r_0-Structure, Partial r-Structure, and Nitrogen Nuclear Quadrupole Coupling Constants of N-Nitroso-dimethylamine

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The microwave spectra of $(CH_3)_2{}^{15}NNO$, $(CH_3)_2N^{15}NO$, syn-$^{13}CH_3{}^{12}CH_3NNO$ and anti-$^{13}CH_3{}^{12}CH_3NNO$ have been studied and the rotational constants evaluated. With these data and former results [1] the r_s-structure of the carbon-nitrogen frame has been found to be planar. An r_0-structure has also been calculated. From the hyperfine structure of the spectra the nuclear quadrupole coupling constants of the nitrogen nuclei have been determined. Further studies to complete the r_s-structure are in progress.

Introduction

In a preceding paper [1] an investigation of the microwave spectra of the two isotopic species $(CH_3)_2NNO$ and $(CH_3)_2{}^{15}N^{15}NO$ and the measurement of the electric dipole moment have been reported.

To obtain better structural data and the nuclear quadrupole coupling constants of the two nitrogen nuclei the spectra of the isotopic species $(CH_3)_2{}^{14}N^{15}NO$, $(CH_3)_2{}^{15}N^{14}NO$, syn-$^{13}CH_3{}^{12}CH_3NNO$, and anti-$^{13}CH_3{}^{12}CH_3NNO$ have been investigated.

Table 1. Microwave spectrum of N-Nitroso-dimethylamine-(syn-^{13}C). Frequencies are in MHz. Transitions labeled with ^{a} were used to obtain the rotational constants.

$J_{K_{-1},K_1} \leftarrow J'_{K'_{-1},K'_1}$		ν_{exp}	ν_{calc}	$\Delta\nu_{exp-calc}$
2_{02}	1_{01} ^{a}	15,140.57	15,140.40	0.17
2_{12}	1_{11} ^{a}	13,991.76	13,991.69	0.07
2_{11}	1_{10} ^{a}	16,957.02	16,956.51	0.51
3_{03}	2_{02} ^{a}	21,974.64	21,974.64	0.00
3_{13}	2_{12} ^{a}	20,797.85	20,798.00	−0.15
3_{12}	2_{11} ^{a}	25,197.24	25,196.84	0.40
3_{22}	2_{21} ^{a}	23,210.74	23,211.15	−0.41
3_{21}	2_{20} ^{a}	24,447.22	24,447.66	−0.44
3_{13}	2_{02} ^{a}	23,763.96	23,763.76	0.20
3_{22}	2_{11} ^{a}	35,554.45	35,554.56	−0.11
3_{31}	3_{22}	24,468.14	24,467.90	0.24
3_{30}	3_{21}	22,946.13	22,946.10	0.03
4_{32}	3_{31}	31,494.66	31,495.18	−0.52
4_{31}	3_{30}	31,774.77	31,775.29	−0.52
5_{33}	4_{32}	39,418.12	39,418.87	−0.75
5_{42}	4_{41}	39,422.38	39,423.52	−1.14
5_{41}	4_{40}	39,467.68	39,468.84	−1.16
5_{33}	5_{42}	33,519.98	33,520.69	−0.71
5_{41}	5_{32}	32,337.84	32,338.60	−0.76

Experimental

The samples were prepared according to Rademacher [2]. The microwave spectra have been recorded with a conventional Stark-effect spectrometer operating in the range 6 – 40 GHz, which has been described elsewhere [3, 4]. The measurements using the radio-frequency-microwave double resonance (RFMWDR) technique [5] have been done with a modification of the apparatus as described in [6] and [7]. The error in the frequency measurements is believed to be less than ± 0.03 MHz. The pressure of the gas was about 2 microns and the temperature about – 50 °C.

Spectrum

In all spectra, no effect due to internal rotation has been observed. The assignment was possible by

Table 2. Microwave spectrum of N-Nitroso-dimethylamine-(anti-^{13}C). Frequencies are in MHz. Transition labeled with ^{a} were used to obtain the rotational constants.

$J_{K_{-1},K_1} \leftarrow J'_{K'_{-1},K'_1}$		ν_{exp}	ν_{calc}	$\Delta\nu_{exp-calc}$
2_{02}	1_{01} ^{a}	14,928.49	14,928.25	0.24
2_{12}	1_{11} ^{a}	13,814.63	13,814.49	0.14
2_{11}	1_{10} ^{a}	16,592.86	16,592.81	0.05
3_{03}	2_{02} ^{a}	21,768.71	21,768.62	0.09
3_{13}	2_{12} ^{a}	20,563.68	20,563.79	−0.11
3_{12}	2_{11} ^{a}	24,696.67	24,696.33	0.34
3_{22}	2_{21} ^{a}	22,805.21	22,805.47	−0.26
3_{21}	2_{20} ^{a}	23,842.10	23,842.33	−0.23
3_{13}	2_{02} ^{a}	23,941.96	23,942.06	−0.10
3_{31}	3_{22} ^{a}	26,090.91	26,091.07	−0.16
3_{30}	3_{21} ^{a}	24,813.92	24,813.76	0.16
4_{32}	3_{31}	30,868.33	30,868.90	−0.57
4_{31}	3_{30}	31,072.90	31,072.86	0.04
5_{33}	4_{32}	38,647.45	38,648.29	−0.84
5_{32}	4_{31}	39,319.31	39,320.11	−0.80
5_{42}	4_{41}	38,618.08	38,619.02	−0.94
5_{41}	4_{40}	38,646.41	38,647.82	−1.41
5_{42}	5_{33}	35,873.02	35,873.85	−0.83
5_{41}	5_{32}	34,995.17	35,995.59	−0.42

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Table 3. Microwave spectrum of $(CH_3)_2N^{15}NO$. Frequencies are in MHz. Transitions labeled with ^{a} were used to obtain the rotational constants, with ^{b} for the nuclear quadrupole coupling constants. $\Delta\bar{\nu}=\bar{\nu}-\bar{\nu}_{calc}$, $\Delta\nu_{exp-calc}=\nu_{exp}-\nu_{calc}$.

$J_{K_{-1},K_1} \leftarrow J'_{K'_{-1},K'_1}$		$F \leftarrow F'$		ν_{exp}	$\bar{\nu}$	$\bar{\nu}_{calc}$	$\Delta\bar{\nu}$	ν_{calc}	$\Delta\nu_{exp\text{-}calc}$
2_{02}	1_{01} ^{a}				15,190.08	15,190.14	−0.06		
2_{12}	1_{11} $^{a,\,b}$				14,048.42	14,048.52	−0.10		
		3	2	14,048.23				14,028.24	−0.01
		2	1	14,048.92				14,048.90	0.02
		2	2	14,049.54				14,049.56	−0.02
		1	1	14,046.86				14,046.84	0.02
2_{11}	1_{10} $^{a,\,b}$				16,938.05	16,937.83	0.22		
		3	2	16,937.96				16,938.00	−0.04
		2	1	16,938.46				16,938.53	−0.07
		2	2	16,937.39				16,937.30	0.09
3_{03}	2_{02} ^{a}				22,106.34	22,106.41	−0.07		
3_{13}	2_{12} ^{a}				20,899.54	20,899.72	−0.18		
3_{12}	2_{11} ^{a}				25,193.01	25,192.89	0.12		
3_{22}	2_{21} $^{a,\,b}$				23,239.63	23,239.76	−0.13		
		4	3	23,239.50				23,239.49	0.01
		3	2	23,240.15				23,240.11	0.04
3_{21}	2_{20} $^{a,\,b}$				24,373.06	24,373.12	−0.06		
		4	3	24,373.05				24,373.02	0.03
		2	2	24,374.08				24,374.11	−0.03
2_{12}	1_{01} ^{a}				18,416.11	18,415.70	0.41		
2_{21}	2_{12} ^{a}				17,435.36	17,435.49	−0.13		
3_{13}	2_{02}				24,124.33	24,125.28	−0.95		
3_{03}	2_{12}				18,880.32	18,880.84	−0.52		
4_{32}	3_{31}				31,488.79	31,489.43	−0.64		
4_{31}	3_{30}				31,726.09	31,726.73	−0.64		
		5	4	31,725.98				31,726.00	−0.02
		4	3	31,726.41				31,726.39	0.02
4_{40}	4_{31}				34,911.91	34,915.11	−3.20		
4_{41}	4_{32}				35,187.67	35,188.67	−1.00		
5_{42}	4_{41}				39,402.33	39,403.78	−1.45		
		6	5	39,402.20				39,402.23	−0.03
		5	4	39,402.66				39,402.64	0.02
5_{41}	4_{40}				39,437.40	39,439.36	−1.96		
1_{01}	0_{00}				12,113.53	12,113.77	−0.24	(disturbed line)	

using the RFMWDR technique. By this way, some *a*-type lines were easily detected and the full set of *a*-type lines from $J=1$ up to $J=3$ was obtained. The lines of the *b*-type spectrum were about 8 times weaker and sometimes not detectable, when they were obscured by other lines. So we did not succeed in obtaining the same set of *b*-type lines from the different isotopic species.

In the spectra of syn- and anti-$^{13}CH_3{}^{12}CH_3NNO$, no attempt was made to resolve the fine structure resulting from the nuclear quadru-

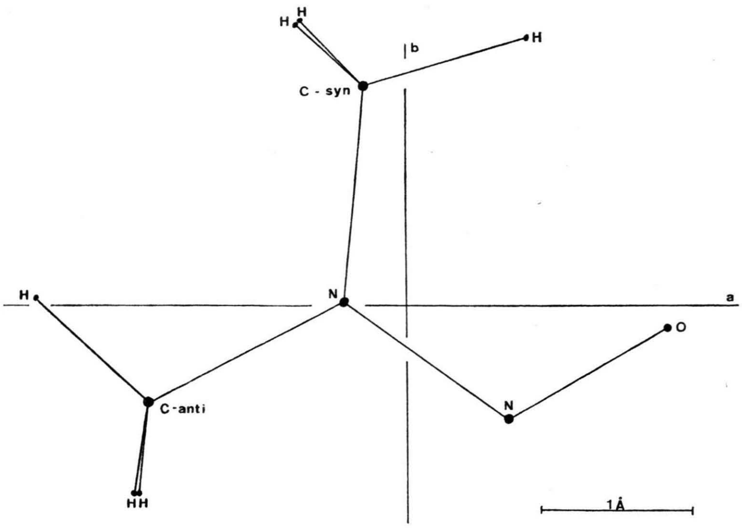

Fig. 1. N-Nitroso-dimethylamine in the principal axis system.

Table 4. Microwave spectrum of $(CH_3)_2{}^{15}NNO$. Frequencies are in MHz. Transitions labeled with [a] were used to obtain the rotational constants, with [b] for the nuclear quadrupole coupling constants. $\Delta\bar{\nu}=\bar{\nu}-\bar{\nu}_{calc}$, $\Delta\nu_{exp-calc}=\nu_{exp}-\nu_{calc}$.

$J_{K_{-1},K_1} \leftarrow J'_{K'_{-1},K'_1}$		$F \leftarrow F'$		ν_{exp}	$\bar{\nu}$	$\bar{\nu}_{calc}$	$\Delta\bar{\nu}$	ν_{calc}	$\Delta\nu_{exp-calc}$
2_{02}	1_{01} [a]				15,250.84	15,250.78	0.06		
		3	2	15,250.90					
2_{11}	1_{10} [a, b]				16,986.73	16,986.60	0.13		
		3	2	16,986.54				16,986.52	0.02
		2	1	16,987.16				16,987.19	−0.03
2_{12}	1_{11} [a]				14,108.03	14,107.92	0.11		
		3	2	14,108.02					
3_{21}	2_{20} [a, b]				24,432.08	24,432.17	−0.09		
		4	3	24,431.77				24,431.78	−0.01
		3	2	24,432.98				24,432.95	0.03
3_{03}	2_{02} [a]				22,209.59	22,209.61	−0.02		
		4	3	22,209.72					
3_{12}	2_{11} [a]				25,271.21	25,271.19	0.02		
		4	3	25,271.16					
3_{13}	2_{12} [a]				20,992.33	20,992.34	−0.01		
		4	3	20,992.36					
3_{22}	2_{21} [a, b]				23,320.82	23,320.89	−0.07		
		4	3	23,320.70				23,320.68	0.02
		3	2	23,321.26				23,321.27	−0.01
3_{13}	2_{02}				24,296.45	24,296.47	−0.02		
		4	3	24,296.79					
3_{22}	2_{11} [a, b]				36,661.86	36,661.86	0.00		
		4	3	36,662.24				36,662.26	−0.02
		3	2	36,660.50				36,660.47	0.03
2_{20}	1_{11} [b]				32,063.68	32,063.38	0.30		
		3	2	32,063.40				32,063.41	−0.01
		2	1	32,065.03				32,065.00	0.03
3_{21}	3_{30}				24,634.26	24,634.24	0.02		
		4	4	24,634.66					
3_{22}	3_{31}				26,002.83	26,002.84	−0.01		
		4	4	26,002.99					
4_{22}	3_{21}				33,280.94	33,281.10	−0.16		
		5	4	33,280.71					
4_{04}	3_{03}				28,670.47	28,670.64	−0.17		
		5	4	28,670.65					
4_{31}	3_{30} [b]				31,815.50	31,816.29	−0.79		
		5	4	31,815.25				31,815.29	−0.04
		4	3	31,816.18				31,816.13	0.05
4_{13}	3_{12}				33,251.39	33,251.42	−0.03		
		5	4	33,251.91					
4_{32}	3_{31} [b]				31,587.73	31,588.26	−0.53		
		5	4	31,587.53				31,587.56	−0.03
		4	3	31,588.29				31,588.25	0.04
4_{14}	3_{13}				27,721.99	27,722.11	−0.12		
		5	4	27,721.98					
4_{23}	3_{22}			30,861.18		30,861.50	−0.32		
5_{41}	4_{40} [b]				39,556.44	39,558.09	−1.65		
		6	5	39,556.20				39,556.19	0.01
		5	4	39,556.91				39,556.94	−0.03
5_{05}	4_{04}				34,890.80	34,891.10	−0.30		
		6	5	34,890.93					
5_{33}	4_{32}				39,544.63	39,545.60	−0.97		
		6	5	39,544.50					
5_{15}	4_{14}				34,308.98	34,309.19	−0.21		
		6	5	34,308.97					
5_{42}	4_{41} [b]				39,523.10	39,524.55	−1.45		
		6	5	39,522.87				39,522.85	0.02
		5	4	39,523.55				39,523.59	−0.04
5_{24}	4_{23}			38,211.18		38,211.75	−0.57		
5_{41}	5_{32} [b]				34,738.23	34,738.79	−0.56		
		6	6	34,738.56				34,738.57	−0.01
		5	5	34,737.58				34,737.56	0.02

pole coupling of the two ^{14}N-nuclei. The observed and calculated frequencies are listed in Table 1 and 2. For the calculations a rigid rotor fitting procedure has been employed.

In the spectra of $(CH_3)_2N^{15}NO$ and $(CH_3)_2{}^{15}NNO$ with only one coupling nucleus, the fine structure was resolved and the components were assigned. The spectra are listed in Table 3 and 4. From the splittings of the fine structure components the nuclear quadrupole coupling constants of the ^{14}N-nuclei were obtained. They are listed in Table 5. From our measurements it is not possible to obtain the quadrupole coupling tensors in their own principal axis system as χ_{ab} could not be determined.

Table 5. Nuclear quadrupole coupling constants of the ^{14}N-nuclei in N-Nitroso-dimethylamine (MHz).

	$(CH_3)_2{}^{14}N^{15}NO$	$(CH_3)_2{}^{15}N^{14}NO$
χ_{aa}	1.92 ± 0.1	1.83 ± 0.1
χ_{bb}	2.09 ± 0.1	-5.55 ± 0.1
χ_{cc}	-4.11 ± 0.1	3.72 ± 0.1

Structure

The rotational constants which have been evaluated so far are listed in Table 6. From the smallness of the c-coordinates of the atoms as obtained by applying Kraitchman's equations [8] we deduced a planar r_s-structure of the carbon-nitrogen frame. The central nitrogen *b*-coordinate value resulted to be imaginary. A calculation according to Krisher and Pierce [9] failed, due to the insufficient accuracy of the rotational constants. So we put the nitrogen on the *a*-axis. The structural data obtained in this way are listed in Table 7.

The r_0-structure listed in Table 7 was obtained with the assumptions that the molecule is planar and that the methyl groups have C_{3v}-symmetry with the bonding axis as symmetry axis and with identical C – H bonding distances and HCN-angles in both methyl groups. A calculation of the r_0-structure allowing for non-planarity of the molecule failed.

A further calculation of the structure was made using the method proposed by Nösberger et al. [10] and their program. The structure based on moments of inertia and differences of moments of inertia can be considered to be intermediate between the r_0- and r_s-structure. A great advantage of this method is the possibility to determine small coordinates more exactly. The calculated structure is given in Table 7.

Another way to confirm the planarity is to determine the variation of the pseudo-inertial defect Δ * from a planar to an out of plane conformation of the molecule. We have chosen the r_0-structure values from Table 7 as starting parameters and calculated Δ while deforming the molecule so that the two

Table. 6. Rotational constants, asymmetry parameters, moments of inertia and pseudo-inertial defects of N-Nitroso-dimethylamine. Rotational constants are in MHz, moments of inertia and pseudo-inertial defects in amu·Å². The conversion factor is 505 376 MHz·amu·Å². The given errors are the standard errors of the rigid rotor fitting procedure.

	syn-$^{13}CH_3CH_3NNO$	anti-$^{13}CH_3CH_3NNO$	$(CH_3)_2{}^{15}N^{14}NO$	$(CH_3)_2{}^{14}N^{15}NO$	$(CH_3)_2NNO$	$(CH_3)_2{}^{15}N^{15}NO$
A	8724.20 ± 0.13	8987.54 ± 0.04	9053.47 ± 0.03	8962.71 ± 0.07	9052.89 ± 0.08	8963.17 ± 0.07
B	4609.73 ± 0.06	4495.49 ± 0.03	4606.48 ± 0.01	4595.68 ± 0.03	4613.77 ± 0.04	4588.68 ± 0.03
C	3127.32 ± 0.05	3106.33 ± 0.03	3167.15 ± 0.01	3150.85 ± 0.03	3170.46 ± 0.03	3147.59 ± 0.03
I_a	57.9281 ± 0.0009	56.2307 ± 0.0003	55.8212 ± 0.0002	56.3865 ± 0.0004	55.8248 ± 0.0005	56.3836 ± 0.0004
I_b	109.6325 ± 0.0014	112.4184 ± 0.0008	109.7098 ± 0.0002	109.9676 ± 0.0007	109.5365 ± 0.0009	110.1354 ± 0.0007
I_c	161.6003 ± 0.0026	162.6923 ± 0.0016	159.5681 ± 0.0005	160.3935 ± 0.0015	159.4015 ± 0.0015	160.5597 ± 0.0015
$\varkappa$	-0.47027 ± 0.00007	-0.52759 ± 0.00003	-0.51096 ± 0.00001	-0.50280 ± 0.00004	-0.50928 ± 0.00004	-0.50440 ± 0.00004
Δ	-5.9603 ± 0.0016	-5.9568 ± 0.0009	-5.9629 ± 0.0003	-5.9606 ± 0.0009	-5.9598 ± 0.0010	-5.9593 ± 0.0009
Ref.	this paper	this paper	this paper	this paper	(1)	(1)

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* $\Delta = I_c - I_a - I_b$.

	r_s	r_0	r_* [10]
r_{N-N}	1.318 ± 0.006	1.329 ± 0.007	1.327 ± 0.001
r_{N-O}		1.233 ± 0.005	1.234 ± 0.001
$r_{N-C(syn)}$	1.463 ± 0.007	1.444 ± 0.005	1.443 ± 0.001
$r_{N-C(anti)}$	1.439 ± 0.005	1.452 ± 0.003	1.452 ± 0.001
r_{C-H} *		1.065 ± 0.002	1.065 ± 0.001
∢NNC (syn)	120.6 ± 0.5	121.4 ± 0.4	121.4 ± 0.1
∢NNC (anti)	117.7 ± 0.6	116.1 ± 0.4	116.0 ± 0.1
∢NNO		114.0 ± 0.1	114.3 ± 0.1
∢NCH *		111.2 ± 0.2	111.3 ± 0.1

* Assumed to be equal in both methyl groups.

Table 7. Structural parameters of N-Nitroso-dimethylnitrosamine (distances in Å, angles in degrees). The errors in the r_0- and r_*-structure are the standard errors of the fitting procedure. The errors in the r_s-structure are due to the uncertainties on the rotational constants.

methyl groups were raised symmetrically above the NNO-plane. The C – N distances and NNC-angles were kept constant. A second calculation was made rotating the dimethylamino-group around the N – N axis. In Fig. 2 the results are shown, on the left hand side for the out of plane deformation, on the right hand side for the rotation of the dimethylamino-group. In the middle of the figure the experimental values from Table 6 for each isotopic molecule are shown. This figure suggests that the molecule should be planar within an uncertainty of ± 1 degree.

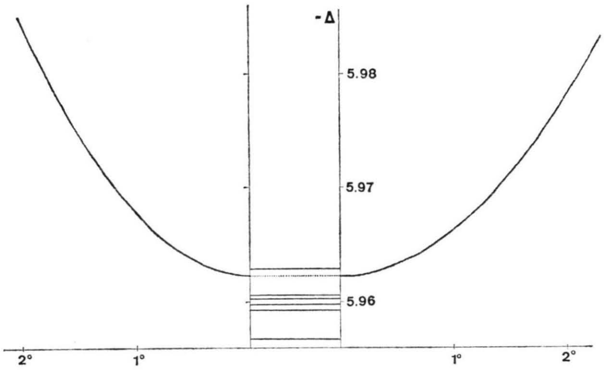

Fig. 2. Pseudo-inertial defect Δ (amu·Å^2) of N-Nitroso-dimethylamine *Left:* Raising the methyl groups above the NNO-plane with constant C—N distances and NNC-angles. *Middle:* Experimental values (continuous lines) and calculated value using the r_0-structure (dotted line). *Right:* Rotating the dimethylamino-group around the N—N axis.

In addition calculations of the bonding energies depending on twisting or bending the molecule were made using the INDO program of Pople and Beveridge [11]. These calculations confirmed the planarity of the molecular frame. Furthermore, the INDO calculations showed a barrier to internal rotation around the N – N axis of 21.9 kcal/mol. The experimental value, obtained by NMR spectroscopy [12], is 23.0 kcal/mol.

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