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# Microwave Spectra of Pyrolytically Produced $CH_3NHCN$ and $CD_3NHCN$, *N*-Cyanomethylamine

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Dimethylcyanamide, $(CH_3)_2NCN$, pyrolyzes (900 °C, 0.01 Torr) to $CH_3NHCN$ as seen by its microwave spectrum (18.6–40.0 GHz). The spectral assignment was greatly facilitated by analysis of the microwave spectrum of $CD_3NHCN$ produced by pyrolysis of $(CD_3)_2NCN$. The resulting structural information on $CH_3NHCN$ is strictly limited by the use of assumed geometric parameters from other molecules ($CH_3NHCl$, $CH_3C{\equiv}CH$ and $CH_3N_3$). An estimated barrier to internal torsion is 260 $cm^{-1}$ with a corresponding torsional frequency of *ca.* 105 $cm^{-1}$. Approximate values of the $\mu_a$ and $\mu_b$ electric dipole moment components are 4.72 and 1.30 Debye, respectively.

During an extended microwave (mw) spectroscopic analysis of products of pyrolysis of $(CH_3)_2NCN$ (1000 °C, $p \sim 0.01$ Torr) where a main and easily identified product is $CH_2{=}NCN$ or $(HCN)_2$,[1] a weaker spectrum was subsequently observed (900 °C, $p \sim 0.01$ Torr; spec. H). In addition, $(CD_3)_2NCN$ was pyrolyzed giving rise to another "weak" spectrum, spec. D. Comparison of spec.'s H and D showed features familiar from mw spectra of molecules with an internally rotating $CH_3$ group and with NH inversion. A reasonable guess at the origin of spec.'s H and D is, therefore, $CH_3NHCN$ (I) and $CD_3NHCN$ (II) since primarily formed $CD_3NDCN$ (III) will exchange mobile nitrogen-bound D by H due to the presence of $H_2O$ in the mw cell. The mw spectrum of II is of greater interest to the present problem because the spectral effects of inversion are conserved whereas the effects of $CH_3$ internal rotation are largely annulled.

A more tangible verification of the formulae of I and II was obtained by calculation of rotational constants (*A*,*B*,*C*) of rigid models of I and II formed from parameters for related molecules (*vide infra*). These models predicted near-prolate symmetric top mw spectra close to their actual positions, without, of course, accounting for the observed spectral multiplicity due to $CH_3$ torsion ('a, e splitting') and NH inversion.

Molecules with both effects have been studied earlier [$(CH_3)_2NH$;[2] $CH_3NHCl$[3]]. Following the usual ± notation for inversion, 8 spectra are expected:

Spec. H: I(a,+); I(e,+); I(a,−); I(e,−).
Spec. D: II(a,+); II(e,+); II(a,−); II(e,−).

Corresponding frequency ($\nu$) differences are expected to obey

$$\nu I(a,+)-\nu I(a,-)\sim\nu II(a,+)-\nu II(a,-)$$
$$\nu I(a,+)-\nu I(e,+)\sim\nu I(a,-)-\nu I(e,-)$$
$$\nu I(a,+)-\nu I(e,+)>\nu II(a,+)-\nu II(e,+)$$
$$\nu I(a,-)-\nu I(e,-)>\nu II(a,-)-\nu II(e,-)$$

in the absence of vibrational interactions. The spectra I(a,+), I(a,−), II(a,+) and II(a,−) are expected to be reproducible by conventional rigid rotor models $M_H(+)$, $M_H(-)$, $M_D(+)$ and $M_D(-)$ whereas this is not possible for 'e' spectra. As a consequence of the subsequent analysis (Tables 1–4) we have restricted ourselves to deriving $M_H(+)$ and $M_D(+)$.

## EXPERIMENTAL

Our equipment for performing pyrolysis and analysis by mw technique has been described else-

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where.[4] $CH_3NHCN$, here prepared conveniently by pyrolysis, has been produced earlier at −10 °C from $CH_3NH_2$ and BrCN (m.p. −40 °C to −50 °C; polymerization at +50 °C).[5] Following Ref. 5 strictly in a single experiment we found that polymerization was dominant even at the final removal of the solvent (dry ether) at low temperature (~ −20 °C). A small yield was, however, collected and its mw spectrum recorded at room temperature (no pyrolysis). Very strong absorption, identical with spec. H, was observed.

When pyrolyzing (1000 °C, $p \sim 0.02$ Torr) vapors from the synthetic product no lines from $CH_2=NCN$ were found. $(CH_3)_2NCN$ may, therefore, pyrolyze in two ways:

$(CH_3)_2NCN \rightarrow CH_2=NCN\ (+CH_4?)$
$(CH_3)_2NCN \rightarrow CH_3NHCN\ (+CH_2?)$

*Table 1.* Observed $2_{02}-3_{03}$ transitions (MHz) of approximately equal intensity in $CH_3NHCN$ (I) and $CD_3NHCN$ (II) in order of increasing frequency. $i$ = inversion effect; a,e = torsional effect.

| | | | | | ⟨i⟩ | ⟨a,e⟩ |
|---|---|---|---|---|---|---|
| I | 28417.73 | 28425.05 | 28463.76 | 28471.54 | | |
| Average | | 28421.39 | | 28467.65 | 46.26 | |
| a,e | | 7.32 | | 7.78 | | 7.55 |
| II | 25348.10 | 25349.54 | 25384.63 | 25387.23 | | |
| Average | | 25348.82 | | 25385.93 | 37.11 | |
| a,e | | 1.44 | | 2.60 | | 2.02 |

*Table 2.* Observed and assigned rotational (a,+) transitions[a] (18.6−40.0 GHz) for $CH_3NHCN$ (I) and $CD_3NHCN$ (II).

| | I(a,+) | | | II(a,+) | | |
|---|---|---|---|---|---|---|
| | Obs. | Obs. − calc. Fit incl. $\Delta_J,\Delta_{JK}$ | Rigid rotor fit | Obs. | Obs. − calc. Fit incl. $\Delta_J,\Delta_{JK}$ | Rigid rotor fit |
| $1_{11}-2_{12}$ | 18492.5[b] | 0.04 | | | | |
| $1_{01}-2_{02}$ | 18959.17 | 0.10 | 0.25 | | | |
| $1_{10}-2_{11}$ | 19435.8[b] | 0.67 | | | | |
| $2_{12}-3_{13}$ | 27735.21 | 0.09 | 0.11 | 24781.50 | 0.08 | 1.49 |
| $2_{02}-3_{03}$ | 28425.05 | 0.03 | 0.11 | 25349.54 | −0.04 | 0.95 |
| $2_{11}-3_{12}$ | 29151.19 | 0.09 | 0.11 | 25948.62 | −0.04 | 1.37 |
| $2_{21}-3_{22}$ | 28447.0 | 0.25 | 0.55 | 25367[c] | 0.60 | |
| $2_{20}-3_{21}$ | 28467.5 | −0.57 | −0.46 | 25386[c] | 0.66 | |
| $3_{13}-4_{14}$ | 36973.68 | 0.13 | −0.27 | 33036.13 | 0.01 | 1.25 |
| $3_{03}-4_{04}$ | 37874.66 | −0.06 | −0.19 | 33777.07 | 0.03 | −0.27 |
| $3_{12}-4_{13}$ | 38861.47 | 0.12 | −0.27 | 34592.39 | 0.11 | 1.34 |
| $3_{22}-4_{23}$ | 37923.8 | −0.58 | −0.62 | 33817.6 | −0.25 | −0.82 |
| $3_{21}-4_{22}$ | 37977.8 | 0.17 | −0.37 | 33865.2 | 0.00 | 2.24 |
| $3_{31}-4_{32}$ | 37940.0 | 0.24 | 0.75 | 33827.5 | 0.15 | −3.20 |
| $3_{30}-4_{31}$ | 37940.0 | 0.01 | 0.52 | 33827.5 | −0.06 | −3.40 |
| rms | | 0.33 | 0.46 | | 0.15 | 2.27 |

[a] Peaks of unresolved quadrupole coupling patterns. [b] Diffuse quadrupole coupling pattern. Not included in fits. [c] Tentative. Not included in fits.

but our experiments do not exclude other mechanisms. The applied $(CD_3)_2NCN$ was prepared as referred elsewhere.[6]

## ASSIGNMENT. DIPOLE MOMENT

Close to the centers of observed 1→2, 2→3 and 3→4 rotational transitions of I and II their mw spectra at 400 V/cm are dominated by quartets as exemplified in Table 1. In agreement with the isotope shift rules for $CH_3NHCN \rightarrow CD_3NHCN$ sketched above transitions in columns 2 and 3 tentatively were assigned to I(a,+), I(e,+), II(a,+) and II(e,+) while transitions in columns 4 and 5 have the inversion character −1. The final assign-

*Table 3.* Observed and assigned rotational (a,−) transitions[a] (18.6−40.0 GHz) for $CH_3NHCN$ (I) and $CD_3NHCN$ (II).

| | I(a,−) | | | II(a,−) | | |
|---|---|---|---|---|---|---|
| | Obs. | Obs.−calc. Fit incl. $\Delta_J$,$\Delta_{JK}$ | Rigid rotor fit | Obs. | Obs.−calc. Fit incl. $\Delta_J$,$\Delta_{JK}$ | Rigid rotor fit |
| $1_{11}-2_{12}$ | 18522.0[b] | 1.00 | | | | |
| $1_{01}-2_{02}$ | 18984.93 | 0.10 | −1.75 | | | |
| $1_{10}-2_{11}$ | 19460.5[b] | −0.4 | | | | |
| $2_{12}-3_{13}$ | 27778.34 | 0.25 | −1.95 | 24819.29 | 0.01 | −2.95 |
| $2_{02}-3_{03}$ | 28463.76 | 0.06 | −1.45 | 25384.63 | 0.05 | −1.86 |
| $2_{11}-3_{12}$ | 29188.15 | 0.23 | −1.98 | 25984.31 | −0.07 | −3.06 |
| $2_{21}-3_{22}$ | | | | | | |
| $2_{20}-3_{21}$ | 28510.5 | −0.68 | −2.13 | | | |
| $3_{13}-4_{14}$ | 37031.17 | −0.01 | −2.41 | 33086.57 | 0.13 | −3.53 |
| $3_{03}-4_{04}$ | 37926.22 | −0.14 | 0.24 | 33823.84 | 0.11 | 0.48 |
| $3_{12}-4_{13}$ | 38910.77 | 0.00 | −2.38 | 34639.93 | 0.19 | −3.45 |
| $3_{22}-4_{23}$ | 37981.7 | −0.12 | 1.09 | 33873.8 | −0.83 | 0.43 |
| $3_{21}-4_{22}$ | 38036.0 | 0.15 | −3.86 | 33921.5 | 0.08 | −6.11 |
| $3_{31}-4_{32}$ | 38004.0 | 0.20 | 7.05 | 33897.5 | 0.25 | 9.18 |
| $3_{30}-4_{31}$ | 38004.0 | −0.03 | 6.77 | 33897.5 | 0.04 | 8.90 |
| rms | | 0.32 | 3.95 | | 0.41 | 5.94 |

[a] Peaks of unresolved quadrupole coupling patterns. [b] Diffuse. Not included in fits.

*Table 4.* Rotational constants *A*, *B*, *C* (MHz) and centrifugal distortion constants $\Delta_J$ and $\Delta_{JK}$ (kHz) for $CH_3NHCN$(a,+), $CD_3NHCN$ (a,+), $CH_3NHCN$ (a,−) and $CD_3NHCN$ (a,−) spectra as analyzed by ROTFIT.

| | I(a,+) | II(a,+) | I(a,−) | II(a,−) |
|---|---|---|---|---|
| *A* | 36090±156 | 28190±64 | 35380±145 | 28390±178 |
| *B* | 4977.13±0.07 | 4422.69±0.04 | 4982.54±0.07 | 4428.16±0.11 |
| *C* | 4505.13±0.07 | 4033.59±0.04 | 4512.58±0.07 | 4039.78±0.11 |
| $\Delta_J$ | 4.3 ±2.0 | 2.9 ±1.3 | 0.4 ±2.1 | 5.0 ±3.4 |
| $\Delta_{JK}$ | −17.4 ±5.3 | 89.1 ±2.5 | −176.7 ±5.2 | −242.7 ±6.7 |
| rms[a] | 0.33 | 0.15 | 0.32 | 0.41 |
| rms[b] | 0.46 | 2.27 | 3.95 | 5.94 |

[a] Fit including $\Delta_J$ and $\Delta_{JK}$. [b] Rigid rotor fit.

ments of I(a,+), II(a,+), I(a,−) and II(a,−) spectra are reported in Tables 2 and 3. A ROTFIT program [7] was used implying rotational constants *A,B,C* and centrifugal distortion constants $\Delta_J$ and $\Delta_{JK}$. Rather large irregularities for $\Delta_J$ and $\Delta_{JK}$ were found (Table 4). For purpose of clarification a ROTFIT for $\Delta_J=\Delta_{JK}=0$ is included in Tables 2 and 3. As seen, this works well for $CH_3NHCN$ suggesting that perturbations not taken into account for the II(a,+), I(a,−) and II(a,−) spectra do occur. For I(a,−) and II(a,−) this may be due to their status as excited states. The $[E(a,-)-E(a,+)]$ energy difference is not known to us because of failure to observe $\mu_c$ transitions. For II(a,+) and II(a,−) it must be noted that $CD_3NHCN$ possesses normal vibrations of lower frequency than $CH_3NHCN$. For these reasons the association of a model $M_H(+)$ with the I(a,+) spectrum involves minimum errors. Larger errors are involved in $M_D(+)$ also presented (*vide infra*) (Table 5) agreeing with the fact (Table 6) that reasonably well predicted a,e splittings are obtained for the I(a,+), I(e,+) spectra only. The applied computer program SEM-4 ignores any interaction between $CH_3$ and $CD_3$ torsion and other modes including inversion.

Following the M = 1 component of the transitions $2_{12}\rightarrow3_{13}$ (300 V/cm), $2_{11}\rightarrow3_{12}$ (300 V/cm), $3_{13}\rightarrow4_{14}$ (800 V/cm) and $3_{12}\rightarrow4_{13}$ (800 V/cm) in the spectrum I(a,+) yielded dipole moment components $\mu_a=4.72$ Debye; $\mu_b=1.30$ Debye while a small $\mu_c$ could not be fixed. The values of $\mu_a$ and $\mu_b$ are approximate. All assigned transitions are of $\mu_a$ type.

*Table 5.* Model rotational constants (MHz) compared to experimental rotational constants of $CH_3NHCN$ and $CD_3NHCN$. Model 2→3 transitions compared to observed transitions.

| | $CH_3NHCN$ Obs. | Model $M_H(+)$ | $CD_3NHCN$ Obs. | Model $M_D(+)$ |
|---|---|---|---|---|
| *A* | 36090 | 33547 | 28190 | 27148 |
| *B* | 4977.13 | 4977.13 | 4422.69 | 4422.69 |
| *C* | 4505.13 | 4505.13 | 4033.59 | 4033.59 |
| $2_{12}-3_{13}$ | 27735.21 | 27735.16 | 24781.50 | 24782.11 |
| $2_{02}-3_{03}$ | 28425.05 | 28423.57 | 25349.54 | 25349.03 |
| $2_{11}-3_{12}$ | 29151.19 | 29151.11 | 25948.62 | 25949.37 |
| $2_{21}-3_{22}$ | 28447.0 | 28446.76 | 25367 | 25368.84 |
| $2_{20}-3_{21}$ | 28467.5 | 28469.96 | 25387 | 25388.65 |
| Angles [a] | | | | |
| α (°) | | 179.92 | | 177.88 |
| *w* (°) | | 112.90 | | 112.50 |

[a] Fig. 1.

*Table 6.* Experimental I(e,+) and II(e,+) frequencies (MHz). Experimental and calculated differences I(a,+)−I(e,+) and II(a,+)−II(e,+). I(a,+) and II(a,+) frequencies in Table 2. I=$CH_3NHCN$; II=$CD_3NHCN$.

| | I(e,+) | I(a,+)−I(e,+) Exp. | Calc. | II(e,+) | II(a,+)−II(e,+) Exp. | Calc. |
|---|---|---|---|---|---|---|
| $1_{01}-2_{02}$ | 18954.28 | 4.89 | 6.36 | | | |
| $2_{12}-3_{13}$ | 27822.18 | −86.97 | −86.64 | 24782.63 | −1.13 | −1.16 |
| $2_{02}-3_{03}$ | 28417.73 | 7.32 | 6.76 | 25348.10 | 1.44 | −0.34 |
| $2_{11}-3_{12}$ | 29051.35 | 99.84 | 93.96 | 25945.33 | 3.29 | −0.79 |
| $3_{13}-4_{14}$ | 37012.0 | −38.32 | −40.85 | 33036.13 | 0.00 | −1.51 |
| $3_{03}-4_{04}$ | 37865.15 | 9.51 | 4.12 | 33775.14 | 1.93 | −2.05 |
| $3_{12}-4_{13}$ | 38805.8 | 55.67 | 39.47 | 34588.90 | 3.49 | −4.54 |

## MOLECULAR MODELS

$M_H(+)$ and $M_D(+)$ models corresponding to ROTFIT rotational constants (Table 4) have been worked out. With only two well-determined rotational constants per species, $B$ and $C$, a number of assumptions has to be made. We have chosen to assume corresponding structural parameters from related $CH_3NHCl$ (method I of Ref. 9). Referring to Fig. 1 we have further taken the N1−C2 distance as 1.400 Å (~1.459 Å as in $CH_3-C\equiv CH$ *minus* a carbon, nitrogen covalent radius difference of 0.055 Å) and the C2≡N2 distance as 1.160 Å. Then the angles $\alpha$ and $w$ were fitted to reproduce $B$ and $C$. The result is reported in Table 5. Obviously, $\alpha$ and $w$ are practically independent of their molecular affiliation. Their dependence on the badly fixed rotational constant $A$ is also slight as seen by the consistency between observed $2_{i,j}\rightarrow 3_{i,j+1}$ transition frequencies and frequencies based on the rigid models. The models $M_H(+)$ and $M_D(+)$ were used for the calculations of 'a,e splittings' to follow.

## TORSIONAL SPLITTINGS IN $CH_3NHCN$ AND $CD_3NHCN$

Unusually large Stark splittings at the band centres where intense spectra could be observed even at an electric field of 1 V/cm, together with our use of SEM-4 (imperfect for our purpose) proved serious enough to prevent unambiguous assignment of about half of the 'e' transitions. Transitions, safely assigned by their Stark patterns and their relatively isolated location (except for the $2_{02}\rightarrow 3_{03}$ and $3_{03}\rightarrow 4_{04}$ transitions), are reported in Table 6. We consider them numerous enough to conclude that SEM-4 with its underlying Hamiltonian works reasonably well only for I(a,+), I(e,+). For I(a,−), I(e,−) and II(a,−), II(e,−) splittings the disagreement using SEM-4 is complete.

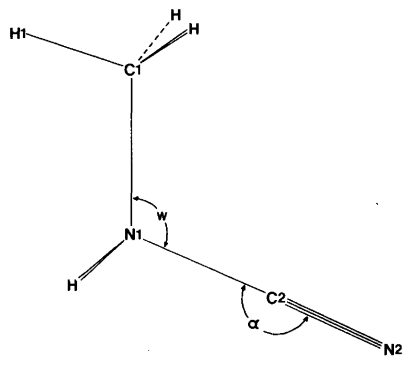


*Fig. 1.* Rigid model of $CH_3NHCN$. Atoms H1, C1, N1, C2 and N2 in plane of paper. Calculated structural parameters $\alpha$ (178−180°) and $w$ (112.5−113°) based on assumed remaining angles and interatomic distances (see text). The resulting angles agree well with corresponding angles in $CH_3CH_2CN$ in which '$\alpha$' = 178.73° and '$w$' = 111.98°.[11]

The I(a,+), I(e,+) splittings correspond to a torsional barrier of 262 $cm^{-1}$. 'Related' $CH_3NHCl$ has a torsional barrier of 1322 $cm^{-1}$.[9] Thus, the torsional barrier of $CH_3NHCN$ is closer to the barrier in $CH_3-N=\overset{+}{N}=\bar{N}$ (250 $cm^{-1}$).[10] The approximate torsional frequency of $CH_3NHCN$ is 105 $cm^{-1}$.

## DISCUSSION

At a slightly higher temperature (1000 °C) $(CH_3)_2NCN$ also forms $CH_2=NCN$ by pyrolysis.[1] Our present observation of transitions in the interval 27 290−29 137 MHz (Table 4 of Ref. 1) again raises the question if we may be dealing with spectra of *trans* and/or *cis* iminoacetonitrile (Fig. 4 of Ref. 1) since their estimated (not experimental) rotational constants $B$ and $C$ are close to experimental $B$ and $C$ for $CH_3NHCN$. However, iminoacetonitrile is still excluded since neither the *trans* nor the *cis* isomer spectrum will exibit a,e splitting or inversion phenomena.

As to the structure of $CH_3NHCN$ it was at first expected that the angle $\alpha$ (Fig. 1) would deviate from 180°. However, assuming $\alpha = 174°$ with any of the assumed N1−C2 or C2≡N2 distances above seriously damaged the calculated, non-assumed distance (C2≡N2 and N1−C2, respectively).

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