. Collin and G. Conde-Caprace, *Intern. J. Mass Spectrom. Ion Phys.*, **1**, 213 (1968); (c) M. Vandewalle, N. Schamp, and K. Van Cauwenberghe, *Bull. Soc. Chim. Belges*, **77**, 33 (1968).

The Microwave Spectrum, Structure, and Dipole Moment of Methylenecyclopropane[1]

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Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey. *Received October 30, 1969*

Abstract: The microwave spectrum of the normal isotopic species and the three monosubstituted ^{13}C species of methylenecyclopropane has been studied in the ground state and effective rotational constants have been obtained. Moments of inertia calculated from the rotational constants lead to the following substitution values for the carbon structural parameters: $r(C_1C_2) = 1.3317 \pm 0.0014$, $r(C_2C_3) = 1.4570 \pm 0.0014$, $r(C_3C_3') = 1.5415 \pm 0.0003$ Å, $\angle C_3C_2C_3' = 63°\,52' \pm 3'$. With assumption of the ethylenic CH bond length to be 1.088 Å, the other H parameters are calculated to be: $r(CH) = 1.09 \pm 0.01$ Å, $\angle HCH$ (ethylenic) $= 114.3 \pm 1°$, $\angle HCH$ (ring) $= 113.5 \pm 1°$ with the HCH plane bisecting $\angle C_2C_3C_3'$. From the Stark effect the dipole moment is determined to be 0.402 ± 0.004 D.

The structures and dipole moments of small ring compounds are interesting because of the unusual geometrical constraints which are imposed. Determination of accurate values for these parameters gives insight into the nature of the bonding and is useful in understanding effects such as angle strain.

A particularly interesting molecule is methylenecyclopropane. Here additional angle strain should be introduced by the presence of a nominally sp^2-hybridized carbon in a three-membered ring. It is of interest, therefore, to ascertain in what way the structural parameters differ from those of cyclopropane and related molecules in which only nominally sp^3-hybridized carbons are present in the ring. Methylenecyclopropane also provides an opportunity to study the interaction between a three-membered ring and a double bond.

In this work we report the microwave spectrum of methylenecyclopropane, including the three monosubstituted ^{13}C isotopic species, and the determination of the molecular structural parameters and dipole moment.

Experimental Section

Methylenecyclopropane was synthesized from 3-chloro-2-chloromethyl-1-propene by the method of Gragson, *et al.*[3] The precursor was obtained from Aldrich Chemical Co. After synthesis the sample was purified by gas chromatography and was stored at −78° to avoid polymerization. ^{13}C species were studied in their naturally occurring abundance.

All transitions except the 2 → 3 R-branch transitions of the main isotopic species were measured on a 100-KHz Stark modulation

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[1] This research was supported by a grant from the National Science Foundation and gifts to Princeton University from the General Electric Foundation and the Olin-Matheson Charitable Fund.

[2] Alfred P. Sloan Fellow.

[3] J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Amer. Chem. Soc.*, **75**, 3344 (1953).

Table I. Ground State Rotational Transitions (MHz) of Normal Methylenecyclopropane

Transition	Obsd[a]	Obsd − calcd
$0_{00} \rightarrow 1_{01}$	12,322.30	+0.07
$1_{11} \rightarrow 2_{12}$	23,212.47	0.00
$1_{01} \rightarrow 2_{02}$	24,528.75	+0.06
$1_{10} \rightarrow 2_{11}$	26,076.44	0.00
$2_{12} \rightarrow 3_{13}$	34,749.02	−0.04
$2_{02} \rightarrow 3_{03}$	36,508.56	−0.02
$2_{21} \rightarrow 3_{22}$	36,966.32	−0.36
$2_{20} \rightarrow 3_{21}$	37,424.43	−0.35
$2_{11} \rightarrow 3_{12}$	39,039.02	−0.12
$3_{13} \rightarrow 3_{12}$	8,585.98	−0.06
$4_{14} \rightarrow 4_{13}$	14,278.70	−0.20
$5_{15} \rightarrow 5_{14}$	21,316.60	−0.54
$7_{26} \rightarrow 7_{25}$	12,090.43	0.00
$8_{27} \rightarrow 8_{26}$	18,487.39	−0.50
$9_{28} \rightarrow 9_{27}$	26,350.97	−1.47

[a] Estimated uncertainty 0.05 MHz.

Table II. Ground State Rotational Transitions[a] (MHz) of ^{13}C Species

	$^{13}C_1$		$^{13}C_2$		$^{13}C_3$	
Transition	Obsd	Obsd − calcd	Obsd	Obsd − calcd	Obsd	Obsd − calcd
$0_{00} \rightarrow 1_{01}$	11,937.54	+0.06	12,309.20	+0.08	12,156.35	+0.06
$1_{11} \rightarrow 2_{12}$	22,529.84	0.00	23,189.26	0.00	22,877.86	0.00
$1_{01} \rightarrow 2_{02}$	23,774.30	0.00	24,503.06	0.00	24,193.45	+0.08
$1_{10} \rightarrow 2_{11}$	25,220.08	0.00	26,047.22	0.00	25,747.31	0.00
$7_{26} \rightarrow 7_{25}$					12,350.09	0.00
$8_{27} \rightarrow 8_{26}$					18,834.22	−0.50
$9_{28} \rightarrow 9_{27}$					26,776.6[b]	−1.59

[a] Estimated uncertainty 0.05 MHz unless otherwise specified. [b] Estimated uncertainty 0.15 MHz.

Table III. Rotational Constants (MHz) and Moments of Inertia[a] (amu Å^2)

	Normal species	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$
A	19417.6 ± 0.1	19424 ± 10	19422 ± 10	18998.1 ± 0.1
B	6877.11 ± 0.03	6641.30 ± 0.03	6869.05 ± 0.03	6795.51 ± 0.03
C	5455.12 ± 0.03	5296.18 ± 0.03	5440.07 ± 0.03	5360.78 ± 0.03
I_a	26.0268 ± 0.0001	26.02 ± 0.01	26.02 ± 0.01	26.6015 ± 0.0001
I_b	73.4869 ± 0.0004	76.0961 ± 0.0004	73.5731 ± 0.0004	74.3693 ± 0.0004
I_c	92.8128 ± 0.0005	95.4229 ± 0.0005	92.8990 ± 0.0005	94.2730 ± 0.0005
$I_a + I_b - I_c$	6.7009	6.69	6.69	6.6978
ΔI_a		$\sim$0	$\sim$0	0.5747
ΔI_b		2.6092	0.0862	0.8824
ΔI_c		2.6101	0.0862	1.4602

[a] Conversion factor 505,377 amu Å^2 MHz.

spectrometer. Weaker lines were measured using phase-stabilized klystrons. The 2 → 3 R-branch transitions of the main species were measured at the Hewlett-Packard Co. using their commercial spectrometer through the courtesy of Dr. L. H. Scharpen.

Spectrum and Rotational Constants

The spectrum is that of a prolate asymmetric top with a-type selection rules. Low J transitions were identified from their characteristic Stark effects. Assigned transitions for the most abundant isotopic species are given in Table I. Transitions for the ^{13}C species are given in Table II. Rotational constants and moments of inertia are given in Table III.

Several relations were useful in assigning the ^{13}C species. Since the carbon atoms lie in a symmetry plane the quantity $I_a + I_b - I_c$ should be essentially invariant. Also two of the carbon atoms lie on a symmetry axis so that I_a should also be invariant while ΔI_b should equal ΔI_c. These conditions are all fulfilled within experimental uncertainty as can be seen from Table III.

Of the transitions studied, the most sensitive to the rotational constant A are the Q-branch series involving $K_{-1} = 2$. The member of this series with the lowest value of J which was accessible was the $7_{27} \rightarrow 7_{26}$. This transition was used in both the main isotopic species and the off-axis ^{13}C-substituted species to calculate the rotational constant A. In the two other ^{13}C-substituted species A was not required for the structure determination and was calculated from the $1_{01} \rightarrow 2_{02}$.

Structure

Since all monosubstituted ^{13}C species have been studied, the carbon atom coordinates are obtained directly[4] and are given in Table IV. The corresponding structural parameters are given in Table V. The quoted uncertainties are those arising from possible error in frequency measurements and do not include any effects of vibration–rotation interactions. Rotational constants used in obtaining the coordinates have been determined from the same transitions for each isotopic species. In this way it is hoped that vibration–rotation effects such as those of centrifugal distortion will tend to cancel. The coordinates of the two carbon atoms located on the symmetry axis can be obtained from either ΔI_b or ΔI_c. The two values thus calculated are essentially the same.

Although none of the hydrogens has been isotopically substituted, there are four relations which can be used to calculate their coordinates. These are the three moments of inertia of the main isotopic species and the center of mass relation $\Sigma m_i z_i = 0$ (z is the symmetry axis). Since there are five structural parameters to be determined which involve hydrogen atoms, one assumption must be made. Because the off-axis distance of the ethylenic hydrogens makes only a small contribution to the moments of inertia while ethylenic CH bond lengths vary relatively little among hydrocarbons, the

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

Table IV. Atomic Coordinates[a] (Å)

Atom	x	y	z
C_1	0	0	1.6275 ± 0.0002
C_2	0	0	0.2958 ± 0.0012
C_3	±0.7707 ± 0.0001	0	−0.9407 ± 0.0004
H(ethylenic)	±0.914[b]	0	2.217[c] ± 0.001
H(ring)	±1.292[c] ± 0.004	±0.9117[c] ± 0.0001	−1.234[c] ± 0.003

[a] The symmetry axis is z and xz is the plane of the C atoms. Error limits only indicate uncertainties due to possible error in frequency measurements. [b] Based on assumed r_{CH} length of 1.088. [c] Not substitution coordinate.

Table V. Structural Parameters[a]

$r(C_1C_2) = 1.3317 \pm 0.0014$
$r(C_2C_3) = 1.4570 \pm 0.0014$
$r(C_3C_3') = 1.5415 \pm 0.0003$
$\angle C_3C_2C_3' = 63° 52' \pm 3'$
r(CH ethylenic) = 1.088 (assumed)
r(CH ring)[b] = 1.09 ± 0.01
∠HCH (ethylenic)[b] = 114.3 ± 1°
∠HCH (ring)[b] = 113.5 ± 1°
HCH plane ∠ with[b] C_3C_3' = 29.2 ± 1°

[a] For carbon parameters error limits represent frequency uncertainties only. For hydrogen parameters they include an estimate of the uncertainty due to the assumption of ethylenic CH bond lengths. All r given in Å. [b] Not substitution values.

ethylenic CH bond length has been assumed to be that found in isobutylene.[5] The hydrogen coordinates which are then calculated are given in Table IV and structural parameters are given in Table V.

Dipole Moment

Stark effect measurements were made on the $M = 1$, $1_{11} \rightarrow 2_{12}$ and $M = 0$, $1_{01} \rightarrow 2_{02}$ transitions. The observed Stark coefficients are given in Table VI. The cell spacing was determined[6] using the 1 → 2 transition of OCS. The value 0.402 ± 0.004 obtained for the dipole moment can be compared with the value of 0.509 D obtained for isobutylene.[7] The dipole moment of cyclopropanone[8] (2.67 D) is also observed to be lower than that of acetone[9] (2.89 D). The lower dipole moment for the two three-membered ring compounds supports the idea that a three-membered ring behaves somewhat like a double bond.[10] On the other hand, the four-membered systems methylenecyclobutane[11] and cyclobutanone[12] have the same dipole moments within experimental error as isobutylene and acetone, respectively.

Table VI. Stark Effect Coefficients and Dipole Moment[a]

Transition	$\Delta\nu/E^2$, MHz/(V/cm)^2	μ, D
$1_{11} \rightarrow 2_{12}$, $M = 1$	7.174×10^{-6}	0.402
$1_{01} \rightarrow 2_{02}$, $M = 0$	-5.076×10^{-7}	0.402

[a] Relative to OCS value of 0.71521 D (ref 6).

Discussion

For purposes of comparison, CC bond lengths from some related molecules are given in Table VII.

Table VII. Comparison of CC Bond Lengths in Related Molecules

Molecule	Single bond lengths	Double bond lengths
Cyclopropane[a]	1.514	
Cyclopropyl chloride[b]	1.514	
Cyclopropanone[c]	1.475 1.575	
Isobutylene[d]	1.507	1.330
Methylene-cyclopropane	1.457 1.542	1.332

[a] Reference 13. [b] Reference 14. [c] Reference 15. [d] Reference 5.

The lengths of the CC bonds in the ring of methylenecyclopropane are significantly different from those of cyclopropane[13] and closely related molecules such as cyclopropyl chloride.[14] The nominally sp^2-hybridized carbon has caused the CC bond opposite the double bond to become quite long while the two adjacent bonds have become quite short. This result is similar to that found in cyclopropanone,[15] where an even more pronounced lengthening of the CC bond opposite the double bond occurs.

The double bond length is surprisingly close to the value 1.330 ± 0.004 found in isobutylene.[5] According to standard hybridization arguments, the carbon orbitals involved in the ring bonding should have more p character than those of analogous noncyclic compounds. Correspondingly, more s character should be present in the other hybrid carbon orbitals. Bonds involving these orbitals should thus be shortened. This effect has been invoked to explain the variation with ring angle of the carbonyl stretching frequency of cyclic ketones.[16] Since some bonding changes undoubtedly occur in going from isobutylene to methylenecyclopropane the lack of any observable change in the double bond length is unexpected.

In contrast, the carbonyl bond length reported for cyclopropanone[15] is 0.031 Å shorter than that found for acetone.[17] However, because of the rather large experi-

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(5) L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, **39**, 1732 (1963).

(6) J. S. Muenter, *ibid.*, **48**, 4544 (1968).

(7) V. W. Laurie, *ibid.*, **34**, 1516 (1961).

(8) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, **90**, 1072 (1968).

(9) J. D. Swalen and C. C. Costain, *J. Chem. Phys.*, **31**, 1562 (1959).

(10) *Cf.* the quadrupole coupling constants for Cl in cyclopropyl chloride and vinyl chloride: R. M. Schwendeman, G. D. Jacobs, and T. M. Krigas, *J. Chem. Phys.*, **40**, 1022 (1964).

(11) L. H. Scharpen and V. W. Laurie, *ibid.*, **49**, 3041 (1968).

(12) L. H. Scharpen and V. W. Laurie, *ibid.*, **49**, 221 (1968).

(13) W. J. Jones and B. P. Stoicheff, *Can. J. Phys.*, **42** (11), 2259 (1964).

(14) The structure is given in the reference of footnote 10.

(15) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, **91**, 1896 (1969).

(16) For example, P. D. Bartlett and M. Stiles, *ibid.*, **77**, 2806 (1955).

mental uncertainty of 0.02 Å quoted for the cyclopropanone value, the amount of shortening which actually occurs is not well determined and may be less than 0.03 Å.

The CH parameters obtained are similar to those found in related molecules. The parameters of the ring hydrogens are the same within experimental error as those found in cyclopropanone.[15] It is interesting that in both molecules the HCH plane bisects the CCC angle.

(17) R. Nelson and L. Pierce, *J. Mol. Spectrosc.*, **18**, 344 (1965).

The Rotational Isomerism of the Aromatic Amino Acids by Nuclear Magnetic Resonance[1a]

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Abstract: The chemical shifts and coupling constants for the aliphatic protons of tyrosine, tryptophan, and histidine in basic aqueous solution have been obtained as a function of temperature and concentration. The tryptophan anion is nearly identical with the phenylalanine anion previously reported; that is, at low concentration the vicinal coupling constants diverge with increasing temperature while at high concentration they converge. The vicinal coupling constants for the tyrosine dianion are independent of concentration and exhibit the divergent temperature variation typical of phenylalanine at low concentration. On the other hand, those for the histidine anion are nearly temperature independent but vary with concentration in a manner intermediate between tyrosine and phenylalanine. The variations in the vicinal coupling constants may be interpreted in terms of variations with temperature and concentration of the relative energies of the three classical staggered rotamers. In all cases, the two less favorable conformations become less stable with increasing temperature. The effect of concentration is in this same direction; the magnitude of the effect increases in the series tyrosine (no effect) < histidine < tryptophan, phenylalanine. The rotamer energy variations appear to reflect both solute–solvent and solute–solute interactions.

Recent investigations[2] of the nmr spectra of phenylalanine in aqueous solution have shown rather unusual effects of temperature and concentration on the vicinal coupling constants for the α,β protons. These effects have been related to temperature and concentration-dependent changes of the relative energies of the classical staggered rotamers. The rotamer energies appear to be strongly influenced by the nature and extent of intermolecular solute–solvent interactions. In an effort to understand more about such interactions, these studies have been extended to the aromatic amino acids tyrosine, tryptophan, and histidine. We report here the results of this study as applied to the negatively charged species in aqueous solution.

Experimental Section

The nmr spectra were recorded on a Varian Associates DA-60IL spectrometer,[3] equipped with a variable temperature probe and operated at 60 MHz in the internal-lock, frequency-sweep mode. The frequency sweep was calibrated in the vicinity of each resonance peak by counting the difference between fixed and swept oscillators. Line positions were calculated as the averages of at least four recordings taken with alternating upfield and downfield sweep. Precision of the measurements was better than 0.1 Hz. The variable temperature apparatus was calibrated using the internal chemical shifts of ethylene glycol and methanol as standards for the high and low temperature scales, respectively. The reported temperatures are estimated to be accurate to ±2°.

The amino acids were obtained commercially and were stated to be chromatographically pure. The anion of tryptophan was prepared by dissolving the acid in D_2O containing a slight excess of an equivalent amount of NaOH. For the tyrosine dianion and the histidine anion the solvent contained a slight excess of twice an equivalent amount of NaOH.[4] Concentrations are reported in moles of amino acid per liter of solvent. *t*-Butyl alcohol (2% v/v) was added as an internal standard.

Results and Discussion

Analysis of the Spectra. The aliphatic protons of all the amino acids studied give rise to spectra that are similar to corresponding portions of the phenylalanine spectra. These have been discussed previously in detail.[2a] For tryptophan, the α C–H proton of the indole ring couples to the aliphatic β protons, splitting the eight β-proton transitions into doublets. Similarly, the proton adjacent to the carbon–carbon double bond in the imidazole ring of histidine couples to the aliphatic β protons. The splittings in both cases are essentially independent of temperature and concentration. On the basis of a first-order analysis, the values for the coupling constants averaged over all the measurements are as follows: tryptophan, 0.83 and 0.65 Hz for the low- and high-field β proton resonances, respectively; histidine, 0.78 and 0.64 Hz for the low- and high-field β proton resonances, respectively. The three-spin-system transitions of the aliphatic protons appropriate to the β protons were taken as the midpoints of the doublets.[5] The

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(1) (a) Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 7–12, 1969; (b) Agricultural Research Service, U. S. Department of Agriculture.

(2) (a) J. R. Cavanaugh, *J. Amer. Chem. Soc.*, **89**, 1558 (1967); (b) *ibid.*, **90**, 4533 (1968).

(3) Mention of commercial products does not constitute an endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

(4) An excess of twice an equivalent amount of base for histidine was used to ensure that the imidazole ring would not be protonated.

(5) At low temperature, the doublet splitting was masked by an in-