Conformational Studies of Cyclopropylmethylacetylene from Temperature Dependent FT-IR Spectra of Xenon Solutions and Ab Initio Calculations

Gamil A. Guirgis,[†] C. J. Wurrey, Zhenhong Yu, Xiaodong Zhu,[‡] and James R. Durig*

Department of Chemistry, University of Missouri-Kansas City, Kansas City, Missouri 64110-2499

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The infrared (3500 to 30 cm^{-1}) spectra of gaseous and solid and the Raman (3500 to 20 cm^{-1}) spectra of the liquid [with quantitative depolarization ratios] and solid cyclopropylmethylacetylene, *c*-$C_3H_5CH_2CCH$ (ethynylmethylcyclopropane), have been recorded. Additionally, variable temperature (−55 to −100 °C) studies of the infrared spectra (3500 to 400 cm^{-1}) of the title compound dissolved in liquid xenon have been carried out. Utilizing four conformer pairs, an enthalpy difference of 147 ± 14 cm^{-1} (1.76 ± 0.17 kJ/mol) was obtained, with the cis rotamer the more stable conformer. At ambient temperature there is approximately 48% of the cis conformer present. However, the gauche conformer remains in the annealed solid. The optimized geometries, conformational stabilities, harmonic force fields, infrared intensities, Raman activities, depolarization ratios, and vibrational frequencies are reported for both conformers from ab initio calculations. The calculations were carried out at the restricted Hartree−Fock (RHF) level and/or with full electron correlation to second order (MP2), utilizing the following basis sets: 6-31G(d), 6-311G(d), 6-311++G(d,p) and 6-311+G(2d,2p). From the RHF calculations (6-31G(d)) the gauche form was predicted to be the more stable rotamer by 133 cm^{-1} (1.59 kJ/mol), but from all of the calculations with electron correlation, the cis form is predicted to be the more stable rotamer and from the largest basis set by 174 cm^{-1} (2.08 kJ/mol), which is consistent with the experimental results. The other calculated quantities are compared to the experimentally determined values where applicable, as well as with some corresponding results for some similar molecules.

Introduction

For molecules which contain an asymmetrical substituted halomethyl group bonded to a symmetrical three-membered (cyclopropane) ring, two staggered conformers of cis and gauche structure are possible, where the eclipsed forms have been predicted to be unstable.[1] The conformational stability of fluoromethylcyclopropane has not been determined experimentally, apparently because of its stability,[2] but both the gauche (*skew*) (ab initio calculations) and cis (syn) (molecular mechanics) conformers have been predicted[3] to be the more stable rotamer. For the other three halomethylcyclopropane molecules the gauche form is predominant, with chloromethylcyclopropane[4] having 95% gauche conformer, bromomethylcyclopropane[5] having 98% gauche conformer, and the corresponding iodide[6] 100% gauche form in the liquid state at ambient temperature. Thus, as the size of the halogen atom increases, the amount of the cis conformer decreases.[7]

The conformational stability of cyanomethylcyclopropane (the cyano group is frequently considered a pseudohalogen) has also been experimentally determined,[7,8] and in the liquid phase the gauche form is proposed to have 87% abundance at ambient temperature. This value is somewhat surprising because the related molecule, allyl cyanide, $CH_2{=}CHCH_2CN$, has the cis conformer more stable in the liquid state[9] with an enthalpy value of 245 ± 6 cm^{-1} (2.93 ± 0.07 kJ/mol) lower than the gauche form. Ab initio predictions from MP2/6-31G(d) calculations give the cis conformer with lower energy of 114 cm^{-1} (1.36 kJ/mol) for allyl cyanide, so that experiment and theory are in agreement for the conformational stability of this molecule. We[10] recently carried out a conformational study of cyanomethylcyclopropane by an investigation of the variable-temperature infrared spectra of *c*-$C_3H_5CH_2CN$ dissolved in liquid xenon. These studies gave an enthalpy difference of 54 ± 4 cm^{-1} (0.65 ± 0.05 kJ/mol) with the gauche conformer more stable, where the estimated amount of this rotamer is 72% at ambient temperature. In support of the vibrational study we also carried out ab initio calculations with the 6-31G(d) basis set at both the restricted Hartree−Fock (RHF) level and with full electron correlation by the perturbation method[11] to the second order (MP2). However, the MP2/6-311+G(2d,2p) calculations predicted the cis conformer more stable by 134 cm^{-1} (1.60 kJ/mol). These results indicate that the ab initio calculations, even with relatively large basis sets, cannot correctly predict the stable conformers of these three-membered rings when the energy differences are relatively small.

As a continuation of our conformational studies of these three-membered rings, we have investigated the vibrational spectrum of cyclopropylmethylacetylene, *c*-$C_3H_5CH_2CCH$. There has been a recent conformational study of this molecule from a microwave investigation and ab initio calculations.[12] It was concluded that the cis conformer was more stable than the gauche rotamer by 64 ± 30 cm^{-1} (0.77 ± 0.36 kJ/mol) from relative intensity measurements of the microwave transitions.[12] This result is in contrast to the ab initio calculations at the RHF/6-31G(d) level, which predict the gauche conformer more stable by 132 cm^{-1} (1.58 kJ/mol), and the electron diffraction investigation, which indicated that the gauche rotamer is more stable by 152 ± 45

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* Corresponding author.

[†] Permanent address: Analytical R/D Department, Organic Products Division, Bayer, Bushy Park Plant, Charleston, SC 29411.

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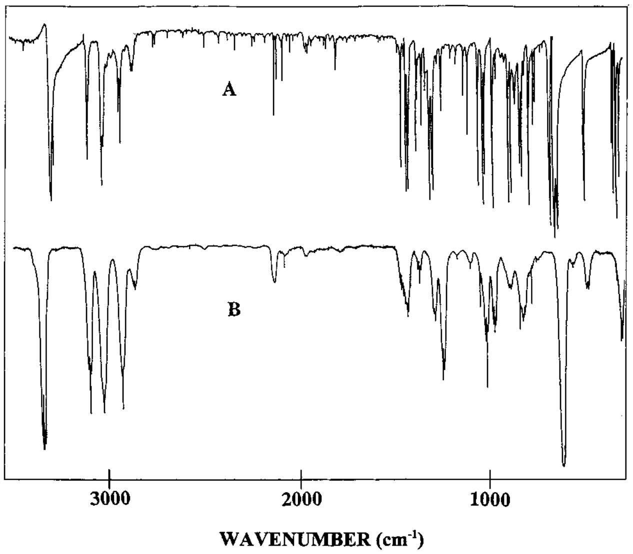

Figure 1. Infrared spectra of cyclopropylmethylacetylene: (A) solid; (B) gas.

cm^{-1} (1.82 ± 0.54 kJ/mol). These latter results were quoted in the microwave study[12] as a private communication. Therefore, the experimentally determined stability of the cis conformer is still in question when one considers the difficulty in making accurate microwave intensity measurements, so we felt another experimental determination of the conformer stability of cyclopropylmethylacetylene was appropriate. Therefore, we have recorded the infrared and Raman spectra of the fluid and solid states, and we have carried out an investigation of the variable temperature mid-infrared study of xenon solutions of this molecule. Additionally, we have performed ab initio calculations with much larger basis sets than were previously used[12] with full electron correlation by the perturbation method[11] to second order (MP2). The conformational stabilities, optimized geometries, harmonic force fields, infrared intensities, Raman activities, depolarization ratios, and vibrational frequencies have been obtained for comparison with the experimental quantities when appropriate. The results of this spectroscopic and theoretical study are reported herein.

Experimental Section

The cyclopropylmethylacetylene sample was prepared by the previously reported[12] method with modification. 1.34 gm (0.01 mol) of cyclopropyl methylbromide in 5 mL of dry dimethyl sulfoxide was added dropwise over a period of 20 min to 3.2 gm (0.012 mol) of 18% sodium acetylide slurry in xylene (Aldrich Chemical Co.) and 15 mL dry dimethyl sulfoxide. During the addition the temperature was maintained between 13 and 15 °C, and after the addition was complete, the sample was stirred for 20 min at room temperature. The reaction vessel was placed in a bath at −100 °C and all volatile material (acetylene) was pumped away.

The mid-infrared spectrum of the gas (Figure 1) was recorded using a Perkin−Elmer model 2000 Fourier transform spectrometer equipped with a Ge/CsI beam splitter and DTGS detector. Atmospheric water vapor was removed from the spectrometer housing by purging with dry nitrogen. The spectrum of the gas was obtained by using a 10-cm cell fitted with CsI windows. The spectrum of the solid was obtained by condensing the sample on a CsI substrate held at the temperature of boiling liquid nitrogen, housed in a vacuum cell fitted with CsI windows. The sample was condensed as an amorphous or glassy solid and repeatedly annealed until no further changes were observed in the spectrum.

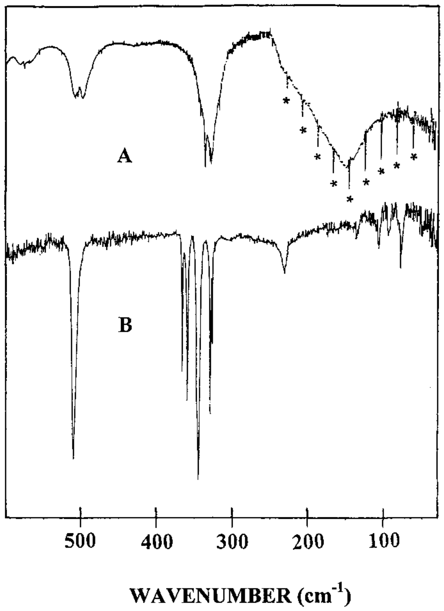

Figure 2. Far-infrared spectra of (A) gaseous and (B) solid cyclopropylmethylacetylene. The absorptions marked by asterisks in (A) are due to HCl.

The mid-infrared spectra of the sample dissolved in liquefied xenon as a function of temperature were recorded on a Bruker model IFS 66 Fourier transform spectrometer equipped with a globar source, a Ge/KBr beam splitter, and a TGS detector. In all cases 100 interferograms were collected at 1.0 cm^{-1} resolution, averaged, and transformed with a boxcar truncation function. A specially designed cryostat cell was used to obtain the spectral data. It consisted of a copper cell with a path length of 4 cm, with wedged silicon windows sealed to the cell with indium gaskets. This cell was cooled by boiling liquid nitrogen, and the temperature was monitored with two Pt thermoresistors. The complete cell was connected to a pressure manifold, allowing the filling and evacuation of the cell. After the cell had cooled to the desired temperature, a small amount of the compound was condensed into the cell. Next, the pressure manifold and the cell were pressurized with the noble gas, which immediately started to condense in the cell, allowing the compound to dissolve.

The far-infrared spectrum of the gas (Figure 2A) was recorded on a Bomem model DA3.002 Fourier transform spectrometer equipped with a vacuum bench, 6.25 and 25 μm Mylar beam splitters, and a liquid helium-cooled Si bolometer. The spectrum was obtained from the sample contained in a 1-m folded path cell equipped with mirrors coated with gold, and fitted with polyethylene windows with an effective resolution of 0.010 cm^{-1}. To remove traces of water from the sample, activated 4 Å molecular sieves were used. The far-infrared spectra of the amorphous and crystalline solids (Figure 2B) were obtained with the Perkin-Elmer model 2000 equipped with a metal grid beam splitter and a DTGS detector.

The Raman spectra were recorded on a SPEX model 1403 spectrophotometer equipped with a Spectra-Physics model 164 argon ion laser operating on the 514.5 nm line. The laser power used was 0.5 W with a spectral band-pass of 3 cm^{-1}. The spectrum of the liquid was recorded with the sample sealed in a Pyrex glass capillary held in a Miller−Harney apparatus.[13] Depolarization measurements were obtained for the liquid sample using a standard Ednalite 35-mm camera polarizer with

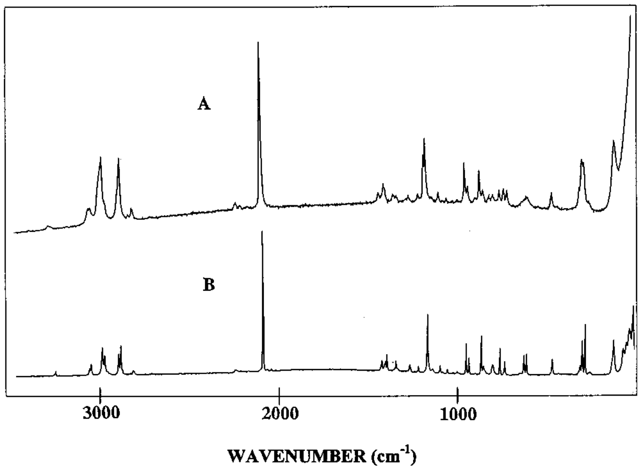

Figure 3. Raman spectra of cyclopropylmethylacetylene: (A) liquid; (B) solid.

38 mm of free aperture affixed to the SPEX instrument. Depolarization ratio measurements were checked by measuring the polarization values of the Raman bands of CCl_4 immediately before depolarization measurements were made on the liquid sample. The Raman wavenumbers are expected to be accurate to ±2 cm^{-1}, and typical spectra are shown in Figure 3. All of the observed bands in both the infrared and Raman spectra, along with the proposed assignments, are listed in Table 1S in the Supporting Information.

Ab Initio Calculations. The LCAO-MO-SCF RHF calculations were performed with the Gaussian-94 program,[14] using Gaussian-type basis functions. The energy minima with respect to the nuclear coordinates were obtained by the simultaneous relaxation of all geometric parameters using the gradient method of Pulay.[15] The 6-31G(d) basis set was employed at the RHF level and with full electron correlation with Moller−Plesset perturbation (MP2) at second order.[11] The predicted structural parameters are listed in Table 2S. Additional calculations were carried out with the 6-311+G(d,p), 6-311++G(d,p), and 6-311+G(2d,2p) basis sets with full electron correlation with Moller−Plesset perturbation to second order (MP2). All MP2 calculations predict the cis conformer to be the more stable form.

The ab initio MP2/6-31G(d) calculations were utilized to obtain harmonic force constants for both conformers, and the resulting vibrational wavenumbers were used for comparison with the experimental results. To obtain the approximate description of the normal modes, it was necessary to transform the ab initio force field in terms of Cartesian coordinates into a force field expressed in terms of the more convenient internal coordinates. The corresponding transformation matrix, B, was generated using the Cartesian coordinates obtained for the optimized geometries, and the complete set of internal coordinates are shown in Figure 4. This complete set of internal coordinates was used to form the symmetry coordinates listed in Table 3S. The resulting force field in internal coordinates for both conformers, which can be obtained from the authors, was used along with the unsymmetrized G-matrix to produce the pure ab initio calculated vibrational frequencies. A scaling factor of 0.9 for all the coordinates was used to obtain the “fixed scaled” force field and vibrational wavenumbers along with the potential energy distributions (PED) among the symmetry coordinates. All of these data are listed in Tables 1and 2.

Conformational Stability. A comparison of the Raman spectrum of the liquid with that of the solid (Figure 3) shows several bands disappear upon solidification of the sample. Raman lines at 579, 751, 851, 928, 1051, 1214, and 1366 cm^{-1} in the spectrum of the liquid can be assigned as resulting from fundamentals of the cis conformer, and all of these lines are absent from the spectrum of the solid. Therefore, the gauche conformer is the rotamer present in both the Raman and infrared spectra of the solid. Similarly, infrared bands at 576, 748, 852, 924, 1057, 1213, and 1364 cm^{-1} in the spectrum of the gas are not present in the spectrum of the solid. Therefore, in the spectra of both the gas and the liquid there is clear evidence for the existence of the two conformers, and the ab initio calculations clearly show that the bands that disappear are those due to the cis conformer.

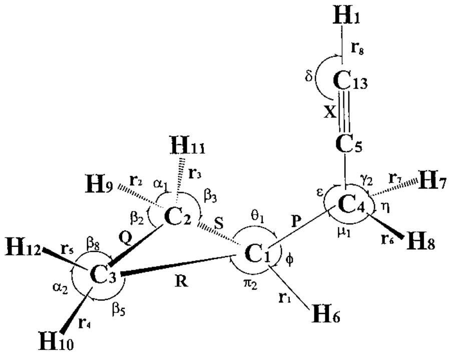

Figure 4. Internal coordinates of cyclopropylmethylacetylene.

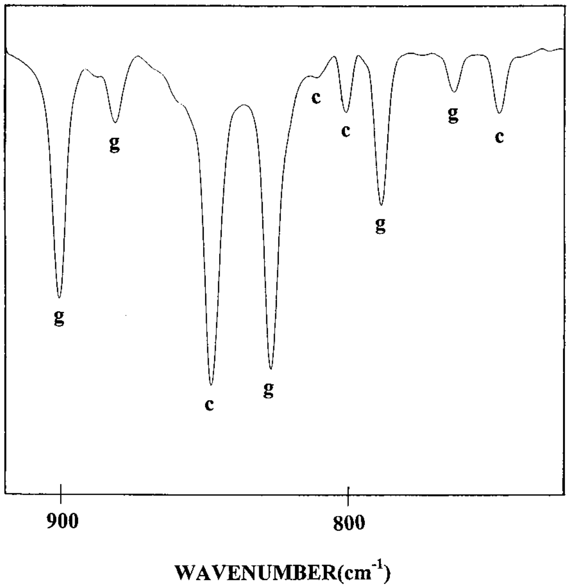

Figure 5. Infrared spectrum of cyclopropylmethylacetylene in liquid xenon at −95 °C from 720 to 920 cm^{-1} (*c* = cis, g = gauche).

The conformer pairs at 1052/1045, 1021/1019, 848/828, and 575/502 cm^{-1} (Figure 5), with the first listed frequency due to the cis rotamer, were used to determine the enthalpy difference between the conformers. The spectral changes are shown in Figures 6 and 7 for two of these pairs. From these spectral data it is obvious that the increase in the intensity of the infrared bands assigned to the cis conformer as the temperature decreases confirmed the stability of the cis rotamer over the gauche conformer in the xenon solution.

To obtain the enthalpy difference between these two conformers, 10 spectral data points were obtained for these lines over the temperature range −55 to −100 °C (Table 3). The intensities of each conformer pair were fit to the equation $-\ln K = (\Delta H/RT) - (\Delta S/R)$, where K is the intensity ratio of I_{cis} to I_{gauche} and it is assumed that ΔH is not a function of temperature. Using a least-squares fit, and from the slope of the line, ΔH values ranging from a low value of 103 ± 15 (1.23 ± 0.18

TABLE 1: Observed and Calculated Frequencies and Potential Energy Distribution (PED) for cis Cyclopropylmethylacetylene

species	vib. no.	species fundamental[a]	ab initio[b]	fixed scaled[c]	IR int[d]	Raman act[e]	obs. [f]	PED
A′	ν_1	$\equiv$C−H Stretch	3522	3349	52.4	30.04	3332	$95S_1$
	ν_2	CH_2 antisymmetric stretch	3306	3137	11.1	27.03	3083	$100S_2$
	ν_3	C−H stretch	3215	2051	10.0	224.13	3019	$68S_3,31S_4$
	ν_4	CH_2 symmetric stretch	3208	3044	9.9	53.64	3007	$68S_4,31S_3$
	ν_5	*CH_2 symmetric stretch	3085	2925	20.0	127.43	2923	$100S_5$
	ν_6	C$\equiv$C stretch	2168	2150	0.0	91.13	2127	$84S_6,12S_{12}$
	ν_7	CH_2 deformation	1572	1492	3.8	4.54	1462	$74S_7,17S_{11}$
	ν_8	*CH_2 deformation	1540	1461	2.8	13.91	1432	$98S_8$
	ν_9	CH bend	1451	1376	4.0	3.56	1362	$46S_9,20S_7,12S_{11}$
	ν_{10}	*CH_2 wag	1385	1316	1.9	8.48	1311	$65S_{10},16S_{14}$
	ν_{11}	ring breathing	1283	1217	1.8	21.12	1213	$48S_{11},27S_9$
	ν_{12}	CH_2 twist	1159	1101	3.2	1.22	1101	$25S_{12},17S_{10},16S_9,16S_{16}$
	ν_{13}	CH_2 wag	1106	1050	9.2	1.27	1021	$84S_{13}$
	ν_{14}	C_1−C_4 stretch	1045	993	13.9	15.82	983	$25S_{14},30S_{17},13S_{11},10S_{13}$
	ν_{15}	C_4−C_5 stretch	956	912	4.2	7.11	931	$55S_{15},13S_{17}$
	ν_{16}	CH_2 rock	822	780	0.9	1.07	802	$63S_{16},22S_{12}$
	ν_{17}	ring deformation	792	756	1.3	15.88	748	$43S_{17},26S_{14},10S_{12}$
	ν_{18}	$\equiv$C−H in-plane bend	602	638	16.1	4.32	632	$83S_{18}$
	ν_{19}	$C_1C_4C_5$ bend	538	559	34.3	0.74	575	$35S_{19},18S_{18},16S_{20},11S_{21}$
	ν_{20}	ring-C_1C_4 bend	332	329	0.3	7.40	328	$58S_{20},35S_{21}$
	ν_{21}	C−C$\equiv$C in-plane bend	144	146	0.1	5.00	150	$46S_{21},43S_{19}$
A″	ν_{22}	CH_2 antisymmetric stretch	3296	3128	0.6	79.94	3091	$100S_{22}$
	ν_{23}	CH_2 symmetric stretch	3207	3043	10.8	27.80	3007	$100S_{23}$
	ν_{24}	*CH_2 antisymmetric stretch	3130	2968	11.5	91.54	2928	$100S_{24}$
	ν_{25}	CH_2 deformation	1520	1442	3.3	6.57	1426	$100S_{25}$
	ν_{26}	*CH_2 twist	1285	1220	0.5	3.56	1255	$91S_{26}$
	ν_{27}	CH_2 twist	1239	1175	0.5	9.84	1171	$41S_{27},46S_{32},12S_{28}$
	ν_{28}	CH bend	1181	1120	1.5	1.14	1104	$60S_{28},34S_{27}$
	ν_{29}	CH_2 wag	1116	1059	2.6	0.56	1052	$97S_{29}$
	ν_{30}	*CH_2 rock	1060	1011	0.8	3.41	1015	$53S_{30},18S_{31},11S_{34}$
	ν_{31}	ring deformation	909	864	9.4	14.04	848	$78S_{31},14S_{30}$
	ν_{32}	CH_2 rock	844	802	2.1	2.85	811	$40S_{32},22S_{28},18S_{27},16S_{30}$
	ν_{33}	$\equiv$C−H out-of-plane bend	532	604	51.1	1.79	622	$100S_{33}$
	ν_{34}	ring −C_1C_4 bend	345	327	0.6	9.85	328	$77S_{34}$
	ν_{35}	C−C$\equiv$C out-of-plane bend	302	325	0.1	0.25	328	$78S_{35},12S_{34}$
	ν_{36}	asymmetric torsion	111	112	0.0002	1.97	−	$87S_{36},12S_{35}$

[a] The asterisk on the CH_2 group indicates the group attached to the ring. [b] From MP2/6-31G(d) calculations. [c] Scaling factors of 0.9 for stretches and bends, except 1.0 for C$\equiv$C stretch, 1.2 for C−C$\equiv$C bends and 1.3 for C$\equiv$C−H bends, and 1.0 for torsion with MP2/6−316(d) calculations. [d] Calculated infrared intensities in km/mole at the MP2/6-31G(d) level. [e] Calculated Raman activities in Å^4/amu, using RHF/6-31G(d) level. [f] Frequencies are obtained from the spectra of the xenon solution or gas.

kJ/mol) to a high value of 203 ± 30 cm^{-1} (2.43 ± 0.36 kJ/mol) were obtained. The average value from these determinations is 147 ± 14 cm^{-1} (1.76 ± 0.17 kJ/mol), with the cis conformer the more stable rotamer. This value should be near the value for the gas[16−20] because both conformers have similar sizes and polarities. The value of the enthalpy implies at room temperature a gas-phase equilibrium mixture of 48% cis conformer and 52% gauche rotamer, which is a slightly smaller amount of the gauche conformer than previously suggested from the microwave data.[12]

Vibrational Assignment. Since there are no previous vibrational assignments proposed for this molecule, the presently obtained Raman and infrared spectra have been used to provide a complete assignment for the normal modes for both the cis and gauche conformers. The assignments are based on the frequencies obtained from the ab initio calculations, along with relative intensities and the band contours, along with assignment given earlier for some other monosubstituted methylcyclopropyl molecules. The assignments made for the fundamentals associated with the carbon−hydrogen modes should be considered tentative in the absence of selective deuteration studies, but the other assignments are reasonably definitive.

To aid the vibrational assignment, we have predicted the Raman and infrared spectra from the ab initio data. The evaluation of Raman activity by using the analytical gradient method has been previously developed.[21,22] The activity S_j can be expressed as

$$S_j = g_j\,(45\alpha_j^2 + 7\beta_j^2)$$

where g_j is the degeneracy of the vibrational mode j, α_j is the derivative of the isotropic polarizability, and β_j is that of the anisotropic polarizability. The Raman scattering cross sections, $\partial\sigma_j/\partial\Omega$, which are proportional to the Raman intensities, can be calculated from the scattering activities and the predicted wavenumbers for each normal mode using the relationship:[23,24]

$$\frac{\partial\sigma_j}{\partial\Omega} = \left(\frac{2^4\,\pi^4}{45}\right)\left(\frac{(\nu_0 - \nu_j)^4}{1 - \exp\left[\frac{-hc\nu_j}{kT}\right]}\right)\left(\frac{h}{8\pi^2 c\nu_j}\right)Sj$$

where ν_0 is the exciting wavenumber, ν_j is the vibrational wavenumber of the jth normal mode, and S_j is the corresponding Raman scattering activity. To obtain the polarized Raman scattering cross sections, the polarizabilities are incorporated into S_j by $S_j[(1 - \rho_j)/(1 + \rho_j)]$ where ρ_j is the depolarization ratio of the jth normal mode. The Raman scattering cross sections and calculated wavenumbers obtained from the standard Gaussian program were used together with a Lorentzian function to obtain the calculated spectra. Because the calculated wavenumbers are approximately 10% higher than those observed,

TABLE 2: Observed and Calculated Frequencies and Potential Energy Distribution (PED) for Gauche Cyclopropylmethylacetylene

species	vib. no.	species fundamental[a]	ab initio[b]	fixed scaled[c]	IR int[d]	Raman act[e]	obs.[f]	PED
A	ν_1	≡C−H Stretch	3524	3350	52.1	30.17	3273	$95S_1$
	ν_2	CH_2 antisymmetric stretch	3302	3132	14.1	41.89	3086	$98S_2$
	ν_3	C−H stretch	3223	3058	6.8	96.62	3015	$97S_3$
	ν_4	CH_2 symmetric stretch	3207	3042	6.4	126.90	3002	$92S_4$
	ν_5	*CH_2 symmetric stretch	3084	2924	15.2	103.73	2912	$99S_5$
	ν_6	C≡C stretch	2171	2152	0.0	109.65	2116	$84S_6,12S_{15}$
	ν_7	CH_2 deformation	1574	1493	1.8	3.88	1453	$76S_7,16S_{11}$
	ν_8	*CH_2 deformation	1536	1458	3.8	10.30	1433	$82S_8,15S_{25}$
	ν_9	CH bend	1462	1387	1.5	3.55	1375	$40S_9,15S_7,13S_{11},12S_{14}$
	ν_{10}	*CH_2 wag	1360	1292	10.9	5.53	1299	$77S_{10}$
	ν_{11}	ring breathing	1271	1205	0.3	22.04	1200	$48S_{11},27S_9$
	ν_{12}	CH_2 twist	1185	1127	0.4	1.45	1128	$13S_{12},18S_{26},13S_{14},12S_9$
	ν_{13}	CH_2 wag	1103	1046	8.7	0.69	1033	$85S_{13}$
	ν_{14}	C_1-C_4 stretch	1043	992	11.4	14.01	984	$19S_{14},16S_{17},16S_{30},11S_{31}$
	ν_{15}	C_4-C_5 stretch	1020	971	2.5	7.69	967	$30S_{15},16S_{31}$
	ν_{16}	CH_2 rock	801	761	0.4	8.98	770	$40S_{16},44S_{12}$
	ν_{17}	ring deformation	956	910	7.7	7.99	901	$23S_{17},36S_{15},29S_{31}$
	ν_{18}	≡C−H in-plane bend	538	599	50.8	2.53	651	$92S_{18}$
	ν_{19}	$C_1C_4C_5$ bend	490	484	4.4	3.80	510	$34S_{19},21S_{21}$
	ν_{20}	ring-C_1C_4 bend	324	328	0.4	2.63	348	$46S_{20},25S_{36},12S_{35}$
	ν_{21}	C−C≡C in-plane bend	140	141	0.1	4.96	175	$40S_{21},40S_{19},14S_{34}$
	ν_{22}	CH_2 antisymmetric stretch	3290	3121	0.4	91.68	3076	$98S_{22}$
	ν_{23}	CH_2symmetric stretch	3202	3037	12.0	34.32	3002	$94S_{23}$
	ν_{24}	*CH_2 antisymmetric stretch	3132	2970	10.9	77.34	2924	$98S_{24}$
	ν_{25}	CH_2 deformation	1525	1447	3.2	11.24	1425	$85S_{25},15S_8$
	ν_{26}	*CH_2 twist	1302	1236	2.2	5.34	1250	$52S_{26},18S_{12}$
	ν_{27}	CH_2 twist	1235	1171	0.7	11.47	1173	$38S_{27},47S_{32},14S_{26}$
	ν_{28}	CH end	1174	1114	0.6	1.05	1088	$53S_{28},31S_{27}$
	ν_{29}	CH_2 wag	1108	1051	2.8	0.65	1056	$95S_{29}$
	ν_{30}	*CH_2 wag	924	882	0.9	6.11	887	$37S_{30},26S_{16}$
	ν_{31}	ring deformation	875	832	10.4	10.04	840	$30S_{31},19S_{32},14S_{17},11S_{28},10S_{27}$
	ν_{32}	CH_2 rock	831	792	2.7	9.60	798	$18S_{32},21S_{17},10S_{16},10S_{30}$
	ν_{33}	≡C−H out-of-plane bend	558	609	49.2	3.07	665	$100S_{33}$
	ν_{34}	ring −C_1C_4 bend	297	315	0.2	4.86	332	$46S_{34},25S_{21},19S_{35}$
	ν_{35}	C−C≡C out-of-plane bend	355	347	0.1	10.33	359	$44S_{35},30S_{20},12S_{36}$
	ν_{36}	asymmetric torsion	80	81	0.01	2.31	122	$82S_{36}$

[a] The asterisk on the CH_2 group indicates the group outside the ring. [b] From MP2/6−316(d) calculations. [c] Scaling factors of 0.9 for stretches and bends, 1.0 for torsion, except 1.0 for C≡C stretch, 1.2 for C−C≡C bends, and 1.3 for C≡C−H bends. [d] Calculated infrared intensities in km/mole at the MP2/6-31G(d) level. [e] Calculated Raman activities in Å^4/amu, using RHF/6-31G(d) level. [f] Frequencies are obtained from the spectra of Raman solid.

the wavenumber axis of the theoretical spectrum was compressed by a factor of 0.9.

The predicted Raman spectrum of the pure cis form is shown in Figure 8D and that of the pure gauche conformer in Figure 8C. The predicted Raman spectrum of the mixture of the two conformers with an enthalpy difference of 150 cm^{-1} is shown in Figure 8B. The experimental Raman spectrum of the liquid is shown in Figure 8A for comparative purposes. The agreement is considered satisfactory and it is clear that these calculated spectra can be very useful in making the vibrational assignment. For example, the predicted Raman line at 494 cm^{-1} for the gauche form is readily identified as the Raman line at 510 cm^{-1} (Figure 8). In general, the spectrum of the liquid showed very good correspondence with the predicted intensities.

Also, the theoretical infrared spectra of the cis and gauche conformers were calculated. The infrared intensities were predicted on the basis of the dipole moment derivatives with respect to the Cartesian coordinates. The derivatives were taken from the ab initio calculations transformed to normal coordinates by:

$$\left(\frac{\partial \mu_u}{\partial Q_i}\right) = \sum_j \left(\frac{\partial \mu_u}{\partial X_j}\right) L_{ij}$$

where Q_i is the ith normal coordinate, X_j is the jth Cartesian

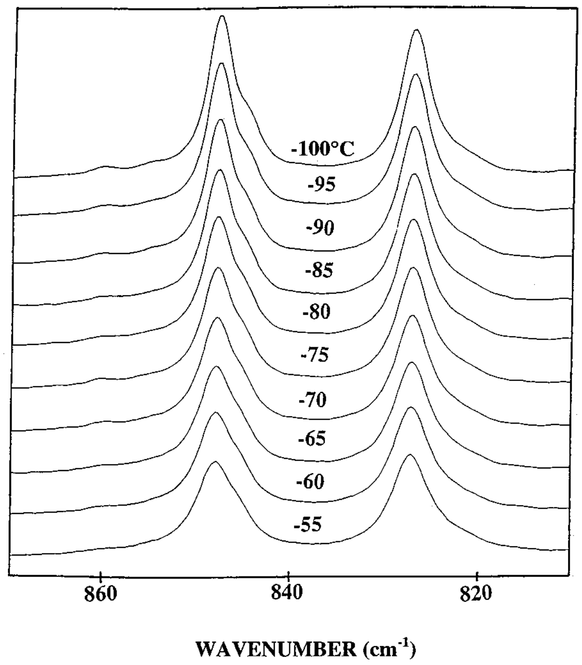

Figure 6. Temperature-dependent infrared spectra (810−870 cm^{-1}) of cyclopropylmethylacetylene in liquid xenon.

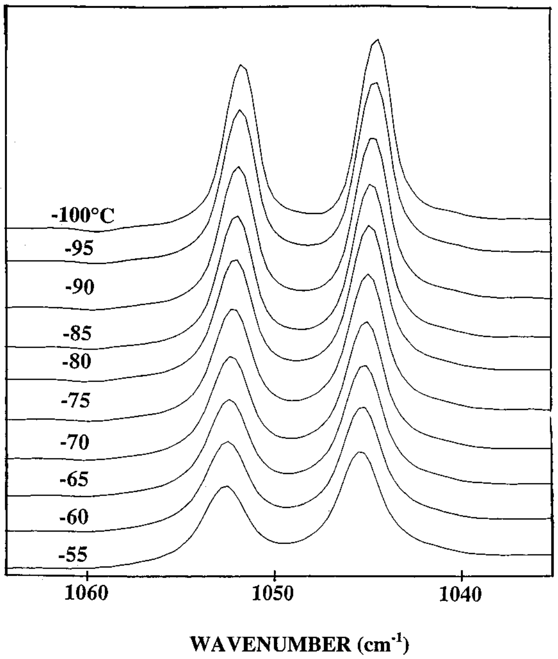

Figure 7. Temperature-dependent infrared spectra (1065−1035 cm^{-1}) of cyclopropylmethylacetylene in liquid xenon.

TABLE 3: Temperature and Intensity Ratios from Conformational Study of Cyclopropylmethylacetylene

T (°C)	1000/T (K)	I_{1052}/I_{1045}	I_{1021}/I_{1019}	I_{848}/I_{828}	I_{575}/I_{502}
−55	4.58	0.758	0.778	–	0.236
−60	4.69	0.786	0.826	0.850	0.233
−65	4.80	0.786	0.856	0.876	0.241
−70	4.92	0.788	0.881	0.890	–
−75	5.05	0.806	0.874	0.886	0.241
−80	5.18	0.817	0.920	0.898	0.268
−85	5.31	0.878	0.955	0.906	0.288
−90	5.46	0.894	0.995	0.922	0.308
−95	5.61	0.908	1.008	0.970	0.300
−100	5.78	0.932	1.029	1.033	–
ΔH^a (cm^{-1})		124 ± 10	157 ± 10	103 ± 15	203 ± 30

[a] Average value of ΔH is 147 ± 14 cm^{-1} (1.76 ± 0.16 kJ/mol) with the cis conformer the more stable form.

displacement coordinate, and L_{ij} is the transformation matrix between the Cartesian displacement coordinates and normal coordinates. The infrared intensities were then calculated by:

$$\mathrm{I_i} = \frac{N\pi}{3c^2}\left[\left(\frac{\partial\mu_x}{\partial Q_i}\right)^2 + \left(\frac{\partial\mu_y}{\partial Q_i}\right)^2 + \left(\frac{\partial\mu_z}{\partial Q_i}\right)^2\right]$$

In Figure 9D is the predicted spectrum of the cis form, and in Figure 9C, that of the gauche conformer. The predicted infrared spectra of the mixture with an enthalpy difference of 150 cm^{-1} is shown in Figure 9B. The experimental infrared spectrum of the sample dissolved in liquid xenon at −55 °C is also shown for comparison in Figure 9A. The agreement between the observed and calculated spectra is quite good, and these data were valuable for making the vibrational assignment. Again, the predicted gauche fundamental at 494 cm^{-1} is clearly observed at 502 cm^{-1} with reasonable intensity prediction. However, the predicted cis band at 539 cm^{-1} must be assigned to the relatively weak band at 575 cm^{-1} even though the predicted intensity is one of the highest in the spectrum. Nevertheless, this appears to be an exception, so the predicted infrared spectrum provided quite useful information in making the vibrational assignment.

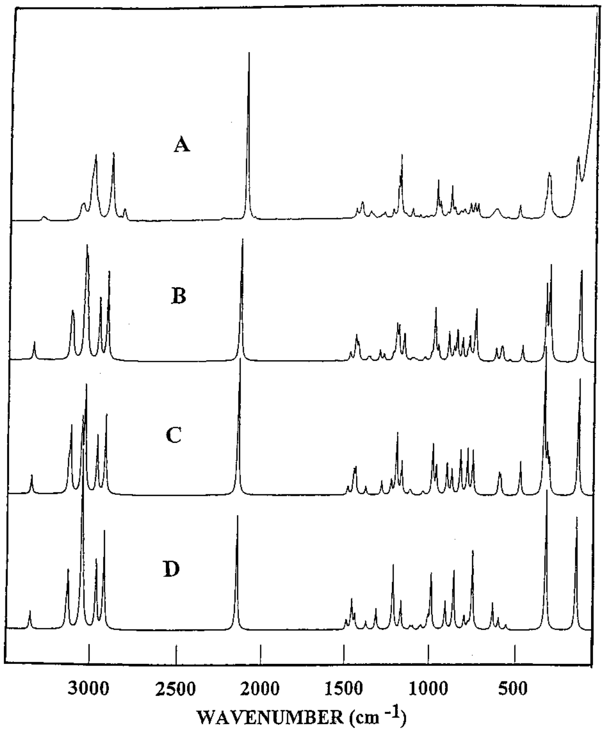

Figure 8. Comparison of experimental and calculated Raman spectra of cyclopropylmethylacetylene: (A) observed Raman spectrum of cyclopropylmethyl acetylene in liquid phase; (B) simulated Raman spectrum of a mixture of the cis and gauche conformer; (C) simulated Raman spectrum of the pure gauche conformer; and (D) simulated Raman spectrum of the pure cis conformer.

The frequencies for the carbon−hydrogen modes for the hydrogens attached to the ring carbons are remarkably similar to those of the corresponding modes for cyanomethylcyclopropane.[10] The normal modes for the CH_2 motions of the methylene group are highly correlated with the similar modes for the cyanomethylcyclopropane molecule, even though the CN and C≡C−H groups are expected to affect these motions significantly. Therefore, the carbon−hydrogen stretches and bends have very similar frequencies for the two molecules with, of course, the additional modes for the C≡C−H stretch and two bends. Also, it should be noted that the solid has the pure gauche conformer present, so it is easy to assign the fundamentals for this form. However, in the gas and liquid where the cis conformer is the more stable form, one must assume that many of the fundamentals have the same frequencies for the cis form as those for the gauche conformer. Therefore, the listed fundamentals for the cis conformer (Table 1) are observed frequencies in the gas or xenon solutions, whereas the fundamentals for the gauche form (Table 2) are observed frequencies from the infrared or Raman spectra of the solid.

In the carbon−hydrogen stretching regions the C≡C−H stretch is observed at 3332 cm^{-1} in the gas and at 3319 cm^{-1} in the xenon solution, and it shifts to 3270 cm^{-1} in the spectrum of the solid. The four carbon−hydrogen stretches for the two methylene groups in the ring appear as two groups, with the higher frequency one split and the other C−H stretch of the ring falling (3019 cm^{-1}) near the lower frequency absorption at 3007 cm^{-1}. The two carbon−hydrogen stretches of the methylene group attached to the ring fall approximately 100 cm^{-1} lower, at 2928 and 2923 cm^{-1}. These assignments are very similar to those given for the corresponding modes for cyanomethylcyclopropane.[7]

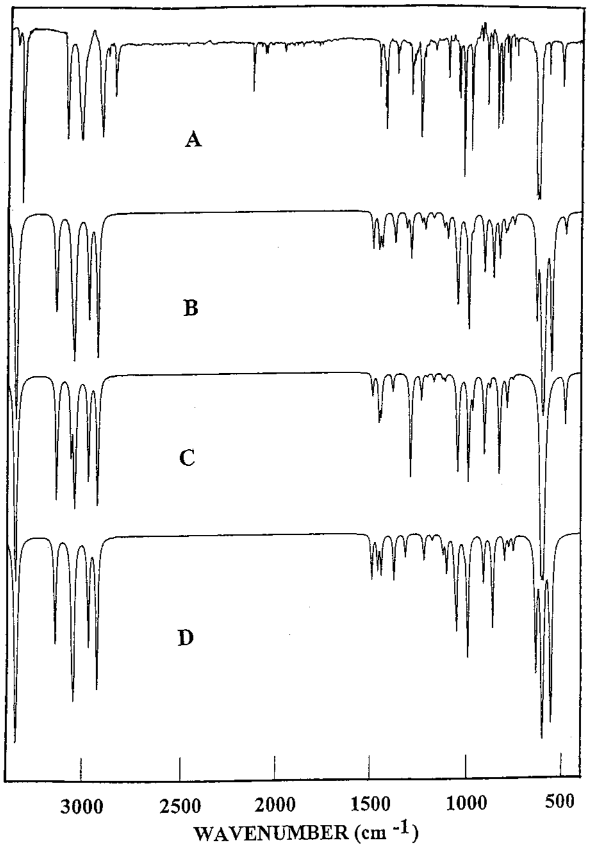

Figure 9. Comparison of experimental and calculated infrared spectra of cyclopropylmethylacetylene: (A) observed infrared spectrum of cyclopropylmethylacetylene in liquid xenon; (B) simulated infrared spectrum of a mixture of the cis and gauche conformers; (C) simulated infrared spectrum of the pure gauche conformer; and (D) simulated infrared spectrum of the pure cis conformer.

In the fingerprint region the carbon−hydrogen bends have very similar frequencies to those of the corresponding modes of cyanomethylcyclopropane with the addition of the two C≡C−H bends which fall at 632 and 622 cm^{-1}. These two fundamentals are predicted too low by ab initio calculations, so a scaling factor of 1.3 is needed for reasonable frequency predictions for these modes.[25] The frequencies for the skeletal stretching modes show excellent correlation with the frequencies for the corresponding vibrations of cyanomethylcyclopropane.[7]

The most challenging region for assignment is the low-frequency region where the skeletal bending modes are found. For example, in the far-infrared spectral region there is a broad, nondescript band centered at 328 cm^{-1} which arises from three fundamentals of the cis conformer as well as three bending fundamentals of the gauche conformer. In the infrared spectrum of the solid, the higher and lower frequency fundamentals of the gauche conformer show very distinctive factor group splitting, whereas the middle frequency fundamental gives rise to a single broad but strong absorption.

The assignment of the C−C≡C in-plane bend must be at 151 cm^{-1} in the infrared spectrum of the gas for the cis conformer, which shifts to 175 cm^{-1} in the Raman spectrum of the solid with a large loss in intensity in the infrared spectrum. The asymmetric torsion is predicted to be too weak to be observed for the cis conformer, and it is expected to also be quite weak in the infrared spectrum for the gauche conformer. Therefore, it is assigned at 136 cm^{-1} in the infrared spectrum and 122 cm^{-1} in the Raman spectrum of the solid, with the difference in frequency being ascribed to factor group splitting. The remaining low-frequency bands in both the infrared and Raman spectra of the solids are assigned as lattice modes, with the 232 cm^{-1} infrared band believed to arise from a two-phonon mode. Because of the splitting of several of the infrared bands in the spectrum of the solid, it is clear that there are at least two molecules per primitive cell.

Discussion

The spectroscopic data in the xenon solution clearly show that the cis conformer is the more stable form. The value of 147 ± 14 cm^{-1} (1.76 ± 0.17 kJ/mol) for the enthalpy difference between the two conformers is significantly larger than the previously reported[12] value of 64 ± 30 cm^{-1} (0.76 ± 0.36 kJ/mol) which was obtained from the microwave relative intensity measurements. This experimental result also indicates that the $\Delta G°$ value of 152 ± 45 cm^{-1} with the gauche conformer more stable from the electron diffraction result (given in ref 12) is in error. Also, it should be noted that the ab initio calculations at the RHF level with the 6-31G(d) basis set also predict the wrong conformer stability. It is necessary to utilize electron correlation to obtain meaningful predictions of conformer stabilities for these monosubstituted methyl cyclopropane molecules.[10,25,26] However, increasing the basis set sizes beyond the MP2/6-311+G(d) calculations did not significantly change the predicted enthalpy difference between the two stable conformers.

In our recent investigation of the conformer stability of cyanomethylcyclopropane, we[10] found the enthalpy difference between the two stable conformers to have a value of 54 ± 4 cm^{-1} (0.65 ± 0.05 kJ/mol), but with the gauche conformer the more stable form. However, the ab initio calculations at the MP2/6-311+G(2d,2p) level predict the cis form to be more stable by 134 cm^{-1}. Therefore, the ab initio predictions for the cyano- and ethynyl-substituted methylcyclopropane molecules are essentially the same at the same level of calculation, although the experimental results clearly show a difference in the conformational stability. As pointed out earlier,[7] there is a strong correlation of the increasing abundance of the cis conformer with the electronegativity of the substituent, but the amount of the cis form for ethynylmethylcyclopropane (48%) compared to the 40% of cis form of cyanomethylcyclopropane[10] does not follow the electronegativities of these two groups [C≡N (3.2) and C≡CH (3.1)].[27] Nevertheless, as a further indication of the importance of the substituent's electronegativity in determining the amount of the cis conformer present at ambient temperature of these monosubstituted methylcyclopropane molecules, it is interesting to consider the differences between chloromethylcyclopropane and ethylcyclopropane. The former molecule has 12% of the cis form present (Cl electronegativity of 3.0), whereas ethylcyclopropane[26] has about 2% (methyl group electronegativity 2.2) of the cis rotamer. The chlorine atom and the methyl group have approximately the same van der Waals radii. Therefore, the conformational stability of fluoromethylcyclopropane would be of interest for comparison with this series.

The major difference in the structural parameters between the two conformers is the C_1-C_4 bond distance, which is predicted to be about 0.006 Å shorter in the gauche conformer compared to the similar distance in the cis conformer. Also, the C_4-C_5 bond distance is predicted to be about 0.002 Å longer in the gauche rotamer. The remaining parameters are very similar for the two conformers, which results in many of the normal modes having nearly the same frequencies. The rotational constants (previously reported[12] from the microwave study) of A = 10 691, B = 1985, and C = 1808 MHz for the gauche conformer are predicted to have values of 10,559, 1998, and 1814 MHz, respectively, from the calculations at the MP2/6-311+G(d,p) level. Only the A rotational constant is predicted to have a significantly different value (10,735 MHz) from the MP2/6-311+G(2d,2p) calculation. Similarly, the determined microwave rotational constants of A = 6896, B = 2621, and C = 2269 MHz for the cis conformer differ by about the same amount from the predicted values of 6850, 2640, and 2277 MHz, respectively, from the MP2/6-311+G(d,p) calculations. There is significantly poorer agreement of the experimental values with those predicted from the MP2/6-311+G(2d,2p) calculations. These calculations predict the C−H distances to be too short, so the carbon−hydrogen parameters from the MP2/6-311++G(d,p) calculation along with the heavy atom parameters from the MP2/6-311+G(2d,2p) calculation were used with adjustments to fit the microwave rotational constants. The predicted differences of the parameters between the two conformers from the ab initio calculations were maintained, and the final parameters for the heavy atoms differed little from those from the ab initio values.

For the cis conformer, the PED indicates extensive mixing for only three of the fundamentals of the A′ modes, i.e., ν_{12}, ν_{14}, and ν_{19}. The bands assigned to the CH_2 twist of the ring methylene group and the C_1-C_4 stretch have only 25% contributions from these motions. Also, the $C_1C_4C_5$ bend is extensively mixed with the ring−C_1C_4, the $C-C\equiv C$, and $\equiv C-H$ bends. Similarly, for the gauche form the bands assigned to the first two modes have even smaller contributions from the indicated motions. Several other bands for the gauche form have major contributions from three or four motions, so the mixing is quite extensive for the gauche conformer.

There is little difference between the corresponding diagonal force constants for the two conformers except for those of the C_1-C_2 stretch and the angle bendings around the C_1 carbon atom. For the C_1-C_2 stretching force constant, the value is 0.040 mdyn/Å^2 smaller for the gauche conformer (3.915 versus 3.955 mdyn/Å^2 for the cis rotamer) compared to that of the cis rotamer. Similarly, the two angle bends for the heavy atoms around the C_1 atom ($C_2C_1C_4$ and $C_3C_1C_4$), as well as those associated with the H_6 atom (Figure 4), which includes θ_1, θ_2 and ϕ, are all about 0.40 mdyn/Å^2 smaller for the gauche conformer for the first two and 0.30 mdyn/Å^2 smaller for ϕ compared to the corresponding ones for the cis rotamer. Also, the value for ϵ is about 0.20 mdyn/Å^2 smaller for the gauche compared to the corresponding force constant for the cis form. Therefore, the skeletal bending modes have the most significant differences in frequencies between the two conformers.

The predicted dipole moment of 0.778D for the gauche conformer from the MP2/6-311+G(d,p) calculation is only 3% higher than the experimental value of 0.754 ± 0.007D, which is as good agreement as can be expected from the ab initio calculations. Similarly, the predicted dipole moment of 0.671D for the cis conformer agrees well with the experimental value of 0.639 ± 0.010D. The individual dipole moment components are also predicted rather well from the ab initio calculations, which indicates good estimates of the electron distributions.

Because of the relatively poor signal-to-noise ratio in the far-infrared spectrum (Figure 2) of the gas, it was not possible to confidently assign the weak absorption in the 100 to 80 cm^{-1} region to the asymmetric torsional fundamentals and associated hot bands. Since the predicted infrared intensity for this mode for the cis form is so low (0.0002 km/mol), one does not expect to observe the asymmetric torsion for the cis rotamer. Nevertheless, the asymmetric torsion for the gauche conformer should be observed, and there is an indication of an absorption maxima at 86 cm^{-1}. This value is in good agreement with the predicted torsional frequency of 70 ± 20 cm^{-1} obtained from the microwave intensity data from an excited state.[12] This value is also in good agreement with the ab initio prediction of 81 cm^{-1} for this fundamental. The frequency for the next-lowest-frequency bending mode of the gauche conformer was also predicted[12] from the microwave study to have a value of 120 ± 30 cm^{-1}, and it is observed at 150 cm^{-1}. Similarly, the asymmetric torsion of the cis conformer was predicted [12] to be 85 ± 20 cm^{-1} from the microwave intensity data, and the ab initio predicted value is 112 cm^{-1}, so the agreement is considered satisfactory. Therefore, we have used the torsional frequency of 86 cm^{-1} for the gauche rotamer and 112 cm^{-1} for the cis conformer, along with the experimental enthalpy value and gauche dihedral angle, to obtain the potential constants V_1, V_2, and V_3 which govern the conformational interchange. The V_2 term was dropped because it was so small, and the fit to the data was not affected. These potential function coefficients are listed in Table 4.

TABLE 4: Potential Function Coefficients (cm^{-1}) for the Asymmetric Torsion of Cyclopropylmethylacetylene and Barriers to Interconversion (cm^{-1})

coefficient	experimental value[a]	MP2/6-311+G(d)
V_1	205 ± 20	188
V_2	−	−10
V_3	1057 ± 35	1156
V_4	−	78
V_6	−	−47
gauche dihedral angle	118.9	116.6
ΔH (cm^{-1})	147	184
cis to gauche barrier	815	1254
gauche to cis barrier	668	1070
gauche to gauche barrier	809	1165

[a] Calculated using $F_0 = 0.885440$, $F_1 = 0.041087$, $F_2 = 0.017145$, $F_3 = 0.001205$, $F_4 = 0.000397$, $F_5 = 0.000036$, $F_6 = 0.000010$, and $F_7 = 0.000001$.

The V_1 and V_2 terms have values very similar to those obtained from the ab initio predictions from the MP2/6-311+G(d) calculation. However, the cis-to-gauche barrier as well as the gauche-to-gauche barriers obtained from the ab initio calculations are 55% and 44% higher, respectively, than those obtained from the experimental data. No barriers were given from the potential function proposed from the microwave study[12] for comparison with the ones obtained in this study.

The allyl cyanide molecule has the cis conformer as the more stable form in the liquid state by 245 ± 6 cm^{-1} (2.93 ± 0.07 kJ/mol), and the enthalpy difference is only slightly larger from the xenon solution. The correct conformer stability is predicted from the ab initio calculations with an energy difference of 114 cm^{-1} (1.36 kJ/mol) from the MP2/6-31G(d) calculations.[9] Thus, the ab initio calculations at this level underestimate the energy difference between the two conformers of allyl cyanide. From the same level of calculation for cyanomethylcyclopropane, the cis conformer is predicted to be more stable than the gauche form by 153 cm^{-1} (1.83 kJ/mol), whereas the gauche form is the more stable species for this molecule. Thus, it appears that the ab initio calculations are not able to predict the relative stability of the monosubstituted methylcyclopropane conformers where the energy differences are small (~100 cm^{-1}), unless very large basis sets at a high level of calculation are utilized. Therefore, further studies of the theoretical and experimental conformational stabilities of monosubstituted methylcyclopropane molecules such as those substituted with fluoride and $C\equiv$

CCH_3, as well as some other groups such as SiH_3, OH, or CF_3, would be of considerable future research interest.

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Supporting Information Available: (Table 1S) Observed infrared and Raman frequencies (cm^{-1}) and assignments for cyclopropylmethylacetylene; (Table 2S) structural parameters, rotational constants, dipole moments, and energy for cyclopropylmethylacetylene; (Table 3S) symmetry coordinates for cyclopropylmethyl acetylene. This material is available free of charge via the Internet at http://pubs.acs.org.

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