Conformational Equilibrium in (Cyclopropylmethyl)acetylene: A Microwave Spectroscopy and ab Initio Calculation Study

Walther Caminati

Dipartimento di Chimica "G. Ciamician" dell'Universita', Via Selmi 2, I-40126 Bologna, Italy

Roberto Danieli

Instituto di Spettroscopia Molecolare del C. N. R., Via de'Castagnoli 1, I-40126 Bologna, Italy

Marwan Dakkouri* and Ralf Bitschenauer

Abteilung für Elektrochemie, Universität Ulm, D-89069 Ulm, Germany

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The microwave spectrum of (cyclopropylmethyl)acetylene (a newly prepared compound) was investigated in the frequency range 28–40 GHz. Both *gauche* and *cis* conformers were observed, the latter being 64 ± 30 cm⁻¹ lower in energy. The geometries of these conformers were obtained combining the ab initio and microwave spectroscopy results. A large-amplitude motion (the methylacetylene group torsion) was studied by assigning the rotational spectra of several torsionally excited states.

Introduction

The main objectives for synthesizing and studying (cyclopropylmethyl)acetylene (CPMAC), in which the acetylene group and the ring are separated by a saturated sp³-hybridized carbon atom, are the following: (i) to investigate whether the interaction between the acetylene group and the cyclopropyl ring occurs through the bonds or through space; (ii) to study the conformation and the role of the acetylene moiety as a strong σ and π acceptor by the conformational preference of CPMAC. The conformational behavior of a number of cyclopropylmethyl derivatives has been studied by various spectroscopic methods.¹⁻⁶ In most of these compounds the gauche conformer has been found to be predominant. This result has been accounted for mainly by the "gauche effect".⁷ We, however, thought that the situation could be different when the substituent is a strong electron acceptor which might interact with the surface orbitals of the cyclopropane ring. For these reasons we undertook the investigation of the microwave spectrum of CPMAC. Depending on the value of the angle τ between the ethynyl group and the bisector of the ring angle $C_2C_1C_3$, three conformations are possible, the cis, the gauche, and the trans (Figure 2). Figure 1 shows the atom numbering used through the text. Information on the torsion of the methylacetylene group with respect to the ring was expected to be obtained from the analysis of the vibrational satellites.

Experimental Section

CPMAC was synthesized by the reaction of cyclopropylmethyl bromide with lithium acetylide-ethylenediamine complex in dry dimethyl sulfoxide. The product was removed from the reaction mixture by trapping it in vacuum and fractioning it to yield 25% of CPMAC (bp 74.5-75.0 °C at 718 Torr). The purity of the sample was checked by IR and mass spectroscopy. Details of the preparation of this and other various cyclopropylmethyl derivatives will be published elsewhere.⁸

We investigated the microwave spectrum of CPMAC in the frequency range of 28-40 GHz using a computerized



Figure 1. (Cyclopropylmethyl)acetylene. Molecular model which shows the numbering of the atoms.

conventional Stark modulated spectrometer.⁹ The cell was kept cold at about -20 °C.

Results and Discussion

(a) Ab Initio Calculations. The optimization of the geometry of CPMAC was performed using standard gradient procedures^{10,11} and the program BRABO.¹² The 4-21G* basis set was applied for the calculations.

The most important structural parameters obtained from the ab initio calculations are displayed in Table 6.

Two rotamers, the *gauche* and the *cis*, were calculated to be the most stable conformations, where the *cis* form is more stable than the *gauche* only by 20 cal/mol.

We also optimized the geometry and investigated the conformational stability of CPMAC at the 6-31G* level.¹³ It is worth noting that in contrast to the 4-21G* basis set the 6-31G* basis set predicts a higher stability of the *gauche* conformer in comparison to the *cis* one. The difference in total energy in this case is 376 cal/mol.

(b) Assignment of the Rotational Spectra. The ab initio geometries were used to calculate the preliminary values of the rotational constants.

Because the μ_a -type bands of the *gauche* form dominated the spectrum, the assignment of this conformer was relatively easy to achieve. A few μ_a -R-type K_a asymmetry doublets were assigned by using the radiofrequency microwave double reso-

^{*} Author to whom correspondence should be addressed.

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$J'(K_a',K_c') \leftarrow J''(K_a'',K_c'')$		$v_t = 1$	$v_t = 2$	v _t = 3	$v_x = 1$	(1,1)
$8(0.8) \leftarrow 7(0.7)$	30 125.27	30 159.06			30 166.53	30 202.30
$8(1.8) \leftarrow 7(1.7)$	29 586.91	29 621.00	29 653.44	29 684.00	29 624.41	29 661.20
$8(1.7) \leftarrow 7(1.6)$	30 994.93	31 032.15	31 067.04	31 099.53	31 041.86	31 080.81
$8(2.7) \leftarrow 7(2.6)$	30 312.09					
$8(2.6) \leftarrow 7(2.5)$	30 531.05	30 569.25		30 638.80	30 574.61	
$8(3.6) \leftarrow 7(3.5)$	30 374.29	30 410.75	30 445.38	30 477.19	30 416.99	30 455.49
$8(3,5) \leftarrow 7(3,4)$	30 380.56	30 417,10	30 452.05	30 484.29	30 423.23	30 461.92
$8(4) \leftarrow 7(4)^a$	30 365.06	30 401.50	30 435.98	30 467.86	30 407.55	
$8(5) \leftarrow 7(5)^a$	30 360.54	30 396.88	30 431.27	30 463.27	30 403.11	
$8(6) \leftarrow 7(6)^a$	30 359.14	30 395.33	30 429.71	30 461.76	30 401.50	
$9(0.9) \leftarrow 8(0.8)$	33 828.11	33 865.48	33 900.93	33 933.96	33 874.15	
$9(1.9) \leftarrow 8(1.8)$	33 270.09	33 308.22	33 344.74	33 378.65	33 312.07	33 353.16
$9(1.8) \leftarrow 8(1.7)$	34 849.53	34 891.12	34 930.17	34 966.34	34 902.21	34 945.74
$9(2.8) \leftarrow 8(2.7)$	34 089.41					
$9(2.7) \leftarrow 8(2.6)$	34 398.02	34 441.70	34 482.74	34 520.63	34 447.32	34 493.16
$9(3.7) \leftarrow 8(3.6)$	34 176.87	34 217.95	34 256.67	34 292.79	34 224.84	
$9(3.6) \leftarrow 8(3.5)$	34 188,49	34 229.78	34 268.93	34 305.26	34 236.45	34 280.31
$9(4) \leftarrow 8(4)^a$	34 164.74	34 205.88	34 244.55	34 280.49	34 212.69	34 256.00
$9(5) - 8(5)^a$	34 157.96	34 199.00		34 273.58	34 205.88	34 249.20
$9(6) \leftarrow 8(6)^a$	34 155.27	34 196.23	34 234.81	34 270.95	34 203.24	34 246.36
$10(0.10) \leftarrow 9(0.9)$	37 511.90	37 552.67	37 591.51	37 627.79	37 562.68	
$10(1.10) \leftarrow 9(1.9)$	36 948.65	36 990.87	37 031.12	37 068.74	36 995.14	37 040.27
$10(1.9) \leftarrow 9(1.8)$	38 696,40	38 742.28	38 785.42	38 825.44	38 754.84	38 802.90
$10(2.9) \leftarrow 9(2.8)$	37 862.57					
$10(2.8) \leftarrow 9(2.7)$	38 279.40	38 328.32	38 374.46	38 416.99	38 334.50	38 385.92
$10(3.8) \leftarrow 9(3.7)$	37 980.96	38 026.82	38 069.79	38 110.17	38 034.34	38 082.48
10(3,7) - 9(3,6)	38 000.58	38 046.99	38 090.66	38 130.72	38 054.13	38 103.04
$10(5) - 9(5)^a$	37 956.27	38 001.76	38 044.81	38 084.88	38 009.41	
$10(6) - 9(6)^a$	37 952.40	37 997.71	38 040.67	38 080.74	38 005.56	38 053.50
$10(7) \leftarrow 9(7)^a$		37 996.55	38 039.55	38 079.49	38 004.46	38 052.13

^a Asymmetry degenerate K_a doublets.

nance technique (RFMWDR).¹⁴ Several transitions were then measured with Stark modulation.

In spite of the fact that the *cis* conformer is more stable (see later), its signals, however, were weaker because, with respect to the *gauche* form, (i) it does not have a double degeneracy; (ii) the observed transitions have smaller line strengths; (iii) the μ_a dipole moment is smaller. Nevertheless, it has been possible to assign its spectrum with the help of RFMWDR.

We also assigned the rotational spectra of several low-energy vibrational satellites belonging to the methylacetylene group torsion in both conformers. They have been labeled $v_t = 1, 2, 3$. One vibrational satellite of a second low-energy vibration ($v_x = 1$) and the combination excited state (1,1) has been assigned too, but only for the *gauche* conformer.

Measured rotational transitions of the *gauche* form are reported in Table 1, while those of the *cis* species are listed in Table 2. The spectroscopic constants obtained treating the experimental frequencies with a quadratic Watson Hamiltonian¹⁵ are reported in Tables 3 and 4, respectively, for the two species. Some statistical parameters of the fits are also shown.

It is, however, worth noting that the given vibrational energies are obtained from MW relative intensity measurements.¹⁶

(c) Dipole Moment. The dipole moment has been measured for both conformers. In the case of gauche-CPMAC two transitions have been classifed, which have *M*-dependent Stark coefficients (ΔB^{g}) much smaller than the coefficients (ΔA^{g}) which do not depend on M.¹⁷ For them, just a single giant Stark lobe appears when an electric field is applied. We have used this technique to determine the dipole moment for various kinds of heavy asymmetric tops.¹⁸ For one more transition it has been possible to measure the displacements of three single Stark lobes. The $\Delta \nu/E^2$ slopes of five Stark lobes of two transitions have been measured for *cis*-CPMAC.

Table 5 displays the transitions chosen for the dipole moment measurements. Moreover, the obtained dipole moment components for both conformers are listed at the bottom of this table.

TABLE 2: Experimental Transition Frequencies of cis-CPMAC (MHz)

$J'(K_a',K_c') \leftarrow J''(K_a'',K_c'')$	G.S.	$v_t = 1$	$v_t = 2$
$6(0,6) \leftarrow 5(0,5)$		28 603.56	
$6(1,6) \leftarrow 5(1,5)$	28 136.35		
$6(1,5) \leftarrow 5(1,4)$	30 208.81		29 975.20
6(2,5) - 5(2,4)	29 246.94		
$6(2,4) \leftarrow 5(2,3)$	29 908.92	29 779.20	
6(3,4) - 5(3,3)	29 435.57	29 326.94	29 221.29
$6(3,3) \leftarrow 5(3,2)$	29 478.42	29 366.40	29 258.35
$6(5) \leftarrow 5(5)^a$	29 394.44		
7(0,7) ← 6(0,6)	33 242.41	33 162.68	33 083.77
$7(1,7) \leftarrow 6(1,6)$	32 767.20	32 683.94	
$7(1,6) \leftarrow 6(1,5)$	35 139.85	35 007.27	34 879.20
$7(2,5) \leftarrow 6(2,4)$	35 053.79	34 898.20	34 747.96
$7(4,4) \leftarrow 6(4,3)$	34 334.38	34 207.20	34 084.04
$7(4,3) \leftarrow 6(4,2)$	34 337.06	34 209.88	34 086.18
$8(0,8) \leftarrow 7(0,7)$	37 766.84	37 681.16	37 596.20
$8(1,8) \leftarrow 7(1,7)$	37 379.24	37 286.84	37 194.90
8(2,7) - 7(2,6)	38 867.06		38 616.45
$8(3,6) \leftarrow 7(3,5)$	39 283.00	39 137.67	38 996.35
$8(3,5) \leftarrow 7(3,4)$	39 468.53	39 309.49	
$8(4,5) \leftarrow 7(4,4)$	39 264.52	39 118.19	38 975.90
$8(4,4) \leftarrow 7(4,3)$	39 272.04	39 125.02	38 982.13
$8(5) \leftarrow 7(5)^a$	39 223.81	39 079.29	38 938.86
$8(6) \leftarrow 7(6)^a$	39 201.20	39 057.76	38 918.29
$8(7) \leftarrow 7(7)^a$	39 188.28	39 045.38	38 906.45

^{*a*} Asymmetry degenerate K_a doublets.

Calibration of the cell was undertaken using the 3–2 transition of OCS ($\mu = 0.71521$ D).¹⁹

The values of the μ_a dipole moment components data have been used for the determination of the relative energy of the two conformers in the following section.

(d) Conformation and Structure. Optimized geometries as well as the relative total energies of the three conformers obtained from *ab initio* calculations at the 4-21G* level are given in Table 6. The values of the corresponding calculated rotational constants are compared to the two experimental sets in Table

TABLE 3: Spectroscopic Constants of gauche-CPMAC (I r Representation)

	G.S.	$v_t = 1$	$v_t = 2$	$v_t = 3$	$v_x = 1$	(1,1)
A/MHz	10690.7(11) ^a	10631.9(13)	10575.5(20)	10528.7(22)	10763.5(12)	10696.0(22)
<i>B/</i> MHz	1984.990(5)	1987.454(7)	1989.762(10)	1991.888(11)	1988.240(6)	1990.804(11)
C/MHz	1808.226(6)	1810.277(7)	1812.267(10)	1814.125(11)	1810.277(6)	1812.532(11)
Δ_J/kHz^b	0.75(3)	0.72(3)	0.77(5)	0.80(5)	0.74(3)	0.82(6)
Δ_{JK}/kHz	-8.39(7)	-8.33(7)	-8.30(10)	-8.5(1)		-8.25(10)
$E_{\rm v}/{\rm cm}^{-1}$	_	70(20)	140(30)	200(40)	120(30)	200(40)
N^{d}	29	27	24	26	27	19
σ/MHz ^e	0.07	0.09	0.13	0.14	0.08	0.11
J_{\max}	10	10	10	10	10	10

^{*a*} Errors in parentheses in units of the last digit. ^{*b*} Δ_K (the first-order centrifugal distortion parameter), δ_J , δ_K were not determined from the fit and were fixed at zero. ^{*c*} Vibrational energy from MW relative intensity measurements. ^{*d*} Number of transitions in the fit. ^{*e*} Standard deviation of the fit.

 TABLE 4: Spectroscopic Constants of cis-CPMAC (l r Representation)

TABLE 6:	Structural	Parameters	CPMAC	(Å and deg)	and
ab Initio Ca	lculated (4-	-21G*) and	Effective	Geometries (See
Text) (See H	Figure 1 for	· Atom Nun	nbering)		

	G.S.	$v_t = 1$	$v_t = 2$
A/MHz	6895.8(5) ^a	6909.6(5)	6930.3(12)
<i>B</i> /MHz	2621.430(9)	2608.674(10)	2596.496(20)
C/MHz	2268.913(11)	2264.234(12)	2259.548(32)
Δ_{J}/kHz^{b}	1.56(7)	1.39(8)	1.67(20)
Δ_{JK}/kHz	-4.48(13)	-3.88(13)	-3.38(28)
$E_{\rm v}/{\rm cm}^{-1}$ c	_	85(20)	185(30)
N^{d}	23	19	17
σ/MHz ^e	0.10	0.09	0.19
J_{max}	8	8	8

^{*a*} Errors in parentheses in units of the last digit. ^{*b*} Δ_K (the first-order centrifugal distortion parameter), δ_J , and δ_K were not determined from the fit and were fixed at zero. ^{*c*} Vibrational energy from MW relative intensity measurements. ^{*d*} Number of transitions in the fit. ^{*e*} Standard deviation of the fit.

 TABLE 5: Stark Coefficients and Dipole Moment of CPMAC

Stark Coefficients						
$d\nu/dE^2$ (Hz V ⁻² cm ²)						
$\frac{J'(K_{a},K_{c}) \leftarrow J''(K_{a},K_{c})}{K_{a}}$	exp	calc				
	(a) Gauche					
$9_{2,7} \leftarrow 8_{2,6}$	-0.423(11)	-0.424 (M=2)				
. ,	-0.924(32)	-0.927 (M=3)				
	-1.637(42)	-1.631 (M=4)				
$9_{1.8} \leftarrow 8_{1.7}$	$-0.065(10)^{a}$	-0.065 (M=1)				
		-0.071 (M=4)				
$10_{1.9} - 9_{1.8}$	$-0.040(10)^{a}$	-0.034 (M=1)				
	. ,	-0.038 (M=4)				
	(b) Cis					
$6_{2,4} - 5_{2,3}$	-0.389(6)	-0.393 (M=1)				
_,,.	-1.222(21)	-1.202 (M=2)				
	-2.460(42)	-2.444 (M=3)				
$6_{25} - 5_{24}$	0.905(42)	0.947 (M=2)				
	2.333(85)	2.365 (M=3)				
Dipole	Moment Componen	its				
gauche cis						

	0	,	
μ_{a}	0.700(6)	0.489(3)	
$\mu_{\rm b}$	0.21(3)	0.411(12)	
$\mu_{\rm c}$	0.18(6)	0.0^{b}	
$\mu_{ m tot}$	0.754(7)	0.639(10)	

^{*a*} For these lines the ΔB^{g} Stark coefficients are much smaller than the ΔA^{g} ones (g = a, b, c) and almost all Stark lobes overlap each other. ^{*b*} By symmetry.

7. It is easy to infer that the observed spectra belong to the *gauche* and *cis* conformers. Plausible partial r_0 structures which reproduce the rotational constants within a few megahertz are proposed in Table 6, and the corresponding values of the rotational constants are also reported in Table 7. These plausible structures have been obtained using empirical corrections²⁰ to the 4-21G* geometry of the corresponding conformers of

	gau	che	cis		trans
	ab initio	corr ^a	ab initio	corr ^a	ab initio
bond lengths					
C_1C_2	1.4950	1.4950	1.4959	1.4959	1.4982
C_2C_3	1.4995	1.4995	1.4959	1.4995	1.4967
C_1C_4	1.5199	1.5199	1.5253	1.5253	1.5364
C_1H_5	1.0780	1.0850	1.0790	1.0870	1.0763
C_4C_6	1.4743	1.4743	1.4727	1.4727	1.4728
C_6C_7	1.1819	1.2017	1.1825	1.2017	1.1819
C ₇ H ₈	1.0571	1.0640	1.0572	1.0640	1.0571
C_2H_9	1.0775	1.0840	1.0764	1.0840	1.0781
C_2H_{10}	1.0768	1.0840	1.0771	1.0840	1.0771
$C_{3}H_{11}$	1.0779	1.0850	1.0764	1.0840	1.0781
$C_{3}H_{12}$	1.0770	1.0840	1.0771	1.0840	1.0771
C_4H_{13}	1.0883	1.0950	1.0886	1.0950	1.0867
C_4H_{14}	1.0884	1.0950	1.0886	1.0950	1.0867
angles					
$\vartheta^{\mathbf{b}}$	124.8	125.78	127.43	128.52	125.42
$C_2C_1C_3$	60.14	60.14	60.16	60.16	59.93
$C_4C_1C_2$	119.84	119.84	121.73	121.73	120.14
$C_2C_1H_5$	116.38	116.38	115.82	115.82	115.92
$C_6C_4C_1(\alpha)$	112.47	112.47	114.08	112.41	112.49
$C_1C_2H_9$	117.74	117.74	117.64	117.64	117.62
$C_1C_2H_{10}$	118.09	118.09	117.86	117.86	118.21
$C_1C_3H_{11}$	117.95	117.95	117.64	117.64	117.62
$C_1C_3H_{12}$	118.09	118.09	117.86	117.86	118.21
$C_1C_4H_{13}$	109.70	109.70	109.38	109.38	110.39
$C_1C_4H_{14}$	109.99	109.99	109.38	109.38	110.39
dihedral angles					
τ°	119.30	116.30	0.00	0.00	180.00
$C_4C_1-C_2C_3$	-108.88	-108.88			
$C_3C_2-C_1H_5$	106.89	106.89			
$C_3C_1-C_2H_9$	107.82	107.82	107.02	107.02	107.56
$C_3C_1-C_2H_{10}$	-108.02	-108.02	-108.37	-108.37	-108.30
$C_2C_1-C_3H_{11}$	-107.60	-107.60	-107.02	-107.02	-107.56
$C_2C_1-C_3H_{12}$	108.05	108.05	108.37	108.37	108.30
$H_5C_1-C_4H_{13}$	-178.07	-175.03	-58.48	-58.48	121.02
$H_5C_1-C_4H_{14}$	-60.70	-57.66	58.48	58.48	-121.02
		Energie	s		
oh init		ah init	io a	vn (h initio

	au muu	exp	ao muo	Слр	ao muo
E^{d}	-145200.08	_	-145200.10	_	-145196.79
ΔE^e	0.00	0.00	-0.020	-0.18(8)	3.29
^a E	mpirically corre	ected an	nd adjusted valu	ues: see tex	t. ^b See Figure

1. ^c See Figure 2. ^d Absolute ab initio energy (kcal/mol). ^e ΔE = relative energy with respect to the *gauche* conformer (kcal/mol).

CPMAC and refining the $C_5C_4C_1$ valence angles (α of Figure 1) and either the ϑ or $C_4C_1-C_2C_3$ dihedral angles in order to reproduce the experimental rotational constants.

By combining microwave relative intensity measurements and the μ_a component dipole moment values it was possible to calculate the relative energy of the two conformers in their

TABLE 7: Calculated and Experimental Rotational Constants (MHz) for the Various Conformers of CPMAC

		Α	В	С
gauche	ab initio	10 899.7	1978.2	1806.2
0	corrected ^a	10 692.6	1986.3	1806.5
	experimental	10 690.7	1985.0	1808.2
cis	ab initio	7 032.8	2601.9	2260.5
	corrected ^a	6 902.0	2624.4	2266.1
	experimental	6 895.8	2621.4	2268.9
trans	ab ⁱ nitio	12 565.3	1743.6	1729.2
^a See tex	t.			

vibronic ground state, $\Delta E_{0,0} = (E_{cis} - E_{gauche})$, by using the following equation:

$$\Delta E_{0,0} = kT \ln[(g_{\rm C}\alpha_{\rm G}\Delta\nu_{\rm G}\mu_{\rm a,C}^2\gamma_{\rm C}\nu_{\rm C}^2)/(g_{\rm G}\alpha_{\rm C}\Delta\nu_{\rm C}\mu_{\rm a,G}^2\gamma_{\rm G}\nu_{\rm G}^2)]$$
(1)

where g, α , $\Delta \nu$, γ , and ν are degeneracy, peak height, line width, line strength, and transition frequency, respectively.

From this equation we obtained $\Delta E_{0,0} = -64 \pm 30 \text{ cm}^{-1}$. It is worth noting that this value is in poor agreement with the value of -7 cm^{-1} provided by the *ab initio* calculations using the 4-21G* basis set and it is in contrast with values of 132 cm⁻¹ obtained from the 6-31G* basis set and the ΔG^0 value of 152 ± 45 cm⁻¹ provided by our currently undertaken electron diffraction study.13

(e) Potential Energy Surface of the Methylacetylene Group Internal Rotation. For the determination of potential energy surface with respect to the torsion of the methylacetylene group we used the above-mentioned value for $\Delta E_{0,0}$, the vibrational energies from MW relative intensity measurements, the changes of the rotational constants in going from the gauche to the cis conformer, and the shifts of second moments of inertia upon torsional excitation.

In order to define the second moments of inertia, the following equations were used:

$$M_{\rm aa}(v) = (h/16\pi^2)(-1/A_v + 1/B_v + 1/C_v)$$
, etc. (2)

From the shifts in the second moment upon torsional excitation, we gain some indication of the corresponding extensions and contractions of the molecule along the different principal axes, helping us to visualize the structural effects of the torsional excitation.

A one-dimensional flexible model,²¹ previously used to study large-amplitude motions and related structural relaxations, was applied to the available data. It calculates the correct quantummechanical energy levels for an arbitrary motion and also provides the rotational constants in the corresponding state. The hindering potential for the torsional motion around the C_1-C_4 bond has the form given in eq 3:

$$V(\tau) = (1/2) \{ V_1 [1 - \cos(\tau)] + V_3 [1 - \cos(3\tau)] \}$$
(3)

The ϑ and α angles of Figure 1 were allowed to relax upon torsional excitation according to the following equations:

$$\vartheta = \vartheta_0 + \delta\vartheta (1 - \cos\tau)^2$$
(4)
$$\alpha = \alpha_0 + \delta\alpha (1 - \cos\tau)^2$$

Table 8 shows the complete results of the fitting. First the calculated values are compared to the experimental data, and then, at the bottom of the table, the obtained parameters are given. More precise values of the vibrational spacings, as from 2266.4

TABLE 8: Flexible Model Results for the Internal Rotation of the Methylacetylene Group

1. Vibrational Spacings (cm ⁻¹)							
$v_u - v_1$ expt calc							
gauche	1-0		70(20)	65.3			
Ū	2-0		140(30)	128.6			
	3-0		200(40)	190.0			
cis	1-0		80(20)	72.6			
	2-0		170(40)	142.8			
$\Delta E_{0,0}$			-64(30)	-61.2			
2. Ground-State Rotational Constants (MHz)							
		Α	В	С			
gauche	exp	10 690.7	1985.0	1808.2			
0	calc	10 690.5	1985.8	1807.0			
cis	exp	6895.8	2621.4	2268.9			

6894.6 3. Shifts of Second Moments $[M_{gg}(v) - M_{gg}(0)]$ (uÅ²)

2621.4

2624.3

cis

exp calc

		g = a		g =	= b	g = c	
	v	expt	calc	expt	calc	expt	calc
gauche	1	-0.447	-0.523	0.130	0.025	0.132	0.043
0	2	-0.875	-1.082	0.251	0.055	0.264	0.090
cis	1	0.775	0.547	-0.314	-0.338	0.168	0.026
	2	1.570	1.130	-0.646	-0.696	0.282	0.055

4. Determined Parameters

$V_1 (\mathrm{cm}^{-1}) = 87(28)^a$
$V_3 (\rm cm^{-1}) = 616(43)$
$\alpha_0 (deg) = 111.16(13)$
$\theta_0 (\text{deg}) = 125.63(19)$
$\delta \alpha (\text{deg}) = 0.08(4)$
$\delta\theta$ (deg) = 1.07(6)

a Errors in parentheses in units of the last digit.



Figure 2. Three possible conformations of the (cyclopropylmethyl) acetylene molecule. The gauche and the cis have been observed.

a far-infrared spectrum, would be very important for a better determination of the parameters, and even for a better choice of the shape of the potential energy function.

The internal rotation angle τ was allowed to vary over the range of 2π (cyclic motion) in the numerical calculations. This range was resolved into 57 equidistant mesh points²¹ in order to reach the proper convergence without using too much computer time. For each mesh point the molecular structure as well as the potential energy were specified.

Conclusions

Two conformers, the gauche and the cis have been detected in the microwave spectrum of CPMAC (Figure 2). In spite of the fact that the gauche conformer dominates the MW spectrum, it is less stable by about 60 cm^{-1} than the *cis* conformer. This is because the gauche conformer is doubly degenerate, and

 TABLE 9:
 Comparison between Relevant Bond Distances

 (Å) in Cyclopropylacetylene (CPA) and CPMAC As

 Obtained from *ab Initio* Calculations

	СРА		CPMAC (cis)		CPMAC (gauche)	
	4-21G*	6-31G*	4-21G*	6-31G*	4-21G*	6-31G*
$\overline{\begin{array}{c}C_1-C_2\\C_1-C_3\end{array}}$	1.5060	1.5057	1.4959	1.4959	1.4950 1.4974	1.4974 1.4947
$C_2 - C_3$ $C - C \equiv$	1.4909 1.4500	1.4906 1.4504	1. 4994 1.4727	1.5004 1.4722	1.4995 1.4743	1.5001 1.4734

because the μ_a dipole moment component of the *cis* is smaller. The *trans* form could not be observed. This finding is in accordance with the obtained potential energy function of the methylacetylene group torsion which indicates that the trans conformer represents an energy maximum. Furthermore, this result is in good agreement with the magnitude of the total energy obtained from ab initio calculations for the *trans* from. This value is higher than the values for the *gauche* and the *cis* conformers by 3.3 and 2.9 kcal·mol⁻¹ respectively (Table 6).

The conformational behavior of various (halomethyl) cyclopropanes¹⁻⁶ and (cyanomethyl)cyclopropane^{6b} has been analyzed using either spectroscopic methods¹⁻⁶ or the electron diffraction technique.²² These studies have demonstrated that all these molecules show a strong tendency toward the gauche conformation. Such a trend has been generally rationalized on the basis of increasing steric crowding as a result of the increase of the size of the substituent residing above the ring plane in the cis conformation. This means that there are apparently no electronic interactions in these compounds which would tend to stabilize the cis form. In contrast, however, we believe, that the occurrence of the cis conformer in these conformeric equilibria is due to attractive interaction between the substituent situated above the ring and the surface orbitals of the ring. Such kind of rationalization is supported to some extent by the increasing stability of the cis rotamer upon moving from iodoto bromo-, chloro-, cyano-, and ethynylmethylcyclopropane. The abundance of the cis form within this series is 0, 2, 5, 13, and 40%, respectively. Interestingly enough, this trend parallels the increase of the electronegativity of the substituents considered in this series. The values for the electronegativity of I, Br, Cl, C=N, and C=CH are 2.5^{23} 2.8^{23} 3.0^{23} 3.2^{24} and 3.1^{24}

Unfortunately, to our knowledge, no experimental value for the conformational composition of (fluoromethyl)cyclopropane is available so far. However, based on a recent vibrational investigation of the chloro and bromomethyl cyclopropane molecules, Durig et al. ²⁵ concluded that the abundance of the *cis*-fluoromethylcyclopropane should be larger than that of the *cis* form of the corresponding halomethyl derivatives. Should it be the case, this might be considered as an additional support for the electronegativity arguments alluded to above.

Furthermore, a larger percentage of the *cis* conformer in (fluoromethyl)cyclopropane, if verified experimentally, argues equally well for steric effects as it does for their proposed electronic effects. In truth, both of these are really manifestations of generalized "electronic effects" in any case.

As mentioned in the Introduction, one goal of the present study is to elucidate the role of the acetylene group by the distortion of the geometry of the three-membered ring and whether through bond or through space interaction is predominant in CPMAC. If we compare the relevant structural parameters in cyclopropylacetylene (CPA) and CPMAC obtained from $4-21G^*$ and $6-31G^*$ basis sets (Table 9) we come to the conclusion that following indications may substantiate the coupling between the acetylene group and the ring system: (i) as it can be easily seen from Table 9 there is an apparent

shortening of the distal bond and lengthening of the vicinal bonds upon moving from CPA to CPMAC. This is valid regardless of both the level of the calculations and, surprisingly, the conformation of CPMAC. (ii) The C_{ring} — $C \equiv$ bond distance in CPA is about 0.02 Å shorter than the C— $C \equiv$ bond distance in CPMAC. These findings may be interpreted as the result of through-bond coupling between the acetylene group and the ring in the case of CPA. Such kind of rationalization is consistent with the orbital model proposed by Walsh²⁶ and with Hoffmann's prediction²⁷ that substitution of a π -electron acceptor shortens the bond opposite the substituent and lengthens the two adjacent bonds. This, however, also means that the separation of the acetylene group from the ring by an sp³hybridized carbon atom leads partially to a decoupling of the two electron-rich moieties. In conclusion, from the foregoing arguments it can be postulated that through-bond interactions between the substituent and the ring system in CPMAC are less accentuated than in CPA and a substantial contribution of through-space interaction in the case of CPMAC is operative. The latter interaction is most likely the reason for the observed stability of the cis conformation of CPMAC.

Finally, it is of particular interest to note that the computed bond distances in CPMAC remain almost unaffected upon moving from one conformer to the other, except in the case of the exocyclic C-C bond (Table 6). This bond increases by about 0.0054 and 0.016 Å on going from gauche to cis and gauche to trans, respectively. Comparison of the corresponding bond angles in all three conformers indicates a similar feature. Surprisingly, only minor differences exist between the values for these angles in all conformers. The only two exceptions are the angles ϑ and α . While the values for both angles are fairly close to each other in the case of the gauche and trans conformers they deviate, however, by about 2° for ϑ and 1.6° for α when compared with the *cis* form. One probable rationalization for this remarkable structural behavior is that the geometrical relaxation which occurs upon the transition from one conformer to the other takes place at the expense of the exocyclic C–C bond and the angles ϑ and α .

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