Acta Chemica Scandinavica A 31 (1977) 755—758

Pyrolytic Production and Microwave Spectra of Light and Heavy *N*-Methylmethylenimine

B. BAK, N. W. LARSEN and H. SVANHOLT

Chemical Laboratory V, H.C. Ørsted Institutet, DK-2100 Copenhagen, Denmark

$CH_2=N-CH_3$ (I), *N*-methylmethylenimine, and $CD_2=N-CD_3$ (II) have been produced by pyrolysis of $(CH_3)_2NH$ and $(CD_3)_2ND$, respectively, on a quartz surface at 950 °C and $p = ca.$ 30 mTorr. I and II were identified by their microwave spectra (12.5 – 40 GHz). 16 transitions in addition to 12 found in earlier work were assigned to $CH_2=N-CH_3$. 28 transitions were assigned to $CD_2=N-CD_3$. Rotational and centrifugal distortion constants were calculated for both species.

In recent attempts to identify interstellar molecules it has become necessary to produce 'suspect' species in the laboratory. One example of this is $CH_2=NH$, methylenimine.[1] Primarily, only *spectra* of such compounds are wanted so that bulk production is unnecessary. Methylenimine has been obtained by pyrolysis of methylamine and identified by its microwave (m.w.) spectrum.[1] In consequence, interstellar m.w. radiation due to methylenimine has been safely identified.[2] Generally, in the search for interstellar species experience has shown that *methyl* derivatives of small hydrogen-containing molecules are likely to occur.[3] Thus, for $CH_2=NH$, future identification of *cis*, *trans* $CH_3-CH=NH$ and of $CH_2=N-CH_3$ (I) is not unlikely. $CH_3-CH=NH$ has already been produced by pyrolysis of ethylamine.[4] Earlier, I has been prepared from $[CH_2=N-CH_3]_3$ by decomposition on Al_2O_3,SiO_2 at 425 °C.[5] 12 m.w. transitions were measured.[5] We wanted to see if easy production of I from $(CH_3)_2NH$ by pyrolysis would be possible. If so, we wanted to measure a larger number of m.w. transitions to get rotational and centrifugal distortion constants of high precision. A study of the m.w. spectrum of II formed by pyrolysis of $(CD_3)_2ND$ soon proved to be a useful pre-stage to a final analysis of the m.w. spectrum of I. The resulting rotational constants of II add to our knowledge of the structure of *N*-methylmethylenimine [5,6] but a discussion of this is not given in this paper.

EXPERIMENTAL

5 g quantities of commercial $(CH_3)_2NH$ (III) and $(CD_3)_2NH$ (IV) were repeatedly distilled at −80 °C and *ca.* 2 Torr, collecting fractions of constant pressure. Parts of the samples were repeatedly exchanged by 99,5 % D_2O at −10 °C to produce $(CH_3)_2ND$ (V) and $(CD_3)_2ND$ (VI). To obtain dry gases III – VI for pyrolysis, samples were taken at −80 °C where $p(H_2O) = 0.4$ mTorr. Before gases were admitted to the pyrolysis zone, a 20 cm long quartz tube of i.d. 9 mm, their pressure was reduced to ~50 mTorr. At the chosen pumping speed the gases were carried through the electrically heated tube in *ca.* 30 s and directly admitted to the cell of a conventional Stark-modulated m.w. spectrometer. The cell was kept at −30 °C, the entrance and exit pressures being of the order 20 and 10 mTorr, respectively. The consumption of 'parent' compound (III – VI) was of the order 0.1 mg/h.

In an experiment a m.w. line of medium intensity and well-separated from other lines of, say, III was repeatedly scanned while the temperature of the quartz tube was raised. Typically, the line intensity remained constant up to 800 – 850 °C, then started to decrease to *ca.* ½ intensity at 950 °C. When pyrolyzing gases of III 'new' lines turned out to be lines from $CH_2=N-CH_3$ (I), $CH_2=NH$, NH_3 and HCN. The m.w. region scanned by us was 17.5 – 40 GHz. Here, positions of lines from NH_3, ND_3, HCN and DCN are well-known while positions of lines from $CH_2=NH$ and $CD_2=ND$ had to be calculated ignoring centrifugal distortion.[1] A large portion of 'new'

lines was discarded in this way. Positive identification of lines from I and II was based on precalculated relative intensities, Stark-lobe positions, and ^{14}N-quadrupole coupling patterns, all available by using data from Ref. 5.

Pyrolysis of III at 950 °C produced I as expected. Four transitions below 40 GHz earlier found by Sastry and Curl [5] were identified. It was found that complete separation of Stark lobes occurred at an electric field intensity > 1000 V cm^{-1}. The measured intensity of these 4 lines proved very useful in further identification of lines in the spectra of I and II.

ASSIGNMENT

Observation of. m.w. lines from I and II was sometimes questionable due to, for example, strong 'parental' lines. However, both III and V form I by pyrolysis. So, a spectral 'background' of III could be replaced by a background of V and *vice versa* wherever necessary. Following the identification of 4 lines in the m.w. spectrum of I (as mentioned above) we proceeded to pyrolyze IV (or VI) to II ($CD_2=N-CD_3$). For I and II with a barrier to CH_3 and CD_3 torsion of *ca.* 2 kcal mol^{-1} [5] so-called *A,E*-splitting is expected. For II, a preliminary calculation based on the barrier of 1970 cal mol^{-1} from Ref. 5 showed this splitting to be < 1 MHz for transitions observed by us (17.5 – 40 GHz) with $J<10$, $K_{-1}<3$. Thus, the first 10 transitions of Table 1 may be considered a group of firmly established '*A*' components (coinciding with *E*'s). Any further assigned *A*-component ($J>10$) must be agreeable with this group within the framework of a rigid rotor Hamiltonian including centrifugal distortion. Also, for $J>9-10$, *E*-components may split further, while the *A*-components remain single and, therefore, of the larger intensity. Using these two criteria as further guides in the assignment 18 further *A*-components were assigned. Table 1 reviews the total number of transitions assigned, their

Table 1. Number and type of transitions (17.5 – 40 GHz) measured. Maximum rotational quantum number J_{max} involved. ROTFIT r.m.s. deviations in the analysis of microwave spectra of $CD_3-N=CD_2$ and $CH_3-N=CH_2$.

	R-type	Q-type	*P*-type	J_{max}	ROTFIT r.m.s. deviations (MHz)
$CD_3-N=CD_2$	14	6	8	28	0.2498
$CH_3-N=CH_2$	11	0	8	20	0.2125

Table 2. Rotational constants *A,B,C* in MHz for $CH_3-N=CH_2$ and $CD_3-N=CD_2$. Quartic distortion constants Δ_J, Δ_{JK}, Δ_K, δ_j and δ_{jk} in kHz. Sextic constants H_K and H_{KJ} in Hz. Asymmetry parameter $\varkappa$. Both sets correspond to observed *A*-components.

	$CH_3-N=CH_2$	$CD_3-N=CD_2$
A	52 527.265 ±0.12 [a]	34 577.274 ±0.11
B	10 666.1008 ±0.029 [a]	8 161.0836 ±0.027
C	9 377.3587 ±0.023 [a]	7 191.1612 ±0.029
Δ_J	6.566 ±0.75	3.354 ±0.38
Δ_{JK}	−18.327 ±11.	11.294 ±4.6
Δ_K	1 041.818 ±17.	125.885 ±4.1
δ_j	1.3334 ±0.068	0.8779 ±0.085
δ_{jk}	−45.788 ±1.1	−59.730 ±3.7
H_K	3 820.34 ±270.	
H_{KJ}	176.72 ±25.	
$\varkappa$	−0.94026675	−0.92916684

[a] Ref. 5 has $A=52\,523.75\pm1.2$ MHz, $B=10\,666.13\pm0.3$ MHz, and $C=9\,377.19\pm0.3$ MHz.

Table 3. Observed and calculated (SEM-4) [a] frequencies of ν_A and ν_E components (MHz) in the microwave spectrum of $CH_3-N=CH_2$ corresponding to a methyl group torsional barrier of 2007 cal/mol [d] and an angle between the symmetry-axis of CH_3 and the *a*-axis of the entire molecule of 27.52°.[d]

Transition $J_{K_{-1}K_{+1}} \rightarrow J'_{K'_{-1}K'_{+1}}$	ν_A Obs.	ν_A Calc.	$\nu_A - \nu_E$ Obs.	$\nu_A - \nu_E$ Calc.
$1_{0,1} - 1_{1,0}$	43 148.91	43 147.56	18.00	18.76
$2_{0,2} - 2_{1,1}$	44 467.25	44 466.25	19.50	19.57
$3_{0,3} - 3_{1,2}$	46 499.28	46 498.99	20.2	19.95
$4_{0,4} - 4_{1,3}$	49 309.25	49 310.22	19.7	20.30
$2_{1,2} - 3_{0,3}$	19 411.78	19 411.82	−19.0	−18.86
$3_{1,3} - 4_{0,4}$	41 113.35	41 114.17	−18.0	−17.96
$4_{1,3} - 3_{2,2}$	40 963.98	40 964.85	68.4	68.19
$6_{2,5} - 7_{1,6}$	30 183.3	30 183.43 [c]	−47.3	−47.5
$9_{3,7} - 8_{3,6}$	[b]	25 053.36 [c]		66.0
$9_{3,6} - 8_{3,5}$	34 460.8	34 461.53 [c]	45.0	44.4
$9_{3,7} - 10_{1,10}$	26 501.4	26 501.40 [c]	−49.9	−51.9
$10_{3,8} - 11_{1,11}$	34 556.3	34 556.50 [c]	−49.9	−51.8
$10_{3,8} - 11_{2,9}$	22 191.8	22 191.65 [c]	−62.0	−53.0
$11_{3,8} - 12_{2,11}$	20 047.5	20 047.20 [c]	−52.2	−45.7

[a] Internal rotation program valid for any symmetry of the frame and top, N. W. Larsen and Th. Pedersen (to be published). [b] Probably hidden under a very intense NH_3-absorption line at 25056 MHz. [c] Calculated from the data in Table 2, left column. [d] Ref. 5 has a barrier of 1970 ± 25 cal/mol and an angle of 29.9 ± 1°.

type and the r.m.s. deviation at a ROTFIT fit.[7] The complete list of measured frequencies is available on request. The corresponding rotational and centrifugal distortion constants are reported in Table 2 (right column).

Finally the more complicated m.w. spectrum of I was assigned (Table 3). The first seven transitions were taken from Ref. 5 ($J \leq 4$). This group was increased by the following seven *A*, *E* transitions of Table 3 as identified by the positions of the *A*-components (fitted to a rigid rotor/centrifugal distortion Hamiltonian) and *A*,*E*-splittings (calculated by means of the computer-program 'SEM-4'; see footnote *a* in Table 3). Assignment of the remaining 9 *A*-components ($J,K_{-1} \geq 12,3$) was performed as for II but with distortion terms up to the sixth power in $\hat{P}$ (H_K and $H_{KJ} \pm 0$). Observed *A*-components are available on request. Rotational and centrifugal distortion constants of I are given in Table 2 (left column).

DISCUSSION

A rigid molecular model of II derived from the rigid model of I (see Fig. 1), presented in Ref. 5, by replacing all hydrogen atoms by deuterium has $A = 34810$ MHz, $B = 8169$ MHz, and $C = 7219$ MHz. The values found here are (Table 2) $A_{exp} = 34577$ MHz, $B_{exp} = 8161$ MHz, and $C_{exp} = 7191$ MHz. Generally for several isotopic species (like I and II) agreement between experimental rotational constants and rotational constants of a rigid model is not to

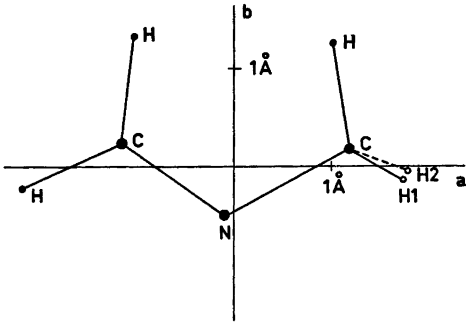

Fig. 1. Position of atoms in *N*-methylmethylenimine (I) in its principal axes system (point group C_s). Atoms in and outside the *ab* plane represented by ● and O, respectively. H1 above and H2 below the *ab* plane. A rigid model (C_s) has 12 geometric parameters. For assumed threefold symmetry of CH_3 (axis N – C) the model has 9 parameters.

be expected. Furthermore the non-rigidity of I and II will add to this disagreement. However, in view of the large number of assumed geometric parameters it is, so far, of little use to discuss the nature and magnitude of the disagreement found.

In the search for interstellar $CH_3-N=CH_2$ observation of emission lines at frequencies higher than 40 GHz may be necessary. The spectroscopic constants derived in this paper (Table 2) should facilitate this.

REFERENCES

1. Johnson, D. R. and Lovas, F. J. *Chem. Phys. Lett. 15* (1972) 65.
2. Godfrey, P. D., Brown, R. D., Robinson, B. J. and Sinclair, M. W. *Astrophys. Lett. 13* (1973) 119.
3. Winnewisser, G., Mezger, P. G. and Breuer, H. D. *Interstellar Molecules.* In *Fortschr. Chem. Forsch. 44* (1973).
4. Lovas, F. J., Clark, F. O. and Tiemann, E. *J. Chem. Phys. 62* (1975) 1925.
5. Sastry, K. V. L. N. and Curl, R. F., Jr. *J. Chem. Phys. 41* (1964) 77.
6. Yardley, J. T., Hinze, J. and Curl, R. F., Jr. *J. Chem. Phys. 41* (1964) 2562.
7. Sørensen, G. O. This laboratory 1975.

Received June 1, 1977.