Table I. Observed Frequencies for the In-Plane Vibrational Fundamentals of $C_3H_3^+$, $C_3D_3^+$, and $C_3H_2D^+$ (in cm^{-1})[a]

		$C_3H_3^+$		$C_3D_3^+$				$C_3H_2D^+$	
		IR	Raman	IR	Raman			IR	Raman
a_1'	ν_1		3183		2480[b]	a_1	ν_1	3175	3166[b]
	ν_2		1626		1490		ν_2	2387	2404[b]
							ν_3		1584
a_2'	ν_3						ν_4	1266	1267
							ν_5	905	923
e'	ν_4	3137	3138	2348	2349				
	ν_5	1295	1290	1250	1248	b_1	ν_7	3132	3134
	ν_6	920	927	670	675		ν_8	1289	1286
							ν_9		
							ν_{10}	720	717

[a] IR spectra were recorded on a Perkin-Elmer 580B spectrometer. Raman spectra were obtained with a Nicolet 1180-computer-assisted Spex Ramalog 5 instrument. Excitation was with the 514.5-nm line of a Coherent CR6 argon ion laser. [b] Average of Fermi resonance doublet.

Table II. Comparison of the Calculated and Observed Frequencies for $C_3H_3^+$, $C_3D_3^+$, and $C_3H_2D^+$ (in cm^{-1})

		$C_3H_3^+$		$C_3D_3^+$				$C_3H_2D^+$	
		obsd	calcd[a]	obsd	calcd			obsd	calcd
a_1'	ν_1	3183	3182	2480	2480	a_1	ν_1	3166	3169
	ν_2	1626	1633	1490	1482		ν_2	2404	2395
							ν_3	1584	1584
a_2'	ν_3		1119		909		ν_4	1267	1262
							ν_5	923	925
e'	ν_4	3138	3138	2349	2349				
	ν_5	1290	1295	1248	1243	b_1	ν_7	3134	3138
	ν_6	927	927	675	670		ν_8	1286	1290
							ν_9		1083
							ν_{10}	717	723
		av diff	2.6		3.6				4.2

[a] These modes are characterized with summed potential energy distributions in symmetry coordinate space as follows:[6] ν_1 (94 s CH str), ν_2 (94 s CCC str), ν_3 (100 s CH bd), ν_4 [95 a CH str(1), 4 a CH str(2)], ν_5 [70 a CCC str(1), 18 a CCC str(2), 7 a CH bd(1), 3 a CH bd(2)], ν_6 [85 a CH bd(1), 5 a CH bd(2), 5 a CCC str(1), 4 a CCC str(2)]. s = symmetric, a = antisymmetric, str = stretch, bd = bend; only one mode of each degenerate pair in the e′ species is characterized here.

the 2.6, 3.6, and 4.2 cm^{-1} average differences in frequencies. The fitted force constants (with statistical dispersions) for the cyclopropenyl cation are (in mdyn $Å^{-1}$ for stretch–stretch, mdyn Å rad^{-2} for bend–bend, and mdyn rad^{-1} for stretch–bend): CC str, 7.91 (17); CH str, 5.28 (02); CH bd, 0.60 (01); CC str/CC str, –0.37 (09); CC str/CH str (same C), –0.20 (03); CC str/CH str (different C), 0.19 (05); CC str/CH bd (same C), 0.16 (05).

For benzene Pulay, Fogarasi, and Boggs have used the scaled ab initio method to resolve discrepancies between various sets of empirical force constants.[8] Their preferred values are 6.578 for CC stretching, 5.176 for CH stretching, and 0.514 for CH in-plane bending. Each of the force constants in the cyclopropenyl cation is larger than the corresponding one in benzene. Adopting the customary correlation between bond strength and magnitude of force constants (e.g., CC stretching constants; saturated, acyclic hydrocarbons 4.70;[9] cyclopropane 4.29[10]), we conclude that both the CC and CH bonds are stronger in the cyclopropenyl cation than in benzene. A stronger CC bond in $C_3H_3^+$ also correlates with a shorter CC bond in cyclopropenyl cations than in benzene. For $C_3Ph_3^+$, r_{CC} = 1.373 Å and, for $C_3[N(CH_3)_2]_3^+$, r_{CC} = 1.363 Å;[11] for benzene, r_{CC} = 1.397 Å.[8] Ab initio calculations for the $C_3H_3^+$ ion also predict CC bond lengths shorter than in benzene.[2,12]

Previous work on empirical force constants for the $C_3H_3^+$ ion is limited to a Urey–Bradley force field (UBFF) derived from incomplete frequency data.[13,1b] UBFF constants have also been fitted to single-isotope vibrational assignments for $C_3Cl_3^+$ and $C_3Br_3^+$.[14] Not only are these several calculations underparameterized, but the resulting UBFF constants are not directly comparable to valence force constants. Of direct interest is Takada and Ohno's ab initio calculation (minimal basis set + C3d + CI) for the $C_3H_3^+$ ion itself, which gave 7.92 for the CC stretching force constant.[2] This surprisingly large value is now supported by our experiments.

The apparently greater CC bond strength in the cyclopropenyl cation than in benzene is remarkable in view of the lower bond order and the strained "σ" bonds in the ion. However, the positive charge on the ion should draw electrons into the bonding region of the ring, and the short CC bonds should give enhanced overlap in the delocalized π bonds.

It is well-known that force constants for stretching of CH bonds increase as the amount of s character in carbon orbitals increases in going from sp^3 in alkanes (4.9) to sp^2 in alkenes (5.1) to sp in acetylenes (5.9).[14] The dissociation energy of CH bonds also increases in this way but not as dramatically.[16] Thus, the CH bond in the cyclopropenyl cation with a force constant of about 5.3 is a strong bond with considerable sp character. A similar conclusion about the sp character of the CH bond in this ion was drawn from the large value of the ^{13}CH coupling constant in this ion[1b] and from the ab initio calculations.[2]

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Gas-Phase ^{1}H NMR Spectra and Nitrogen Inversion of Trimethylene Imine

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Gaseous trimethylene imine ($\overline{\mathrm{HN{-}CH_2{-}CH_2{-}CH_2}}$) produces ^{1}H NMR spectra indicative of an intramolecular chemical-exchange process whose characteristics are compatible with pyrimidal nitrogen inversion. In the liquid phase this process is obscured by very rapid intermolecular imine proton exchange[1] and has not been observed in cyclic imines larger than ethylene imine. Two major conclusions immediately follow from the temperature-dependent gas-phase NMR spectra shown in Figure 1: two magnetically inequivalent conformers are present in a 0.32/1.00 ratio at 30.0 °C, and the free energy for conversion between these conformers, $\Delta G^{\ddagger}$ is 17.9 (0.3) kcal/mol. These results are described more fully below and are discussed in relation to previous studies.

Trimethylene imine (Columbia Organic Chemical) and chloroform (Mallinkrodt) were degassed via five freeze–pump–thaw cycles prior to use. A gaseous sample containing 21.7 torr of trimethylene imine, 210 torr of Ar, and 15.8 torr of $CHCl_3$ (frequency and resolution reference) was prepared in a 3-cm-long 12-mm NMR tube using previously described methods.[2,3] ^{1}H

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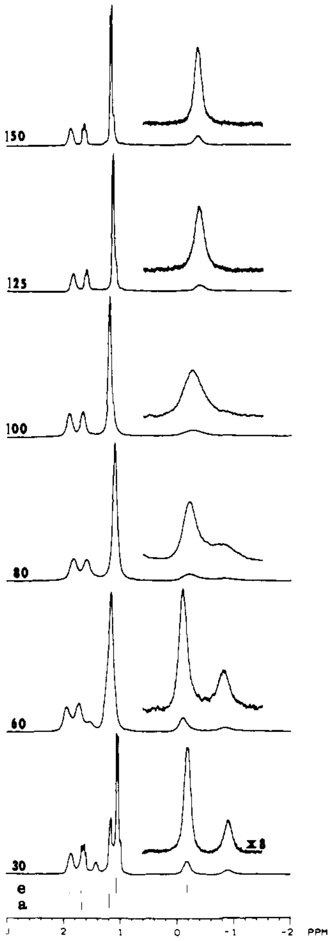

Figure 1. Temperature-dependent ^{1}H NMR spectral traces of gaseous trimethylene imine. The imine proton trace has been multiplied by a factor of 8. Spectral labels refer to the acquisition temperatures in °C. Resonances labeled e and a respectively correspond to equatorial and axial N–H conformers which are resolved at 30 °C. For the equatorial conformer, resonances (referenced to gaseous CHCl$_3$) at −30.0, 209.5, 320 (overlapped), and 371.1 Hz correspond to the imino, α, and inequivalent β protons, respectively. For the axial conformer resonances centered at −102, 232, 202, and 320 Hz (overlapped) correspond to the imino, α, and inequivalent β protons, respectively. The spectra were acquired at 200.067 MHz and referenced to gaseous CHCl$_3$ which is 7.102 ppm downfield from gaseous Me$_4$Si.

NMR spectra were acquired with a Nicolet WB-200 spectrometer on nonspinning samples in the unlocked mode using a sweep width of 3003.0 Hz, a 60° flip angle, and a delay of eight T_1's between acquisitions. At 30.0 °C, T_1 is ca. 250, 350, and 450 ms for the imine, α, and β protons, respectively. Typically, 200 transients were acquired into 4K of memory and Fourier transformed to produce the spectra shown in Figure 1. All spectra were referenced to gaseous CHCl$_3$, which is 7.102 ppm downfield of gaseous Me$_4$Si. For all of the spectra obtained to date we have been unable to completely resolve the coupling constants due to magnetic field inhomogeneity (ca. 1.5 Hz) and rapid T_1's. Despite their low resolution, the preliminary set of spectra do, however, provide insight into the thermodynamic and kinetic parameters which characterize the nitrogen inversion process.

Figure 1 demonstrates that two conformational species of trimethylene imine exist in the gas phase. The indicated spectral assignments are consistent with standard decoupling experiments and peak integrations. The magnetic inequivalency of the β protons in the fast exchange (150 °C) trace is compatible with a nonplanar equilibrium ring conformation. At 30 °C (slow exchange), two sets of resonances are apparent. It is most likely that the more intense set of resonances (e) in the 30.0 °C spectrum arises from the species with the imine proton in the equatorial position. The axial form is then somewhat less stable. At temperatures above 30 °C a process that completely exchanges the inequivalent imine, α, and β protons perturbs the NMR line-shape function. Two processes can result in exchange of axial and equatorial imine protons: *nitrogen inversion* (which proceeds via a transition state in which the N–C bonds are coplanar) and *ring puckering*. However, a combination of ring puckering and nitrogen inversion is required to completely exchange the β protons as is observed spectroscopically. Since the energy requirements for ring puckering are expected to be considerably less than pyrimidal nitrogen inversion, the latter process is rate limiting and gives rise to the observed temperature-dependent line-shape perturbations.

Preliminary rate constants for *nitrogen inversion* were obtained from analyses of the imine proton resonance line shapes using the iterative program DNMR5.[4] An estimated axial/equatorial population ratio of 0.38/1.00 was used at 69.9 °C, along with limiting chemical shifts of −35.0 and −179.6 Hz and a T_2 of 11.2 ms. The respective rate constants obtained [(k (s^{-1}), T (°C); 13.1, 69.9; 41.7, 79.8; 139, 89.8; 321, 99.7] are first order since no pressure dependence was observed. A sample containing 1500 torr of Ar and 20 torr of trimethylene imine showed similar line shapes at the same temperatures. The observed rate constants for interconversion are consistent with a $\Delta G^{\ddagger}$ of 17.9 (0.3) kcal/mol. This preliminary $\Delta G^{\ddagger}$ is similar to the previously reported value of 17.23 (0.05) kcal/mol for nitrogen inversion in gaseous ethylene imine.[5]

Although the above observations and interpretations of the gas-phase NMR spectra of trimethyleneimine are straightforward, our results are especially interesting in light of previous studies which have concerned the *ring puckering* vibration. The reported infrared[6] and Raman[7] spectra of trimethylene imine are consistent with energy levels for the ring-puckering vibration calculated from either a single-[8a] or double-[6]minimum potential function with a low barrier. Vibrational Raman spectral intensities are only consistent with a single-minimum potential function, however.[8b] A recent microwave spectroscopic study reported observation of c-type spectral transitions consistent with an axial conformer.[9] Molecular orbital calculations performed at the STO-3G,[10] STO-4-31G(SCF),[11] and STO-6-31G(RHF)[12] levels have not found a potential energy minimum at the axial conformation along the ring-puckering coordinate.

Despite an NMR spectra assignment ambiguity the present study clearly demonstrates the presence of two conformers, indicating two minima along the nitrogen-inversion coordinate, and that the energy requirements for ring puckering and nitrogen inversion in this four-membered ring are also substantially different and that these two vibrations are not significantly coupled. These results are especially interesting from a dynamical viewpoint, and additional low-pressure studies of nitrogen inversion in trimethylene imine probing intramolecular vibrational redistribution in this system are currently in progress.

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