

# Microwave Spectrum, Conformation, Intramolecular Hydrogen Bonding, Dipole Moment and Centrifugal Distortion Constants of (*N*-Methylamino)-ethanenitrile

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The microwave spectra of  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{N}$  and  $\text{H}_3\text{CNDCH}_2\text{C}\equiv\text{N}$  have been studied in the 18.0–31.5 GHz spectral region at  $-15^\circ\text{C}$ . Only one conformation was assigned and estimated 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  $\pi$ -electrons of the triple bond. The dipole moment is  $\mu_a=2.490(16)$  D,  $\mu_b=1.296(10)$  D,  $\mu_c\approx 0.0$  D, and  $\mu_{\text{tot.}}=2.807(17)$  D. Three vibrationally excited states belonging to two different normal modes were assigned and their frequencies determined by relative intensity measurements. Centrifugal distortion analyses were made for the ground state and the vibrationally excited states.

$\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{N}$  is part of a series of molecules that have recently been studied by spectroscopic methods in order to investigate the possible intramolecular hydrogen-bonding interaction between an aminogroup hydrogen atom and a  $\pi$ -electron system. The other members of this series are 1-amino-2-propyne,  $\text{H}_2\text{NCH}_2\text{C}\equiv\text{CH}$ ,<sup>1,2,3</sup> aminoethanenitrile,  $\text{H}_2\text{NCH}_2\text{C}\equiv\text{N}$ ,<sup>4,5,6</sup> and 1-(*N*-methylamino)-2-propyne,  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{CH}$ .<sup>7</sup> In the cases of  $\text{H}_2\text{NCH}_2\text{C}\equiv\text{CH}$  and  $\text{H}_2\text{NCH}_2\text{C}\equiv\text{N}$  a conformation with both the H–N–C–C dihedral angles close to  $60^\circ$  from *syn* for each molecule, was found to predominate. For  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{CH}$  a similar conformation with both the C–N–C–C and the H–N–C–C dihedral angles close to  $60^\circ$  from *syn*, was found to be the most stable one. These three molecules do therefore have the possibility of forming intramolecular hydrogen bonds in their observed conformations.

There are three different conformational possibilities for  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{N}$ ; these are denoted I, II, and III, and are shown in Fig. 1. In conformations I and II intramolecular hydrogen-bonding interaction may occur between the methylamino group hydrogen atom and the  $\pi$ -electrons of the cyano group, while conformation III does not have this possibility.

It was expected that conformation III should be less stable than I and II since no conformation similar to it has been assigned for the other molecules in this series. Since only a conformation similar to I was observed for  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{CH}$ ,<sup>7</sup> it was also expected that conformation I should be the most stable form of the title compound, as is indeed found in this work.

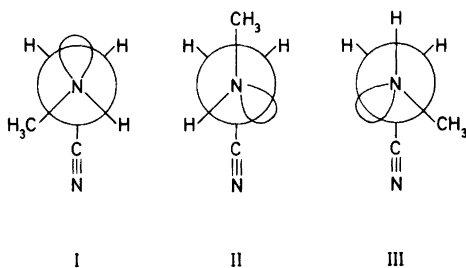


Fig. 1. The three possible conformations of  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{N}$ . Only I was found in this work and estimated to be at least 4 kJ/mol more stable than III and 6 kJ/mol more stable than II.

## EXPERIMENTAL

(*N*-Methylamino)-ethanenitrile was purchased from Tokyo Kasei, Japan, and distilled before use. The distillation had to be carried out because the sample was contaminated with a black insoluble precipitate. The same problem was observed in aminoethanenitrile<sup>6</sup> and might be due to minor amounts of impurities ( $\text{CH}_3\text{OH}$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , etc.)

Studies were made in the 18.0–31.5 GHz spectral region with the absorption cell cooled with dry ice to about  $-15^\circ\text{C}$ . Lower temperatures could not be used because of insufficient vapour pressure of the compound. The spectrum was recorded with pressures in the 1–4 Pa range. Free-running klystrons were employed as radiation sources. With this equipment, fine structure splittings larger than about 0.5 MHz can be resolved. The deuterated species,  $\text{CH}_3\text{NDCH}_2\text{C}\equiv\text{N}$ , was formed by direct exchange between the parent species and  $\text{D}_2\text{O}$  in the wave guide.

## RESULTS

*Spectrum and assignment of the ground vibrational state of I.* Preliminary rotational constants of I were computed by combining structural parameters taken from related compounds (see Table 4), and from these constants a rigid-rotor spectrum was calculated. Bond moment calculations were performed using the values of Ref. 8, and the dipole moment components were predicted to be  $\mu_a=2.6$  D,  $\mu_b=1.8$  D, and  $\mu_c=0.3$  D. This implies that the spectrum of conformation I should contain the strong low- $J$  *R*-branch *a*-type lines, which are easy to assign because of their typical Stark effects. Searches were therefore first made for these lines, and they were soon found. The next step was to look for the *Q*-branch *b*-type lines with medium high values of  $J$ , and these lines were also assigned after some searching. Centrifugal distortion had to be allowed for in this process. Finally, the *P*- and *R*-branch *b*-type lines with high values of  $J$  were assigned.

In the end, about 125 transitions had been assigned, of which 118 were used to derive the spectroscopic constants ( $I'$ -representation,  $A$ -reduction) shown in Table 2. 61 of these transitions are shown in Table 1.\* Maximum values of  $J$  and  $K_{-1}$  (for the coalescing  $K_{-1}$ -doublets) were  $58_{21}\leftarrow 57_{22}$  for the *R*-, and  $51_{23}\leftarrow 52_{22}$  for the *P*-branch transitions. The strongest lines had peak intensities of about  $3\times 10^{-7}$   $\text{cm}^{-1}$ , while the weakest assigned lines had peak intensities of about  $2\times 10^{-8}$   $\text{cm}^{-1}$ . No splittings of the lines due to quadrupole coupling of the  $^{14}\text{N}$  nuclei with the overall rotation, were observed.

*Vibrationally excited states of I.* After the spectrum of the ground vibrational state of conformation I had been assigned, it was evident that this spectrum was accompanied by a

\* The complete spectra of conformation I are available from the authors upon request, or from the Molecular Spectra Data Center, National Bureau of Standards, Bld. 221, Rno. B265, Washington, D.C. 20234, U.S.A., where they have been deposited.

Table 1. Selected transitions for the ground vibrational state of  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{N}$ .

Transition	Observed frequency <sup>a</sup> (MHz)	Obs.-calc. frequency (MHz)	Centrifugal distortion		
			Total (MHz)	Sextic (MHz)	Fixed (MHz)
<b>a-type</b>					
$3_{0,3} \leftarrow 2_{0,2}$	18424.59	0.06	-0.31		
$3_{1,2} \leftarrow 2_{1,1}$	19368.13	0.04	-0.38		
$4_{0,4} \leftarrow 3_{0,3}$	24428.42	-0.11	-0.68		
$4_{1,3} \leftarrow 3_{1,2}$	25785.72	-0.07	-0.96		
$4_{1,4} \leftarrow 3_{1,3}$	23546.45	-0.01	-0.31		
$4_{2,2} \leftarrow 3_{2,1}$	25001.84	-0.14	-0.32		
$4_{2,3} \leftarrow 3_{2,2}$	24703.81	0.00	-0.14		
$5_{0,5} \leftarrow 4_{0,4}$	30326.34	0.11	-1.21		
$5_{1,5} \leftarrow 4_{1,4}$	29382.49	0.04	-0.74		
$5_{2,3} \leftarrow 4_{2,2}$	31422.62	-0.03	-1.19	-0.01	
$5_{2,4} \leftarrow 4_{2,3}$	30841.37	0.05	-0.72	-0.01	
$5_{3,2} \leftarrow 4_{3,1}$	31024.93	-0.12	0.16	-0.01	-0.01
$5_{3,3} \leftarrow 4_{3,2}$	31003.60	-0.03	0.19	-0.01	-0.01
$5_{4,1} \leftarrow 4_{4,0}$	30978.71	-0.11	1.66	-0.03	-0.02
$5_{4,2} \leftarrow 4_{4,1}$	30978.71	0.13	1.67	-0.03	-0.02
<b>b-type</b>					
$4_{2,2} \leftarrow 4_{1,3}$	21050.07	0.14	0.47		
$5_{2,3} \leftarrow 5_{1,4}$	20305.15	0.06	1.18	-0.01	-0.01
$6_{2,4} \leftarrow 6_{1,5}$	19732.84	0.00	1.77	-0.01	-0.01
$5_{2,4} \leftarrow 5_{1,5}$	27666.43	-0.09	-0.41	-0.01	-0.01
$6_{2,5} \leftarrow 6_{1,6}$	29430.07	-0.03	-0.67	-0.01	-0.01
$7_{1,6} \leftarrow 7_{0,7}$	18153.14	-0.01	-4.83	-0.01	-0.01
$9_{1,8} \leftarrow 9_{0,9}$	25742.74	0.02	-13.20	-0.01	-0.01
$8_{2,6} \leftarrow 8_{1,7}$	19610.74	-0.08	1.25	-0.03	-0.03
$10_{2,8} \leftarrow 10_{1,9}$	21513.28	0.06	-4.69	-0.05	-0.05
$12_{2,10} \leftarrow 12_{1,11}$	25970.26	-0.08	-20.80	-0.06	-0.06
$13_{2,11} \leftarrow 13_{1,12}$	29221.11	0.02	-33.85	-0.06	-0.05
$12_{3,9} \leftarrow 12_{2,10}$	30367.54	-0.12	16.87	-0.29	-0.27
$14_{3,11} \leftarrow 14_{2,12}$	29587.67	0.04	8.61	-0.41	-0.39
$15_{3,12} \leftarrow 15_{2,13}$	30098.99	-0.03	-2.75	-0.44	-0.42
$16_{3,13} \leftarrow 16_{2,14}$	31323.77	0.12	-20.39	-0.44	-0.42
$2_{1,2} \leftarrow 1_{0,1}$	19304.13	0.01	0.03		
$5_{0,5} \leftarrow 4_{1,4}$	24977.37	0.16	-1.96		
$9_{2,7} \leftarrow 8_{3,6}$	22702.57	0.07	-19.03	0.01	0.04
$12_{3,9} \leftarrow 11_{4,8}$	24428.42	0.04	-41.21	0.05	0.19
$15_{4,11} \leftarrow 14_{5,10}$	26388.07	-0.05	-68.94	0.11	0.55
$14_{8,6} \leftarrow 15_{7,9}$	23199.43	0.08	-42.93	0.14	-0.02
$18_{5,14} \leftarrow 17_{6,11}$	28234.43	-0.10	-93.25	0.09	1.17
<b>Coalescing <math>K_{-1}</math>-lines<sup>b</sup></b>					
$16_9 \leftarrow 17_8$	26285.56	-0.07	-62.27	0.26	-0.03
$21_{11} \leftarrow 22_{10}$	26133.22	-0.09	-81.86	0.62	-0.67
$26_{13} \leftarrow 27_{12}$	25975.48	0.16	-94.41	1.23	-2.75
$31_{15} \leftarrow 32_{14}$	25820.75	0.07	-95.55	2.16	-7.79
$34_{12} \leftarrow 33_{13}$	18582.36	-0.06	-393.98	2.12	23.23
$38_{13} \leftarrow 37_{14}$	28219.02	-0.03	-629.70	4.29	42.87
$36_{17} \leftarrow 37_{16}$	25676.46	0.05	-80.93	3.49	-18.05
$43_{15} \leftarrow 42_{16}$	28127.85	0.03	-861.77	7.48	77.67
$43_{20} \leftarrow 44_{19}$	28613.46	-0.02	-92.28	7.46	-44.65
$48_{17} \leftarrow 47_{18}$	27998.47	-0.03	-1141.30	12.25	131.96
$51_{23} \leftarrow 52_{22}$	25362.50	0.02	100.75	10.35	-117.75
$58_{21} \leftarrow 57_{22}$	27599.00	0.07	-1857.57	28.50	329.34

<sup>a</sup>  $\pm 0.10$  MHz. <sup>b</sup> The  $K_{-1}$ -energy doublets coalesce for high values of  $K_{-1}$ . Subscripts of  $J$ -quantum numbers refer to  $K_{-1}$  and not to  $K$ .

Table 2. Spectroscopic constants of the ground vibrational states of  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{N}$  and  $\text{H}_3\text{CNDCH}_2\text{C}\equiv\text{N}$ .<sup>a</sup>

Species		$\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{N}$	$\text{H}_3\text{CNDCH}_2\text{C}\equiv\text{N}$
N.o.t. <sup>b</sup>		118	22
R.m.s. <sup>c</sup> (MHz)		0.0780	0.0730
$A_0$	(MHz)	10873.5490(68)	10432.016(20)
$B_0$	(MHz)	3371.7143(20)	3305.4986(33)
$C_0$	(MHz)	2810.1810(26)	2788.9225(28)
$\Delta_J$	(kHz)	3.3556(78)	3.35 <sup>e</sup>
$\Delta_{JK}$	(kHz)	-21.690(85)	-18.54(25)
$\Delta_K$	(kHz)	74.948(47)	74.94 <sup>e</sup>
$\delta_J$	(kHz)	1.0410(60)	0.915(11)
$\delta_K$	(kHz)	7.70(22)	8.69(51)
$\Phi_J$	(Hz)	-0.12376(96)	- <sup>f</sup>
$\Phi_{JK}$	(Hz)	-2.40 <sup>e</sup>	- <sup>f</sup>
$\Phi_{KJ}$	(Hz)	-2.031(65)	- <sup>f</sup>
$\Phi_K$	(Hz) <sup>d</sup>	1.18(12)	- <sup>f</sup>

<sup>a</sup> Uncertainties represent one standard deviation. <sup>b</sup> Number of transitions. <sup>c</sup> Root-mean-square deviation. <sup>d</sup> Further sextic constants preset at zero. <sup>e</sup> Preset at this value. <sup>f</sup> Preset at zero.

satellite spectrum presumably belonging to vibrationally excited states of I. Two such excited states were assigned as shown in Table 3.

The strongest of these two states has about 40 % of the ground state intensity at about -15 °C. For this vibrationally excited state, about 35 transitions were assigned, of which 27 were used to derive the spectroscopic constants shown in Table 3. Maximum value of  $J$  was 16 for the  $16_{3,13} \leftarrow 16_{2,14}$  transition. No  $b$ -type  $P$ - and  $R$ -branch lines were assigned for this vibrationally excited state.

Relative intensity measurements performed as described in Ref. 9, yielded  $151(30) \text{ cm}^{-1}$  for this vibration, and this is in excellent agreement with  $152(20) \text{ cm}^{-1}$  found for the similar vibration of  $\text{CH}_3\text{NHCH}_2\text{C}\equiv\text{CH}$ ,<sup>7</sup> which was assumed to be the first excited state of the heavy-atom ( $\text{H}_3\text{CNH}-\text{CH}_2\text{CCH}$ ) torsional vibration.

In addition to this, the changes of the rotational constants upon excitation are:  $\Delta A=67.96 \text{ MHz}$ ,  $\Delta B=-6.53 \text{ MHz}$ , and  $\Delta C=-4.76 \text{ MHz}$ . The corresponding changes computed by increasing the C-N-C-C dihedral angle of the plausible structure by 1° are  $\Delta A=48.3 \text{ MHz}$ ,  $\Delta B=-16.0 \text{ MHz}$ , and  $\Delta C=-5.1 \text{ MHz}$ . The agreement is good enough to indicate that this is indeed the first excited heavy-atom torsional vibration.

The second excited state of this vibration was also assigned. 17 transitions with  $J \leq 15$  were used to calculate the spectroscopic constants shown in Table 3. The changes of the rotational constants upon excitation from the first excited state to the second excited state of this vibration are:  $\Delta A=69.77 \text{ MHz}$ ,  $\Delta B=-6.97 \text{ MHz}$ , and  $\Delta C=-4.68 \text{ MHz}$ . The fact that these changes are so similar to the changes upon excitation from the ground state to the first excited state, indicates that this is a harmonic mode.

The third excited state of this vibration could not be found, presumably because of too low intensity.

The other excited state that was assigned had about 25 % of the ground state intensity, and relative intensity measurements yielded  $229(40) \text{ cm}^{-1}$  for this vibration. This is close to the value  $222(30) \text{ cm}^{-1}$  found for a similar vibration of  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{CH}$ .<sup>7</sup> Two of the lines assigned to this vibration in  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{CH}$  were split, and this could only be explained

Table 3. Spectroscopic constants of vibrationally excited states of  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{N}$  and  $\text{H}_3\text{CNDCH}_2\text{C}\equiv\text{N}$ .<sup>a</sup>

Vibrational state N.o.t. <sup>b</sup>	First ex. $-\text{H}_2\text{C}-\text{NH}-\text{tors.}$		Second ex. $-\text{H}_2\text{C}-\text{NH}-\text{tors.}$		First ex. methyl tors.		First ex. $-\text{H}_2\text{C}-\text{ND}-\text{tors.}$	
	27	0.0750	17	0.0722	15	0.0608	12	0.0867
R.m.s. (MHz) <sup>c</sup>								
$A_v$ (MHz)	10941.508(16)		11011.273(81)		10908.007(19)		10489.70(16)	
$B_v$ (MHz)	3365.1842(65)		3358.2111(57)		3371.8562(32)		3299.089(16)	
$C_v$ (MHz)	2805.4222(66)		2800.7378(81)		2809.7417(30)		2784.497(14)	
$\Delta_J$ (kHz)	3.35 <sup>e</sup>		3.35 <sup>e</sup>		3.35 <sup>e</sup>		3.35 <sup>e</sup>	
$\Delta_{JK}$ (kHz)	-21.45(25)		-21.14(72)		-21.23(11)		-19.5(12)	
$\Delta_K$ (kHz)	74.94 <sup>e</sup>		74.94 <sup>e</sup>		74.94 <sup>e</sup>		74.94 <sup>e</sup>	
$\delta_J$ (kHz)	1.033(12)		1.016(14)		1.0625(74)		0.884(37)	
$\delta_K$ (kHz)	8.84(58)		8.41(99)		8.62(24)		10.9(21)	
$\Phi_J$ (kHz) <sup>d</sup>	35.6(44)							

<sup>a</sup> Uncertainties represent one standard deviation. <sup>b</sup> Number of transitions. <sup>c</sup> Root-mean-square deviation. <sup>d</sup> Further sextic constants preset at zero. <sup>e</sup> Preset at this value. <sup>f</sup> Preset at zero.

Table 4. Plausible structural parameters<sup>a</sup> (bond lengths in *pm*; angles in *degrees*) of H<sub>3</sub>CNHCH<sub>2</sub>C≡N.

Assumed structural parameters					
C≡N	115.9		∠C-C-C≡N	180.0	
N-CH <sub>3</sub>	146.2		∠NCH	109.47	
N-CH <sub>2</sub>	147.6		∠CNH	108.6	
C-C	146.1		∠HCH	109.47	
C-H	109.4		∠CCH	107.2	
N-H	101.4				
Fitted structural parameters					
∠CCN	114.0(20)				
∠CNC	113.0(20)				
∠HNCC <sup>b</sup>	63(4)	from <i>syn</i>			
Rotational constants (MHz)					
Parent species			Deuterated species		
Obs.	Calc.	Diff.(%)	Obs.	Calc.	Diff.(%)
10873.55	10914.19	0.37	10432.02	10483.85	0.50
3371.71	3390.76	0.56	3305.50	3322.47	0.51
2810.18	2823.09	0.46	2788.92	2800.37	0.41
Kraitchman's coordinates <sup>c</sup> for the methylamino group hydrogen atom					
			a	b	c
From rotational constants:			109.297(7)	40.096(19)	135.672(6)
From plausible structure:			113.97	37.32	134.02
Hydrogen bond parameters					
H...C≡N	270	∠N-H...C	66		
H...N≡C	357	∠N-H...N	77		
		∠N-H, C≡N <sup>d</sup>	75		
Sum of van der Waals radii <sup>e</sup>					
H...C	290 <sup>f</sup>	H...N	270		

<sup>a</sup> See text. <sup>b</sup> H-N-C-C dihedral angle. <sup>c</sup> Ref. 10. <sup>d</sup> Angle between N-H and C≡N bonds. <sup>e</sup> Ref. 17. <sup>f</sup> van der Waals radius of carbon atom taken to be 170 *pm* as for aromatic carbon.

by methyl-group tunnelling. It is therefore assumed that this excited state is the methyl group torsional vibration for H<sub>3</sub>CNHCH<sub>2</sub>C≡N also. No splittings were seen for these transitions.

15 transitions with  $J \leq 17$  were used to derive the spectroscopic constants shown in Table 3. The fact that the changes of the rotational constants upon excitation are so small indicates that little reduced mass is involved in this vibration, and this is consistent with the assumption that this is the methyl group torsional vibration.

Table 5. Stark coefficients and dipole moment of  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{N}$ .<sup>a</sup>

Transition		$\Delta\nu E^2$ (MHz V <sup>-2</sup> cm <sup>2</sup> ) $\times 10^6$	
		Obs.	Calc.
4 <sub>1,4</sub> ← 3 <sub>1,3</sub>	M =2	9.49(9)	9.39
	M =1	-1.99(4)	-1.83
	M=0	-5.25(8)	-5.57
4 <sub>1,3</sub> ← 3 <sub>1,2</sub>	M =3	-23.6(2)	-23.3
	M =2	-8.29(8)	-8.14
	M=0	4.12(4)	4.02
3 <sub>1,2</sub> ← 2 <sub>1,1</sub>	M =2	-93.7(14)	-90.5
	M =1	-25.2(3)	-25.3
	M=0	-3.51(4)	-3.57
3 <sub>0,3</sub> ← 2 <sub>0,2</sub>	M =2	22.1(3)	23.1
5 <sub>0,5</sub> ← 4 <sub>0,4</sub>	M =2	1.08(2)	1.16

## Dipole moment

$\mu_a=2.490(16)$  D<sup>b</sup>,  $\mu_b=1.296(10)$  D,  $\mu_c\sim 0.0$  D<sup>c</sup>,  $\mu_{\text{tot.}}=2.807(17)$  D.

<sup>a</sup> Uncertainties represent one standard deviation. <sup>b</sup> 1 D=3.33564 $\times 10^{-30}$  C m. <sup>c</sup> Preset at zero in order to avoid an imaginary value.

*Deuterated species.* The ground state of  $\text{H}_3\text{CNDCH}_2\text{C}\equiv\text{N}$  was also assigned, and 22 transitions with  $J\leq 17$  were used to calculate the spectroscopic constants shown in Table 2. From these rotational constants and the rotational constants of the ground state of  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{N}$  the substitution coordinates of the hydrogen atom bonded to the nitrogen atom could be determined<sup>10</sup> (Table 4). These coordinates clearly show that the assigned conformation is conformation I and not conformation III which would have very different substitution coordinates for this hydrogen atom, even though the rotational constants would be similar to those of conformation I.

12 transitions with  $J\leq 17$  and belonging to the first excited state of the heavy-atom ( $\text{H}_3\text{CND}-\text{CH}_2\text{CN}$ ) vibration were also assigned. The spectroscopic constants of this state are displayed in Table 3.

*Dipole moment.* The dipole moment was determined from the Stark coefficients shown in Table 5 using standard procedure.<sup>11</sup> Initially, all three dipole moment components were fitted. However,  $\mu_c$  was found to be imaginary. In the final fit  $\mu_c$  was preset at zero. In this manner, the dipole moment components were found as  $\mu_a=2.490(16)$  D and  $\mu_b=1.296(10)$  D (Table 5). These values are reasonably close to those found by the bond-moment method and reported above. The total dipole moment is 2.807(17) D. This value is close to 2.640(7) D found for  $\text{H}_2\text{NCH}_2\text{C}\equiv\text{N}$ .<sup>4</sup>

*Searches for further conformations.* At this point, most of the strong lines and the lines with intermediate intensities had been assigned. Searches were then made among the unassigned transitions for the hypothetical conformations II and III.

The rotational constants and bond moment components of the hypothetical conformation II were predicted to be:  $A=28.1$  GHz,  $B=2.3$  GHz,  $C=2.2$  GHz,  $\mu_a=3.7$  D,  $\mu_b=1.1$  D, and  $\mu_c=1.2$  D. Strong, easily identifiable pile-ups of low- $J$   $a$ -type  $R$ -branch transitions should therefore have been seen at low voltages. Since these pile-ups were not found, it was concluded that conformation I is at least 6 kJ/mol more stable than conformation II.

The predicted values of the rotational constants and bond moment components of the hypothetical conformation III were:  $A=11.3$  GHz,  $B=3.3$  GHz,  $C=2.8$  GHz,  $\mu_a=3.8$  D,  $\mu_b=2.7$  D, and  $\mu_c=1.2$  D. This conformer should therefore have a strong *a*-type spectrum. However, no *R*-branch *a*-type lines could be found, even though they should be easy to detect because of their strength and typical Stark patterns. It was therefore concluded that conformation I is at least 4 kJ/mol more stable than III.

The unassigned lines could not be attributed to impurities either, and the remaining possibility is that they belong to unassigned vibrationally excited states of the title compound.

*Structure.* Since a complete isotopic substitution study was not carried out for (*N*-methylamino)-ethanenitrile, most of the structural parameters had to be taken from related compounds, namely  $\text{H}_2\text{NCH}_2\text{C}\equiv\text{N}^4$  and  $\text{H}_3\text{CNHCH}_3$ .<sup>12</sup> However, three important structural parameters, *viz.* the NC-C-NHCH<sub>3</sub> angle, the C-N-C angle and the C-C-N-H dihedral angle, could be determined by fitting them to the rotational constants and the substitution coordinates of the methylamino group hydrogen atom. In this process, the C-C-N angle and the C-N-C angle were fitted in steps of 0.5° and the dihedral angle C-C-N-H in steps of 1°. The results were:  $\angle \text{CNC}=113.0(20)^\circ$ ,  $\angle \text{CCN}=114.0(20)^\circ$ , and  $\angle \text{CCNH}=63(4)^\circ$  from *syn* ( $\angle \text{CCNC}=57(4)^\circ$  from *syn*) (Table 4). The estimated uncertainties represent approximately three standard deviations for each parameter.

The value of  $\angle \text{CNC}$  found for  $\text{H}_3\text{CNHCH}_3$ <sup>12</sup> is 112.2° and the value of  $\angle \text{CCN}$  found for  $\text{H}_2\text{NCH}_2\text{C}\equiv\text{N}^4$  is 114.5°, and these are very similar to the values found for the corresponding angles of the title compound. However, for  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{CH}^7$  it was found that the CCNH dihedral angle was 57(4)° which is 6° less than the value found in this work. The reason for this difference is difficult to find, but it could be that there is an attraction between the methyl group and the  $\pi$ -electrons of the triple bond, which is of greater importance in the present case than in the case of  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{CH}$ .  $\text{H}_3\text{CCH}_2\text{CH}_2\text{C}\equiv\text{N}$  is isoelectronic with  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{N}$ , and for the former compound both the *gauche* and *anti* forms have been observed.<sup>13,14</sup> However, no accurate energy difference has been determined. In fact, an *IR* work<sup>14</sup> yielded *gauche* more stable than *anti*, while the opposite was found by *ab initio* calculations.<sup>15</sup> The importance of the attraction between the methyl group and the  $\pi$ -electrons is therefore difficult to assess.

The reason for the difference between the CCNH dihedral angles of  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{CH}$  (57(4)°) and  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{N}$  (63(4)°) could also be that the hydrogen-bonding interaction between the methylamino group hydrogen atom and the  $\pi$ -electrons is weaker with a cyano group as hydrogen acceptor than it is with an acetylene group as acceptor. This is found in the cases of  $\text{HOCH}_2\text{CH}_2\text{C}\equiv\text{N}$  and  $\text{HOCH}_2\text{CH}_2\text{C}\equiv\text{CH}$ .<sup>16</sup>

## DISCUSSION

For the title compound, only conformation I was assigned, and this rotamer has the possibility of forming an intramolecular hydrogen bond between the methylamino group hydrogen atom and the  $\pi$ -electrons of the cyano group. This hydrogen bond is, however, rather weak since the  $\text{H}\cdots\text{C}\equiv\text{N}$  distance is only 20 pm shorter than the sum of the van der Waals radii of hydrogen and carbon,<sup>17</sup> and the covalent contribution to this bond is presumably insignificant since the N-H $\cdots$ C angle is 66° which is far from linearity.

It was estimated that conformation I is at least 6 kJ/mol more stable than conformation II. This energy difference cannot be explained by hydrogen-bonding, because both I and II



should be able to form hydrogen bonds of roughly the same strength. Another explanation for this preference is that there is an attraction between the methyl group and the  $\pi$ -electrons of the cyano group. This interaction is not present in conformation II. However, since both the *gauche* and *anti* forms are observed in the microwave spectrum of the isoelectronic compound  $\text{H}_3\text{CCH}_2\text{CH}_2\text{C}\equiv\text{N}$ ,<sup>13</sup> even though it has not been established which of these two forms is the most stable one,<sup>14,15</sup> this interaction is probably rather weak.

There is one more interaction that could be important for these kind of molecules, namely a repulsion between the "lone-pair" electrons of the methylamino group nitrogen atom and the  $\pi$ -electrons of the cyano group. This repulsion would be minimized in conformation I, while it would be about equally important in conformations II and III.

The conformational behaviour of  $\text{H}_3\text{CNHCH}_2\text{C}\equiv\text{N}$  can thus be explained if the repulsion between the "lone-pair" electrons and the  $\pi$ -electrons is the most important interaction in this molecule.

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