Microwave Spectrum, Conformational Composition and Intramolecular Hydrogen Bonding of 3-(Methylamino)propanenitrile

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The microwave spectra of the compound 3-(methylamino)propanenitrile, $H_3C-NH-CH_2-CH_2-C\equiv N$, and one partially deuterated species, $H_3C-ND-CH_2-CH_2-C\equiv N$, have been investigated in the 26.5–38.0 GHz spectral range. Two rotamers were assigned. One of these rotamers is stabilized with an intramolecular hydrogen bond formed between the methylamino-group hydrogen atom and the cyano group, while the second conformer has no hydrogen bond and the heavy atoms are in an *all-anti* arrangement. The hydrogen-bonded rotamer is 5(2) kJ mol^{-1} more stable than the non-hydrogen-bonded conformer.

It is now well established by microwave (MW) spectroscopy that ethylamine derivatives $H_2N-CH_2-CH_2-X$, where X is some proton-accepting atom or group such as F,[1] NH_2,[2] CN,[3] $C\equiv CH$,[4] OCH_3[5] or $C=CH_2$,[6] prefer *two* heavy-atom N–C–C–X *gauche* conformations as their most stable forms in the gaseous state. Each of these *two gauche* conformers is stabilized with an intramolecular hydrogen (H) bond formed between *one* of the amino -group hydrogen atoms and X. There is a very small energy difference between the two different N–H$\cdots$X hydrogen-bonded heavy-atom *gauche* conformers.[1–6]

Only one methylamino derivative of the type $H_3C-NH-CH_2-CH_2-X$ has been studied by MW spectroscopy. In the case of $H_3C-NH-CH_2-CH_2-NH_2$ Caminati *et al.*[7] found that *two* N–C–C–N *gauche* conformers coexist in the free state. In one of these, the methylamino group was the proton acceptor and the amino group the proton donor, while the situation was reversed in the other case.[7] In both these conformers, the methyl group was *anti* to the C–C bond.[7]

The motivation for carrying out this research has been to investigate the ability of methylamino groups to participate in internal H bonding. Apart from the work on $H_3C-NH-CH_2-CH_2-NH_2$,[7] methylamino groups have been shown to participate in this kind of bonding in gaseous $H_3C-NH-CH_2-CH=CH_2$,[8] $H_3C-NH-CH_2-C\equiv N$[9] and $H_3C-NH-CH_2-C\equiv CH$.[10] There are nine all-staggered conformational possibilities for 3-(methylamino)propanenitrile, as shown in Fig. 1. An intramolecular H bond can stabilize conformation I or V, while this interaction is not possible in the other seven cases. Morio *et al.*[11] concluded from an IR study that a mixture of an H-bonded and a

non-H-bonded form is present in dilute carbon tetrachloride solutions, but they could not specifically tell which of the seven conformations of Fig. 1 that they identified in solution. It is shown in this work that the H-bonded conformer I is the most stable conformation of the molecule with VII 5(2) kJ mol^{-1} less stable than I. There is no evidence of large fractions of any other rotamers in the free state.

Experimental

The samples used in this work were purchased from Fluka A. G., Buchs, Switzerland, and purified by gas-phase chromatography before use. The MW spectrum was studied in the 26.5–38.0 GHz spectral region at about $-10\,°C$. Lower temperatures could not be employed owing to insufficient vapour pressure of the compound. The pressure was about 1 Pa during the recording of the spectra. The spectrometer is an improved version of the one described briefly in Ref. 12 employing klystrons as radiation sources. The radiofrequency–microwave-frequency double-resonance technique (RFMWDR) was used as described in Ref. 13, employing the equipment mentioned in Ref. 6. The partially deuterated species was produced by conditioning the cell with D_2O and then introducing the normal species.

Results

Microwave spectrum and assignment of the ground vibrational state of the conformer I. Survey spectra revealed a weak and very dense microwave spectrum for $H_3C-NH-CH_2-CH_2-C\equiv N$. The strongest lines of the spectrum have peak absorption coefficients of roughly 0.7×10^{-7} cm^{-1} at $-10\,°C$. It turned out later that these transitions are

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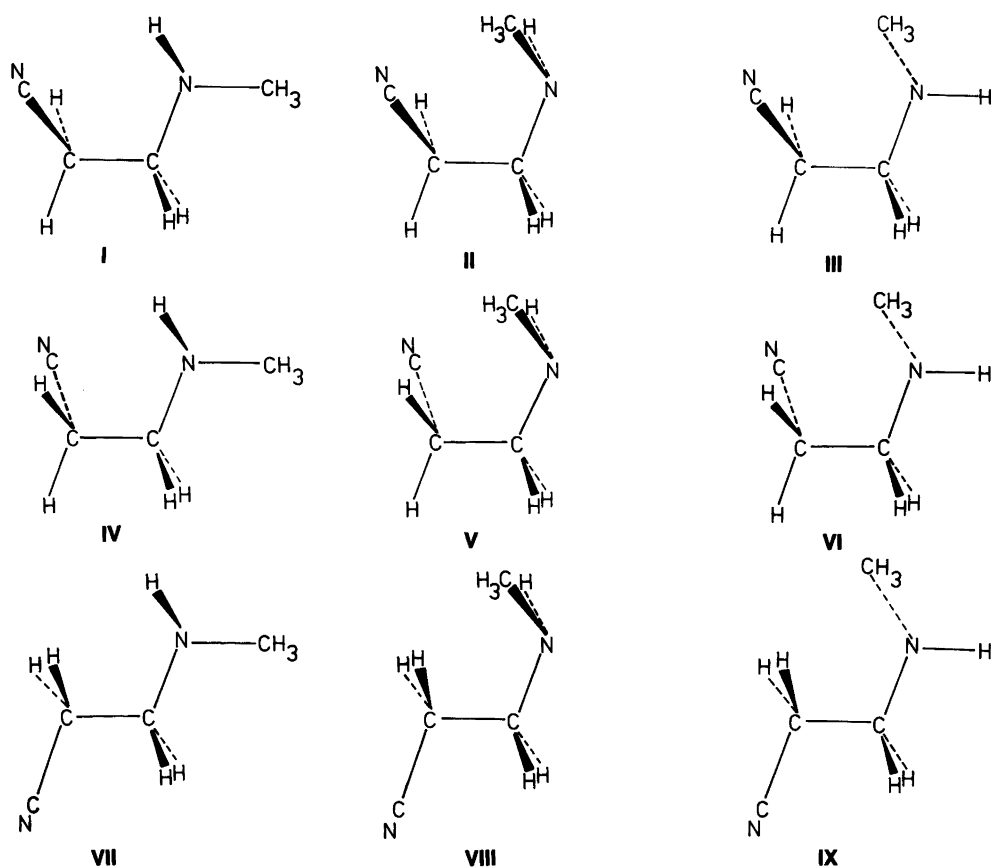* To whom correspondence should be addressed.

Fig. 1. The nine possible all-staggered conformations of 3-(methylamino)propanenitrile. Conformer I (which is stabilized by an internal hydrogen bond) as well as VII have been assigned. I is more stable than VII by 5(2) kJ mol⁻¹.

the high-J, b-type Q-branch or intermediate-J, a-type R-branch transitions of conformer I. The transitions were all rather broad, and also distorted from a Lorentzian shape in some cases, owing to a high dipole moment and the fact that the two nitrogen-14 nucleii produce quadrupole cou-

pling between the overall and nucleii rotations. No completely resolved quadrupole hyperfine structure was identified.

The rotational constants of the nine possible all-staggered conformations shown in Fig. 1 were predicted using the structural parameters shown in Table 7 below. The predicted rotational constants are collected in Table 1. The principal axes dipole moment components were also predicted (Table 1) employing the bond moments suggested by Exner.[14] It is seen that sizable dipole moments are predicted for all nine conformations; in particular, μ_a is predicted to be large for all these nine prolate asymmetrical tops. The high-K_{-1} transitions should therefore be easy to modulate in all nine cases using the RFMWDR technique.[13] This feature was exploited to get the first assignments. A RFMWDR search revealed two series of characteristic pile-ups, one for conformer I, and the other for conformer VII; no further pile-ups belonging to any other rotameric form of 3-(methylamino)propanenitrile were seen.

The low-K_{-1}, a- and b-type R-branch transitions and the intermediate- and high-J, b-type Q-branch transitions of conformer I were searched for next and readily found. The high-J, b-type P- and R-branch transitions were then searched for, but not found presumably because of the absolute weakness of this spectrum. No c-type transitions were identified, presumably because of a small component

Table 1. Rotational constants[a] and principal axes dipole moment components[b] predicted for the all-staggered conformations shown in Fig. 1 of 3-(methylamino)propanenitrile.

Conformation[c]	Rotational constants/GHZ			Dipole moment component/10⁻³⁰ C m		
	A	B	C	μ_a	μ_b	μ_c
I[d]	7.86	1.92	1.65	6.5	8.1	0.8
II	5.51	3.40	2.31	7.6	9.8	4.7
III	6.26	2.32	2.08	12.3	9.6	4.2
IV	7.61	1.94	1.67	9.1	12.9	3.7
V	6.26	2.37	2.11	6.2	6.7	5.4
VI	5.57	3.37	2.27	10.5	8.1	1.1
VII	16.24	1.39	1.32	11.5	5.9	3.2
VIII	11.94	1.62	1.54	11.2	2.9	6.2
IX	11.99	1.62	1.52	13.4	0.3	0.1

[a]Calculated using the plausible structural parameters shown in Table 7 below. [b]Using the bond moments of Ref. 14. [c]See Fig. 1 for definition. [d]The C–C–C–N dihedral angle has been fitted for this conformer as described in the text.

of the dipole moment along this axis. This is in accord with the predictions shown in Table 1. A total of 84 transitions with a maximum J of 32 were ultimately assigned for the ground vibrational state of this rotamer. A portion of this spectrum* is seen in Table 2, and the spectroscopic constants (A-reduction I^r-representation[15]) are found in Table 3.

Unfortunately, the dipole moment could not be determined because the lowest-J transitions generally used for this purpose were too weak to allow quantitative Stark effect measurements to be made.

Table 2. Selected transitions of the ground-state MW spectrum of conformer I of 3-(methylamino)propanenitrile.

Transition	Obs. freq.[a]/MHz	Obs.−calc. freq./MHz	Centrifugal dist./MHz
a-Type			
$8_{0,8} \leftarrow 7_{0,7}$	27752.17	−0.02	−1.46
$8_{1,7} \leftarrow 7_{1,6}$	29371.75	−0.01	−2.52
$8_{1,8} \leftarrow 7_{1,7}$	27194.22	−0.02	−1.12
$8_{2,7} \leftarrow 7_{2,6}$	28359.37	0.02	−1.28
$8_{5,3} \leftarrow 7_{5,2}$	28526.82	0.08	2.85
$8_{5,4} \leftarrow 7_{5,3}$	28526.82	0.10	2.85
$9_{0,9} \leftarrow 8_{0,8}$	31054.18	0.01	−1.90
$9_{1,9} \leftarrow 8_{1,8}$	30548.60	−0.13	−1.62
$9_{3,6} \leftarrow 8_{3,5}$	32243.02	0.15	−1.47
$9_{3,7} \leftarrow 8_{3,6}$	32150.75	−0.16	−1.27
$9_{6,3} \leftarrow 8_{6,2}$	32089.32	−0.06	5.09
$9_{6,4} \leftarrow 8_{6,3}$	32089.32	−0.06	5.09
$10_{0,10} \leftarrow 9_{0,9}$	34331.58	0.02	−2.42
$10_{1,10} \leftarrow 9_{1,9}$	33891.86	−0.02	−2.22
$10_{4,6} \leftarrow 9_{4,5}$	35721.64	−0.02	−0.52
$10_{6,4} \leftarrow 9_{6,4}$	35662.56	−0.11	4.78
$10_{6,5} \leftarrow 9_{6,4}$	35662.56	−0.11	4.78
$10_{8,2} \leftarrow 9_{8,1}$	35649.62	−0.05	12.06
$10_{8,3} \leftarrow 9_{8,2}$	35649.62	−0.05	12.06
$11_{0,1}^{1} \leftarrow 10_{0,10}$	37592.15	0.00	−3.04
b-Type			
$8_{1,8} \leftarrow 7_{0,7}$	30289.98	−0.02	0.13
$9_{1,8} \leftarrow 8_{0,8}$	33086.45	−0.09	−0.03
$10_{0,10} \leftarrow 9_{1,9}$	32299.88	−0.01	−4.29
$11_{0,11} \leftarrow 10_{1,10}$	36000.14	−0.02	−5.11
$10_{3,7} \leftarrow 10_{2,8}$	27869.85	−0.02	6.14
$12_{2,11} \leftarrow 12_{1,12}$	29560.87	0.01	−3.68
$14_{3,12} \leftarrow 14_{2,13}$	43341.90	−0.15	1.04
$17_{1,16} \leftarrow 17_{0,17}$	36684.10	−0.03	−34.53
$19_{4,15} \leftarrow 19_{3,16}$	35534.63	0.10	51.28
$22_{3,19} \leftarrow 22_{2,20}$	27016.54	−0.15	−44.15
$24_{4,20} \leftarrow 24_{3,21}$	30854.00	0.00	51.10
$26_{3,23} \leftarrow 26_{2,24}$	36707.22	−0.10	−153.44
$28_{4,24} \leftarrow 28_{3,25}$	32257.60	−0.02	−49.56
$31_{4,27} \leftarrow 31_{3,28}$	37687.72	−0.08	−202.44
$33_{5,28} \leftarrow 33_{4,29}$	37807.42	−0.02	64.14

[a] ± 0.12 MHz.

*The complete spectra are available from the authors upon request, or from the Molecular Spectra Data Center, Bldg. 221, Room B 268, National Bureau of Standards, Gaithersburg, MD 20899, U.S.A., where they have been deposited.

Table 3. Spectroscopic constants[a,b] for conformer I of 3-(methylamino)propanenitrile in the ground vibrational state.

Constant	Parent species[c]	Deuterated species[d]
A_v/MHz	7868.691(12)	7698.587(17)
B_v/MHz	1919.1777(40)	1918.082(10)
C_v/MHz	1640.4570(39)	1633.2311(99)
Δ_J/kHz	1.122(21)	1.074(51)
Δ_{JK}/kHz	−13.039(31)	−12.783(60)
Δ_K/kHz	56.97(94)	54.3(14)
δ_J/kHz	0.34404(63)	0.3430(11)
δ_K/kHz	2.430(44)	2.664(77)

[a] Uncertainties represent one standard deviation. [b] A-reduction, I^r-representation (Ref. 15). [c] 84 Transitions, r.m.s. deviation 0.088 MHz. [d] 50 Transitions, r.m.s. deviation 0.097 MHz.

Vibrationally excited states. The gound-state transitions were accompanied by a rich satellite spectrum presumably belonging to vibrationally excited states of I. A complete assignment could only be made for the strongest of these satellite spectra, owing to the absolute weakness of the spectrum. The spectroscopic constants of this vibrationally excited state, which is presumed to be the first excited state of the heavy-atom torsional vibration, are shown in Table 4. Relative intensity measurements made largely as described in Ref. 16 yielded 127(25) cm^{-1} for this vibration.

Assignment of conformer VII. As noted above, the other pile-up series seen together with those belonging to conformer I are assigned to conformer VII. Owing to the weakness of these transitions, it was not possible to make assignments for the individual K_{-1} transitions which are necessary in order to determine all three rotational constants. Tables 5 and 6 therefore contain only the most prominent pile-ups which are composed of the high-K_{-1} transitions. It is seen in Table 5 that $B + C \approx 2.69933$ GHz, which is close to 2.71 GHz predicted for this rotamer (Table 1).

Table 4. Spectroscopic constants[a,b] of conformer I of 3-(methylamino)propanenitrile in the first vibrationally excited state heavy-atom torsional vibration.

Constant	I[c]
A_v/MHz	7917.913(46)
B_v/MHz	1917.2831(66)
C_v/MHz	1639.0978(66)
Δ_J/kHz	1.008(39)
Δ_{JK}/kHz	−13.297(74)
Δ_K/kHz	57.4(26)
δ_J/kHz	0.3365(13)
δ_K/kHz	3.79(10)

[a,b] Comments as for Table 3. [c] 50 Transitions, r.m.s. deviation 0.115 MHz.

Table 5. Microwave spectra and spectroscopic constants of conformer **VII** of 3-(methylamino)propanenitrile in the ground vibrational state.

Transition[a]	Parent species		Deuterated species	
	Frequency/MHz	$\approx (B+C)$/MHz	Frequency/MHz	$\approx (B+C)$/MHz
$10 \leftarrow 9$	26992.49	2699.25	26708.24	2670.82
$11 \leftarrow 10$	29693.20	2699.38	29378.98	2670.82
$12 \leftarrow 11$	32391.27	2699.27	$-$[b]	
$13 \leftarrow 12$	35091.15	2699.32	34721.60	2670.89
$14 \leftarrow 13$	37791.97	2699.43	37393.25	2670.95
Average:		2699.33		2670.87

[a] High-K_{-1} pile-ups. [b] Not measured.

Table 6. Microwave spectra and spectroscopic constants of conformer **VII** of 3-(methylamino)propanenitrile in vibrationally excited states.

Transition[a]	1st ex. torsion		2nd ex. torsion		1st ex. bending	
	Freq./MHz	$\approx (B+C)$/MHz	Freq./MHz	$\approx (B+C)$/MHz	Freq./MHz	$\approx (B+C)$/MHz
$10 \leftarrow 9$	27023.73	2702.37	$-$[b]		26986.93	2698.69
$11 \leftarrow 10$	29726.09	2702.37	29759.55	2705.41	29685.77	2698.71
$12 \leftarrow 11$	32429.43	2702.45	32465.24	2705.44	32385.04	2698.75
$13 \leftarrow 12$	35131.41	2702.42	35171.51	2705.50	35084.40	2698.80
$14 \leftarrow 13$	37834.80	2702.49	37877.98	2705.57	37783.93	2698.85
Average:		2702.42		2705.48		2698.76

[a,b] Comments as for Table 5.

The pile-up regions are actually quite crowded with lines. The three most prominent pile-ups besides the ground-state pile-ups are assigned as vibrationally excited states of conformer **VII**, as shown in Table 6. Two of these excited states are presumed to belong to the lowest torsional vibration, and one to the lowest bending mode, or perhaps to the second lowest torsional vibration.

Energy difference between conformers **I** *and* **VII**. In order to determine the internal energy difference between conformers accurately, the dipole-moment components as well as assignment of individual transitions must be known. Such optimum conditions were not met in the present case. The dipole moments have not been determined, and individual transitions were not assigned in the case of rotamer **VII**. The dipole-moment components shown in Table 1 were therefore assumed for both conformers. Rough estimates of the intensities of the unassigned low-K_{-1} a-type transitions of **VII** were carried out. In this manner, conformer **I** was found to be more stable than **VII** with an energy difference, $E^{\circ}_{VII} - E^{\circ}_{I}$, determined to be 5(2) kJ mol^{-1}. The error limit of $\pm$ 2 kJ mol^{-1} has been estimated from likely uncertainties of the dipole moment and intensities of the transitions involved, and is considered to be conservative.

Searches for further conformations. Although a large number of very weak transitions remain unassigned in this spectrum, it is quite clear that many of them must belong to vibrationally excited states of conformer **I** or to the ground and vibrationally excited states of **VII**. There are no obvious spectral features that can be ascribed to any other of the nine rotamers shown in Fig. 1. Any of the remaining conformations depicted in this figure should possess a sizable dipole moment as predicted in Table 1. It is thus concluded that any further conformer of 3-(methylamino)propanenitrile is even less stable than **VII**.

Deuterated species. As shown in Table 1, the hypothetical conformation **IV** is predicted to have rotational constants not widely different from those of the identified rotamer **I** (Table 3). The dipole moment components of **I** and **IV** are not predicted to be very different, as seen in Table 1. The partially deuterated species CH_3–ND–CH_2–CH_2–C$\equiv$N was studied to show beyond doubt that **I** has indeed correctly assigned and is not confused with the hypothetical conformation **IV** which has no internal hydrogen bond. The predicted shifts upon deuteration of the two conformations **I** and **IV** are, however, very different. The rotational constants obtained from the spectrum of the deuterated species (Table 3) are close to those predicted for **I**. There is thus no doubt that **I** has indeed been identified.

Table 7. Plausible structural parameters[a] (bond lengths in pm and angles in °) of 3-(methylamino)propanenitrile.

Assumed structural parameters kept fixed[b]

Distances		Angles	
$C\equiv N$	115.7	$C-C\equiv N$	180.0
$N-CH_3$	147.5	$C-C-N$	108.0
$N-CH_2$	147.5	$C-N-C$	110.0
$C-CN$	146.3	$C-C-C$	110.5
$C-C$	154.0	$C-C-H$	109.47
$N-H$	101.7	$C-N-H$	109.47
$C-H$	109.3	$N-C-H$	109.47

Fitted dihedral angle for conformer I

$C-C-C-N$	65(3) from *syn*

[a]Taken largely from Callomon, J. H., Hirota, E., Kuchitsu, K., Lafferty, W. J., Maki, A. G. and Pote, C. S. *Structure Data of Free Polyatomic Molecules,* Hellwege, K.-H. and Hellwege, A. M. (Ed.), Springer Verlag, Berlin 1976. [b]Used to calculate the rotational constants in Tables 1 and 8.

The shift of $B + C$ predicted for VII upon deuteration was also very closely reproduced (Table 5).

Structure. It is not possible to calculate a full molecular structure for **I** and **VII** from the spectroscopic constants shown in Tables 3 and 5. Assumptions have to be made in order to derive structural parameters of interest. In the case of conformer **I**, only the heavy-atom C–C–C–N dihedral angle was fitted in steps of 1°. This parameter was selected because the rotational constants are strongly dependent upon it, and because it is chemically interesting. The remaining structural parameters shown in Table 7 were taken from accurate studies of related compounds and kept constant in the fit. A value of 65° was derived for the C–C–C–N dihedral angle. The uncertainty limit corresponding approximately to three standard deviations is estimated to be 3°. It is seen in Table 8 that the rotational constants are rather well reproduced using the structural parameters of Table 7 and a dihedral angle of 65°. The substitution coordinates[17] of the methylamino-group hydrogen atom are rather close to those calculated from the plausible structure as far as the *b*- and *c*-axes coordinates are concerned (Table 8), whereas a somewhat larger discrepancy exists for the *a*-axis coordinate. It should be noted that substitution coordinates of hydrogen atoms are not always reliable in cases where large-amplitude vibrations are involved, such as in the present case.[18] Interestingly, the dihedral angle of 65(3)° is very similar to 63(3)° found

Table 8. Rotational constants, substitution coordinates for the methylamino group hydrogen atom and hydrogen bond parameters for 3-(methylamino)propanenitrile.

Rotational constants/MHz

	Parent species			Deuterated species		
	Obs.	Calc.	Diff./%	Obs.	Calc.	Diff./%
Conformer I						
A	7868.69	7861.99	0.09	7698.58	7701.95	0.04
B	1919.18	1922.14	0.15	1918.08	1918.51	0.02
C	1640.46	1650.56	0.62	1633.23	1641.96	0.53
Conformer VII						
B + C	2699.4	2708.7	0.34	2670.9	2680.0	0.34

Substitution coordinates of amino-group hydrogen/pm

	$|a|$	$|b|$	$|c|$
Calc. from rotational constants	21.70(29)	114.91(6)	32.70(20)
Calc. from structure	61.8	110.8	34.4

Hydrogen-bond parameters for conformer I[a]

$H\cdots CN$	255	$\angle N-H\cdots C$	101
$H\cdots N$	303	$\angle N-H\cdots N$	123
$N\cdots C$	292	$\angle N-H, C\equiv N$[b]	4

Sum of van der Waals radii[c]

$H\cdots C$[d]	290
$N\cdots C$[d]	320
$H\cdots N$	270

[a]Calculated from plausible structure; bond lengths in pm, angles in °. [b]Angle between N–H and C≡N bonds. [c]Taken from Ref. 19; in pm. [d]van der Waals radius of carbon assumed to be 170 pm as in aromatic molecules.[19]

for the corresponding conformation of 3-aminopropane-nitrile.[3] This was to be expected, since the hydrogen-bond environments are very similar in the two cases.

In the case of conformer **VII** where only the approximate sums of $B + C$ are available for the parent and the deuterated species, a refinement of the molecular structure was not considered worthwhile. However, it is noted (Table 8) that there is good agreement between the observed and calculated sums of $B + C$. This is indicative of a good correspondence between the real and the plausible structures.

Discussion

There are surely many reasons why 3-(methylamino)propa-nenitrile prefers conformers **I** and **VII** as its most stable forms, with **I** 5(2) kJ mol^{-1} more stable than **VII**. Hydrogen bonding is probably important, although the intramolecular hydrogen bond is rather weak, as can be inferred from the structural paremeters shown in Table 8. It is, for example, seen that the H$\cdots$CN non-bonded distance is about 35 pm shorter than the sum of the van der Waals radii of hydrogen and aromatic carbon.[19] The fact that the N–H and C$\equiv$N bonds are only about 4° from being parallel is very favourable for electrostatic interaction, since the bond moments of said two bonds are rather large.[14]

Steric repulsion is also likely to be a decisive factor for the conformational preferences of the title molecule. The methyl group comes very close to the cyano group in **II** and **VI**. Owing to this very close proximity, it is quite likely that the hypothetical conformations **II** and **VI** are very high in energy, if they at all represent stable forms of the molecule.

Another steric repulsion is presumed to exist within **III**, **V**, **VIII** and **IX**. In these conformations the methyl group comes rather close to methylene hydrogens of the –CH$_2$CN part of the molecule.

Repulsion between the cyano group and the methyl-amino group lone pair seems to be of importance in **III** and **IV**. In **III**, steric conditions are not the best, as noted above, while no steric repulsion is presumed to be present in **IV**. The absence of **IV** is thus thought to be the result of repulsion between the amino group lone pair and the electronegative cyano group.

Steric conditions are ideal in **VII**, and there appears to be no lone-pair–cyano-group destabilization in this conformer. This is probably the explanation why **VII** was found together with **I**.

It is seen in Fig. 1 that a simple 120° rotation around the central C–C bond transforms conformer **I** into **VII**. It has been argued[20] that the energy difference between rotamers which are interchangeable by just *one* such simple rotation may be taken as a measure for the hydrogen-bond strength. The hydrogen-bond strength should thus be roughly 5 kJ mol^{-1} in conformer **I** of the title compound.

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