Microwave Spectrum, Conformation, Intramolecular Hydrogen Bonding, Dipole Moment, ^{14}N Nuclear Quadrupole Coupling Constants, Barrier to Internal Rotation and Centrifugal Distortion Constants of N-Methyl Propargyl Amine

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The microwave spectra of $CH_3NHCH_2C \equiv CH$ and $CH_3NDCH_2C \equiv CH$ have been studied in the 26.5–37.0 GHz spectral region at −40 °C. Only one conformation was assigned and shown to be at least 4 kJ/mol more stable than any other possible conformation. This conformer has a weak intramolecular hydrogen bond formed between the methylamino group hydrogen atom and the π-electrons of the triple bond. The dipole moment is μ_a=0.209(5) D, μ_b=0.480(10) D, μ_c=0.267(4) D, and $\mu_{tot.}$=0.588(10) D. The ^{14}N-quadrupole coupling constants are χ_{aa}=−1.0(7) MHz and χ_{bb}=−0.7(4) MHz. The barrier to internal rotation of the methyl group is 13.79(40) kJ/mol. Five vibrationally excited states belonging to four different normal modes were assigned and their frequencies determined by relative intensity measurements. Extensive centrifugal distortion analyses were made for the ground and the vibrationally excited states.

Recently, propargyl amine, $H_2NCH_2C \equiv CH$,[1–3] and amino acetonitrile, $H_2NCH_2C \equiv N$,[4,5] were studied by microwave[1,4] and infrared[2,3,5] spectroscopic methods. In both these cases, one conformation was found to predominate. This rotamer has both the H−N−C−C dihedral angles close to 60° from *syn*. This allows maximum hydrogen bonding interaction between both the amino group hydrogen atoms and the π-electrons of the acetylene and cyano groups, respectively.

As an extention of these studies, investigation of the N-methyl derivatives, $CH_3NHCH_2C \equiv CH$ and $CH_3NHCH_2C \equiv N$,[6] were undertaken in this laboratory. Our results for $CH_3NHCH_2C \equiv N$ will be reported in this journal in the near future.

Three conformations denoted *I, II,* and *III* and shown in Fig. 1 are possible for $CH_3NHCH_2C \equiv CH$. Intramolecular hydrogen bonding between the hydrogen atoms of the methylamino group and the π-electrons of the triple bond is possible for *I* and *II*, while this kind of interaction is excluded for conformation *III*. The hydrogen bond should be very similar for *I* and *II*. If hydrogen bonding were the most important factor for determining the conformational preferences of $CH_3NHCH_2C \equiv CH$, one would expect a very small energy

Table 1. Selected transitions for the ground vibrational state of $CH_3NHCH_2C \equiv CH$.

Transition		Observed frequency [a,b] (MHz)	Obs.−calc. frequency (MHz)	Centrifugal distortion	
				Total (MHz)	Sextic (MHz)
a-type	$5_{0,5} \leftarrow 4_{0,4}$	29481.40	0.07	−1.05	
	$5_{1,4} \leftarrow 4_{1,3}$	31205.17	0.05	−1.65	
	$5_{1,5} \leftarrow 4_{1,4}$	28567.63	0.00	−0.62	
	$5_{2,3} \leftarrow 4_{2,2}$	30470.00	0.00	−1.00	
	$5_{2,4} \leftarrow 4_{2,3}$	29945.91	0.01	−0.60	
	$6_{0,6} \leftarrow 5_{0,5}$	35123.05	−0.03	−1.63	
	$6_{1,6} \leftarrow 5_{1,5}$	34218.39	−0.11	−1.17	
	$6_{2,4} \leftarrow 5_{2,3}$	36766.72	0.00	−2.26	
	$6_{2,5} \leftarrow 5_{2,4}$	35884.64	−0.03	−1.38	
	$6_{3,3} \leftarrow 5_{3,2}$	36182.70	−0.09	−0.62	
	$6_{3,4} \leftarrow 5_{3,3}$	36134.36	−0.08	−0.55	
b-type	$10_{1,9} \leftarrow 10_{0,10}$	28877.31	−0.06	−16.66	
	$11_{1,10} \leftarrow 11_{0,11}$	33423.12	0.03	−22.69	
	$6_{2,5} \leftarrow 6_{1,6}$	29035.40	−0.04	−0.72	
	$8_{2,7} \leftarrow 8_{1,8}$	33228.29	−0.06	−2.36	
	$11_{3,8} \leftarrow 11_{2,9}$	31712.75	−0.01	−14.16	−0.01
	$13_{3,10} \leftarrow 13_{2,11}$	29814.63	−0.03	14.60	−0.02
	$16_{3,13} \leftarrow 16_{2,14}$	30642.31	0.06	−12.17	−0.03
	$18_{3,15} \leftarrow 18_{2,16}$	34587.19	0.04	−59.13	−0.02
	$2_{2,1} \leftarrow 1_{1,0}$	35023.67	−0.04	−0.79	
	$4_{1,4} \leftarrow 3_{0,3}$	29178.64	0.05	0.07	
	$8_{1,7} \leftarrow 7_{2,6}$	33175.51	−0.08	−11.06	
	$13_{2,12} \leftarrow 12_{3,9}$	28040.38	0.01	2.02	0.10
	$17_{4,14} \leftarrow 16_{5,11}$	34052.93	−0.06	−64.70	0.07
	$22_{6,17} \leftarrow 21_{7,14}$	34337.88	−0.08	−146.63	0.25
	$22_{6,16} \leftarrow 21_{7,15}$	34678.13	−0.11	−156.03	0.26
	$26_{8,19} \leftarrow 25_{9,16}$	27003.25	0.00	−194.23	0.49
	$26_{8,18} \leftarrow 25_{9,17}$	27014.54	0.10	−194.83	0.49
c-type	$8_{3,6} \leftarrow 8_{2,6}$	35247.66	0.06	5.76	
	$11_{3,9} \leftarrow 11_{2,9}$	29361.91	0.13	22.29	−0.02
	$18_{4,15} \leftarrow 18_{3,15}$	35236.77	0.04	122.22	−0.16
	$26_{5,22} \leftarrow 26_{4,22}$	34499.72	−0.10	430.15	−0.93
	$33_{6,28} \leftarrow 33_{5,28}$	35907.41	−0.02	973.04	−3.06
	$40_{7,34} \leftarrow 40_{6,34}$	36296.49	−0.06	1855.41	−8.01
	$48_{8,41} \leftarrow 48_{7,41}$	30330.58	−0.04	3078.25	−17.87
	$55_{9,47} \leftarrow 55_{8,47}$	29603.75	0.00	4683.93	−34.59
	$68_{11,58} \leftarrow 68_{10,58}$	34162.92	−0.01	10004.83	−109.12
Coalescing K_{-1}-lines[c]	$15_9 \leftarrow 16_8$	35192.57	−0.08	−98.05	0.38
	$26_{13} \leftarrow 27_{12}$	30436.56	0.00	−165.01	1.75
	$38_{18} \leftarrow 39_{17}$	35116.07	−0.09	−333.81	8.07
	$48_{22} \leftarrow 49_{21}$	36397.87	−0.01	−448.97	19.66
	$56_{25} \leftarrow 57_{24}$	34369.37	−0.01	−422.23	32.25
	$66_{29} \leftarrow 67_{28}$	35719.58	−0.04	−454.43	62.38
	$37_{12} \leftarrow 36_{13}$	31516.56	−0.02	−499.85	2.58
	$48_{16} \leftarrow 47_{17}$	35861.13	−0.07	−1015.55	8.77
	$57_{20} \leftarrow 56_{21}$	27724.83	0.03	−1364.42	15.20
	$63_{22} \leftarrow 62_{23}$	32787.18	−0.03	−1907.28	26.69
	$74_{26} \leftarrow 73_{27}$	36560.40	0.01	−3023.97	58.34

[a] ±0.10 MHz. [b] Unperturbed frequencies of lines split by ^{14}N-quadrupole interactions were calculated according to Ref. 8. [c] The K_{-1}-energy doublets coalesce for high values of K_{-1}. Subscripts of *J*-quantum numbers refer to K_{-1} and not to K_{+1}.
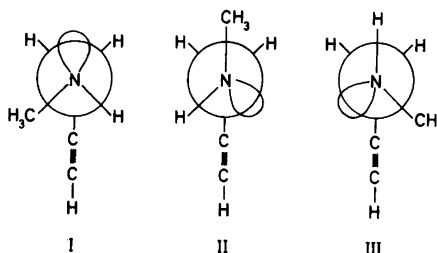
Fig. 1. The three possible conformations of $CH_3NHCH_2C\equiv CH$ viewed along the $N-CH_2-$ bond. Only *I* was found in this work and shown to be at least 4 kJ/mol more stable than *II* or *III*.

difference between *I* and *II*. This, however, was not found. Conformation *I* is the only rotamer which was assigned. This conformer is more stable than any other rotamer by at least 4 kJ/mol.

EXPERIMENTAL

N-Methyl propargyl amine was purchased from EGA-Chemie, Steinheim, West-Germany, and purified by gas chromatography before use. Studies were made mostly in the 26.5−37.0 GHz spectral region with the absorption cell cooled with dry ice to about −40 °C. Lower temperatures could not be used because of insufficient vapour pressure of the compound. The spectrum was recorded with pressures in the 0.5−4 Pa range. Free-running klystrons were employed as radiation sources. With this equipment, quadrupole and internal rotation fine structure splittings larger than about 0.5 MHz were resolved. The deuterated species, $CH_3NDCH_2C\equiv CH$, was formed by direct exchange between the parent species and heavy water in the wave guide.

RESULTS

Spectrum and assignment of the ground vibrational state of I. The microwave spectrum of $CH_3NHCH_2C\equiv CH$ is dense with absorptions occurring every few megahertz. The strongest

Table 2. Spectroscopic constants of the ground vibrational states of $CH_3NHCH_2C\equiv CH$ and $CH_3NDCH_2C\equiv CH$.[a]

Species		$CH_3NHCH_2C\equiv CH$	$CH_3NDCH_2C\equiv CH$
Number of transitions		181	44
Root-mean-square dev. (MHz)		0.0626	0.0543
A_0	(MHz)	10763.1583(29)	10333.8886(91)
B_0	(MHz)	3266.38516(91)	3205.0105(44)
C_0	(MHz)	2735.02663(78)	2716.6320(40)
Δ_J	(kHz)	2.9046(18)	2.806(54)
Δ_{JK}	(kHz)	−19.001(14)	−15.279(60)
Δ_K	(kHz)	75.5639(82)	58.5(11)
δ_J	(kHz)	0.89045(65)	0.7982(21)
δ_K	(kHz)	7.754(59)	6.991(98)
H_J	(Hz)	0.00010(21)	$-$[c]
H_{JK}	(Hz)	−0.1372(11)	$-$[c]
H_{KJ}	(Hz)	−0.493(18)	$-$[c]
H_K	(Hz)[b]	2.223(36)	$-$[c]

[a] Uncertainties represent one standard deviation. [b] Further sextic constants preset at zero. [c] Preset at zero.

Table 3. Spectroscopic constants of vibrationally excited states of $CH_3NHCH_2C\equiv CH$.[a]

Vibrational state	First ex. $-H_2C-N$ tors.	Second ex. $-H_2C-N$ tors.	First ex methyl tors.	First ex. lowest bend.	First ex. second lowest bend.
N.o.t.[b]	131	25	62	23	22
R.m.s. (MHz)[c]	0.071	0.138	0.0921	0.133	0.117
A_v (MHz)	10826.8318(45)	10891.922(20)	10800.781(12)	10736.236(20)	10861.450(20)
B_v (MHz)	3259.6737(14)	3252.4551(56)	3267.8062(33)	3263.9832(48)	3260.7076(42)
C_v (MHz)	2730.5924(17)	2726.1882(58)	2735.4352(33)	2733.1578(49)	2730.9104(44)
Δ_J (kHz)	2.9431(56)	$-^e$	2.965(22)	$-^e$	$-^e$
Δ_{JK} (kHz)	−19.839(41)	−19.97(14)	−18.34(17)	−18.53(14)	−19.62(13)
Δ_K (kHz)	82.429(22)	$-^e$	74.934(42)	$-^e$	$-^e$
δ_J (kHz)	0.9046(27)	0.9302(35)	0.8933(35)	0.9170(35)	0.9308(32)
δ_K (kHz)	8.08(11)	$-^f$	8.07(18)	$-^f$	$-^f$
H_J (Hz)	0.0065(49)	$-^f$	0.153(45)	$-^f$	$-^f$
H_{JK} (Hz)	−0.015(91)	$-^f$	1.50(81)	$-^f$	$-^f$
H_{KJ} (Hz)	−0.559(72)	$-^f$	5.55(59)	$-^f$	$-^f$
H_K (Hz)[d]	2.89(13)	$-^f$	−6.16(54)	$-^f$	$-^f$

[a] Uncertainties represent one standard deviation. [b] Number of transitions. [c] Root-mean-square deviation. [d] Further sextic constants preset at zero. [e] Preset at zero. [f] Preset at zero.

transitions observed which turned out to be the *b*-type *Q*-branch transitions of conformation *I* with *J* between 15 and 19, have peak absorption coefficients of roughly 4×10^{-7} cm^{-1} at about -40 °C.

Prior to this work, the microwave spectrum of $CH_3NHCH_2C \equiv N$ was assigned in this laboratory,[6] and it was known that a conformation similar to *I* predominates. Model rotational constants of conformation *I* of $CH_3NHCH_2C \equiv CH$ predict a characteristic band-head feature of the strong $J_{3,J-3} \leftarrow J_{2,J-2}$ *b*-type *Q*-branch to occur in the lower part of the *R*-band. This was used to get the first determination of $A-C$ and Ray's asymmetry parameter[7] κ. A line at 29178.64 MHz with a well-resolved Stark effect was immediately identified as the $4_{0,4} \leftarrow 3_{1,3}$ transition. Unrefined values of all three rotational constants were thus determined. Assignments were now made for *a*- and *c*-type transitions as well, and gradually extended to high values of the *J* quantum number. A total of about 200 transitions were ultimately assigned; a small selection of which are shown in Table 1. Maximum value of *J* was 74 for the $74_{26} \leftarrow 73_{27}$ transitions.*

Centrifugal distortion is prominent for this molecule as shown in Table 1. It amounts to about 10 GHz for the $68_{11,58} \leftarrow 68_{10,58}$ transition.

The lines which were split by ^{14}N nuclear quadrupole coupling are shown in Table 5. They were included in the final least squares fit after allowance had been made for this effect using Rudolph's first order formula.[8] The final spectroscopic constants (*I'*-representation *A*-reduction) derived from 181 transitions are shown in Table 2.

Vibrationally excited states. The ground state transitions were accompanied by a satellite spectrum presumably belonging to vibrationally excited states of conformation I. Five such excited states were ultimately assigned, as shown in Table 3.

The strongest of these satellites had approximately 40 % of the ground-state intensity at about -40 °C. Relative intensity measurements performed largely as described in Ref. 9 yielded 152(20) cm^{-1} for this vibration which is assumed to be the first excited state of the heavy-atom (the $HCCH_2C-NHCH_3$) torsional vibration. This compares well with 151(30) cm^{-1} found for the similar normal vibration of $CH_3NHCH_2C \equiv N$.[6]

A total of about 145 transitions were measured for this vibrationally excited state, and 131 of these were used to determine the spectroscopic constants appearing in Table 3. Maximum value of *J* for the *Q*-branch lines was found for the $27_{5,23} \leftarrow 27_{4,23}$ transition. For the *R*-branch, the $56_{19} \leftarrow 55_{20}$ coalescing K_{-1}-energy levels, and for the *P*-branch, the $59_{26} \leftarrow 60_{25}$ coalescing transitions involved the maximum *J* and K_{-1} values, respectively.

Apart from its low frequency of 152(20) cm^{-1}, the observed changes of the rotational constants upon excitation indicate that this is indeed the first excited state of the heavy-atom torsional vibration. The changes are (Tables 2 and 3) $\Delta A = +63.67$ MHz, $\Delta B = -6.72$ MHz, and $\Delta C = -4.44$ MHz, respectively. The changes were computed to be $\Delta A = +58.2$ MHz, $\Delta B = -17.0$ MHz, and $\Delta C = -5.7$ MHz by increasing the $H_3C-NH-CH_2-C$ dihedral angle of the plausible structure (Table 7) by 1°, in fair agreement with the experimentally observed changes.

The second excited state of this vibration was also assigned. Its spectroscopic constants are shown in Table 3. They were determined from transitions with $J \leqslant 18$. The fact that the changes of the rotational constants (see Table 2 and 3) upon two successive excitations of this vibrational mode are quite constant, is typical for a harmonic mode.

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* The complete microwave spectra of $CH_3NHCH_2C \equiv CH$ and $CH_3NDCH_2C \equiv CH$ are available from the authors upon request or from the Molecular Spectra Data Center, Bldg. 221, Room B 265, National Bureau of Standards, Washington D.C. 20234, U.S.A., where they have been deposited.

Table 4. Parameters for determination of the barrier to internal rotation of the methyl group of $CH_3NHCH_2C\equiv CH$.

Transition	Observed frequencies (MHz)		Barrier (kJ/mol)
	ν_A^a	ν_A-ν_E^a	
$18_{3,15}\leftarrow 18_{2,16}$	34680.16	−0.54	13.64
$19_{3,16}\leftarrow 19_{2,17}$	37749.12	−0.60	13.93
			Average 13.79

Direction cosines λ_a=0.2689, λ_b=0.8857, λ_c=0.3788

Barrier, reduced barrier, and moment of inertia of methyl top
V_3=13.79(40) kJ/mol, s=94.95, I_a=3.20×10^{-20} u m^2

[a] ±0.10 Mhz.

Table 5. ^{14}N-quadrupole splittings [a] and diagonal elements of the quadrupole coupling tensor of $CH_3NHCH_2C\equiv CH$.

Transition	$F'\leftarrow F$	E_q(obs.) (MHz)	E_q(obs.)-E_q(calc.) (MHz)
$10_{1,9}\leftarrow 10_{0,10}$	$11\leftarrow 11$	−0.24(3)	−0.04
	$10\leftarrow 10$	0.46(2)	−0.01
$11_{1,10}\leftarrow 11_{0,11}$	$12\leftarrow 12$	−0.08(3)	0.12
	$11\leftarrow 11$	0.50(2)	0.05
$5_{2,4}\leftarrow 5_{1,5}$	$6\leftarrow 6$	−0.19(3)	−0.05
	$5\leftarrow 5$	0.43(2)	0.05
$6_{2,5}\leftarrow 6_{1,6}$	$7\leftarrow 7$	−0.19(3)	−0.05
	$6\leftarrow 6$	0.30(2)	−0.06
$7_{2,6}\leftarrow 7_{1,7}$	$8\leftarrow 8$	−0.03(3)	0.11
	$7\leftarrow 7$	0.34(2)	−0.01
$8_{2,7}\leftarrow 8_{1,8}$	$9\leftarrow 9$	−0.24(3)	−0.10
	$8\leftarrow 8$	0.33(2)	−0.11

^{14}N-quadrupole coupling constants χ_{aa}=−1.0(7) MHz, χ_{bb}=−0.7(4) MHz

[a] Uncertainties represent one standard deviation.

Table 6. Stark coefficients and dipole moment of $CH_3NHCH_2C\equiv CH$.[a]

Transition		$\Delta\nu/E^2$ (MHz V^{-2} cm^2)×10^6	
		Obs.	Calc.
$4_{1,4}\leftarrow 3_{0,3}$	M =0	−1.08(1)	−1.11
	|M|=1	−0.540(7)	−0.587
	|M|=2	1.03(3)	0.983
$8_{2,7}\leftarrow 8_{1,8}$	|M|=8	−5.15(4)	−5.08
	|M|=7	−3.84(3)	−3.87
	|M|=6	−2.81(4)	−2.83
$2_{2,1}\leftarrow 1_{1,0}$	M =0	0.900(9)	0.812
	|M|=1	−50.9(4)	−51.1

Dipole moment μ_a=0.209(5) D[b], μ_b=0.480(10) D, μ_c=0.267(4) D, $\mu_{tot.}$=0.588(10) D

[a] Uncertainties represent one standard deviation. [b] 1 D=3.33564×10^{-30} C m.

The third excited state of this vibration could not be found presumably because its intensity is so low; roughly 5 % of that of the ground state.

Another vibrationally excited state having approximately 25 % of the intensity of the ground state was assigned next. Relative intensity measurements[9] yielded 222(30) cm^{-1} for this vibration which is assigned as the first excited state of the methyl group torsional mode for several reasons. Firstly, the rotational constants change little from the ground state values as seen from Tables 2 and 3. This is typical for an excited state involving little reduced mass, which is the case for the methyl group torsion. Secondly, the two Q-branch transitions shown in Table 4 were split. Neither the intensity patterns, nor the splittings themselves are compatible with predictions from the quadrupole coupling constants of Table 5, and can only be explained to be caused by methyl group tunnelling. A barrier of 13.79(40) kJ/mol was calculated from the splittings shown in Table 4 using the computer program described in Ref. 10. This barrier yields 225 cm^{-1} for the methyl group torsional vibration in very good agreement with the relative-intensity value of 222(30) cm^{-1}.

The barrier to internal rotation of the methyl group (13.79(40) kJ/mol) is close to 13.47(8) kJ/mol found for dimethylamine.[11a]

The spectroscopic constants of this torsional mode are shown in Table 3. They were derived from 61 transitions with $45_{15} \leftarrow 44_{16}$ multiplet representing maximum values of J.

The last two excited states shown in Table 3 had relative intensities of about 13 % and 11 %, respectively, of that of the ground state at -40 °C. This yields frequencies of *ca.* 325 cm^{-1} and *ca.* 356 cm^{-1} for these two normal vibrations which are assigned as the two lowest bending modes of the molecule.

^{14}N nuclear quadrupole coupling constants. The two $J_{1,J-1} \leftarrow J_{0,J}$ and $J_{2,J-1} \leftarrow J_{1,J}$ Q-branch series were detectably split into two components due to quadrupole coupling of the ^{14}N nucleus with molecular rotation. The procedure on Ref. 12 was used to determine χ_{aa} and χ_{bb} shown in Table 5.

Assuming the principal nuclear axis quadrupole coupling constant χ_z to be -4.1 MHz as found for NH_3[13] and to be oriented 109.47° with respect to the three bonds of the nitrogen atom, χ_{aa} and χ_{bb} were calculated to be -1.6 and -0.2 MHz, respectively. These values are not very different from those rather inaccurate parameters shown in Table 5.

Dipole moment. The Stark coefficients shown in Table 6 were used to determine the dipole moment using standard procedure.[12] The results were (Table 6): $\mu_a=0.209(5)$ D, $\mu_b=0.480(10)$ D, and $\mu_c=0.267(4)$ D, respectively. The bond moments of Ref. 14 yield $\mu_a=0.6$ D, $\mu_b=0.5$ D and $\mu_c=0.7$ D, respectively. If a modified bond moment of 0.8 D is used for the sp^3-sp carbon-carbon bond with the sp-end assumed to be negative as explained in Ref. 15, $\mu_a=0.1$ D, $\mu_b=0.0$ D and $\mu_c=0.7$ D were obtained. Both these procedures are thus seen to predict dipole moments of about the same quality in this case.

The total dipole moment of 0.588(10) D found for $CH_3NHCH_2C\equiv CH$ is quite similar to 0.736(2) D determined for $H_2NCH_2C\equiv CH$.[1]

Deuterated species. The deuterated species was studied in order to determine the position of the methylamino group hydrogen atom. 44 transitions with $J \leqslant 22$ were used to determine the spectroscopic constants listed in Table 1. The substitution coordinates[16] of this atom are shown in Table 7, and they clearly show that conformation *I* has not been confused with the hypothetical conformation *III* which is predicted to possess similar rotational constants as *I*, but very different substitution coordinates for the hydrogen atom in question.

Searches for further conformations. Nearly 500 transitions in the 26.5–37.0 GHz spectral region were assigned as described above. This includes all the strongest lines of the spectrum

Table 7. Plausible structural parameters[a] (bond lengths in *pm*; angles in *degrees*) of $CH_3NHCH_2C\equiv CH$.

Assumed structural parameters

C−N	149.5	∠H−C≡C	180.0
C≡C	119.6	∠C−C≡C	180.0
C−C	146.1	∠CCN	113.6
H−C$_{acetylene}$	107.3	∠CCH	109.47
H−C	109.3	∠HCH	109.47
H−N	101.7	∠CNH	109.47
		∠NCH	109.47

Fitted structural parameters

∠CNC   112.0(15)
∠HNCC[b]   57(4) from *syn*

Rotational constants (MHz)

Parent species			Deuterated species		
Obs.	Calc.	Diff. (%)	Obs.	Calc.	Diff. (%)
10763.16	10629.88	1.24	10333.89	10207.95	1.22
3266.39	3251.04	0.47	3205.01	3189.38	0.49
2735.03	2731.97	0.11	2716.63	2713.81	0.10

Kraitcman's coordinates[c] for the methylamino group hydrogen atom

	$|a|$	$|b|$	$|c|$
From rotational constants:	106.046(18)	33.816(25)	136.697(6)
From plausible structure:	106.37	30.70	137.97

Hydrogen bond parameters

H···C≡CH	268	∠H···C≡C	130
∠N−H···C	68	∠N−H, C≡C[d]	70

Sum of van der Waals radii[e]
H···C[f]   290

[a] See text. [b] H−N−C−C dihedral angle. $H_3C-N-C-C$ dihedral angle found to be 63(4)° from *syn*; see text. [c] Ref. 16. [d] Angle between N−H and C≡C bonds. [e] Ref. 17. [f] van der Waals radius of carbon atom taken to be 170 *pm* as for aromatic carbon.[17]

as well as the large majority of the transitions of intermediate intensities and many fairly weak lines.

The hypothetical conformation *II* was predicted to have the following rotational constants and dipole moment components using the modified value[15] for sp^3-sp carbon-carbon bonds: $A=27.0$ GHz, $B=2.27$ GHz, $C=2.16$ GHz, $\mu_a=0.8$ D, $\mu_b=0.1$ D, and $\mu_c=1.1$ D. The corresponding values for the hypothetical conformation *III* were predicted to be: $A=10.7$ GHz, $B=3.28$ GHz, $C=2.69$ GHz, $\mu_a=1.3$ D, $\mu_b=1.0$ D, and $\mu_c=0.8$ D. Searches for these two hypothetical conformations among the relatively few unassigned lines of intermediate intensities were negative. It was also noted that the absolute intensities of the assigned conformation *I* transitions were as intense as one would expect with only one

conformation being present. It is concluded that conformation *I* is at least 4 kJ/mol more stable than *II* or *III*.

Structure. Only two isotopic species were studied for *N*-methyl propargyl amine. A complete geometrical structure cannot, therefore, be determined for the compound and some assumptions must be made. The structural parameters which were kept fixed are shown in Table 7. They were taken largely from the substitution values of $H_2NCH_2C\equiv CH$.[1] The $H-C\equiv C-C$ chain of atoms was assumed to be linear. Two structural parameters, *viz.* the $C-N-C$ angle and the rotational angle about the $H_2C-NHCH_3$ bond were fitted to reproduce the rotational constants and substitution coordinates of the methylamino group hydrogen atom. The $H-N-C-C$ (and $H_3C-N-C-C$) dihedral angle was fitted in steps of 1° and the $C-N-C$ angle in steps of 0.5°. The best values (see Table 7) were found with $\angle CNC=112.0(15)°$ and $\angle H-N-C-C=57(4)°$ from *syn* ($\angle H_3C-N-C-C=63(4)°$ from *syn*). The estimated uncertainties of these two angles are approximately three standard deviations.

The fact that the $H-N-C-C$ dihedral angle tends to be a bit less than 60° (and $\angle H_3C-N-C-C$ to be larger) perhaps reflects hydrogen-bonding interaction between the methylamino group hydrogen atom and the π-electrons of the triple bond. The CNC angle of 112.0(15)° is very similar to 112.2° found for dimethylamine.[11b]

DISCUSSION

The intramolecular hydrogen bond of $CH_3NHCH_2C\equiv CH$ is rather weak since the $H\cdots C\equiv CH$ is only approximately 20 *pm* shorter than the sum of the van der Waals radii of carbon and hydrogen (Table 7).[17]

Moreover, the fact that the hypothetical conformation *II* is much less stable than *I*, indicates that forces other than hydrogen-bonding are of importance. The most likely such force is repulsion between the π-electrons of the triple bond and the lone-pair electrons of the nitrogen atom. This repulsion is minimized in conformation *I*, but might be of importance in the hypothetical conformations *II* and *III*. If this repulsion were larger than hydrogen bonding, one would expect to find that *I* would be considerably more stable than the hypothetical rotamer *II*, in accord with the present finding.

It is also noted that a possible attraction between the methyl group and the π-electrons of the triple bond might help stabilize the identified conformation *I*. This attraction is presumed to be rather insignificant, however, since in $CH_3CH_2CH_2C\equiv CH$ which is isoelectronic to the title compound, the *gauche* and *anti* forms are very close in energy.[18]

Our final conclusion then is that two factors seem to decide the conformational behaviour of $CH_3NHCH_2C\equiv CH$, namely hydrogen bonding and repulsion between the π-electrons of the triple bond and the lone-pair electrons, perhaps with the latter being more important.

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