A Contribution to the Structure of N-nitroso-dimethylamine Microwave Spectra of Isotopic Substituted Forms

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Microwave spectra of trideuterated and perdeuterated N-nitroso-dimethylamine have been investigated. On the basis of these measurements an improved structure has been calculated.

Introduction

In two preceeding papers [1, 2], investigations on the microwave spectra of six isotopic species of N-nitrosodimethylamine (DMNA) have been reported.

A r_s-structure of the carbon-nitrogen frame and a r_0-structure of the molecule as well as the dipole moment and the nuclear quadrupole coupling constants of both nitrogen atoms were deduced from the measurements. A reasonable r_0-fitting was only possible by making the assumption of equivalence of both methylgroups because of the lack of informations and data on the deuterium substituted molecules. A knowledge of the complete structure of DMNA is important for medical purposes because of the cancerogenic properties of this class of substances.

With the purpose of performing a better determination of the structure, we report in this paper the results of investigations on the microwave spectrum of the following deuterium substituted molecules:

CH_3CD_3NNO-anti, CD_3CH_3NNO-syn,
$(CD_3)_2NNO$ and $(CD_3)_2{}^{15}N^{15}NO$.

With the obtained data a further approximation has been worked out to the whole structure of the molecule. However it must be emphasized here that a complete knowledge of the molecular structure would be available only after an investigation of the isotopic forms with partial deuterated methylgroups.

The necessarily simultaneous presence in the sample to be investigated of at least four isotopic species which cannot be separated chemically, makes the assignment of the microwave spectrum particularly difficult. Low intensity and overlap of lines prevent sometimes any assignment which seems to be feasible only after an improvement of the present microwave techniques.

We present these data as a help in future investigations particularly for the precalculation of the rotational spectrum of these d_1-substituted molecules.

Experimental

The samples were prepared according to Rademacher [3] and stored in traps at room temperature.

During the investigation the microwave cell was kept at about −50 °C. The sample pressure was about 0.2 Pa (3 mTorr). The microwave spectra have been recorded with a conventional Stark-effect spectrometer operating in the range 6–40 GHz, which has been described elsewhere [4, 5].

The measurements using the radiofrequency microwave doubleresonance (RFMWDR) technique [6] have been performed with a modification of the apparatus described in [7] and [8].

The error of the frequency measurements is believed to be less than ±0.03 MHz.

The frequencies of the measured lines are listed in Tables 1 to 4. The determination of the rotational constants has been made using the frequencies of the same type of transitions for all four molecules whenever possible. Other measured lines have been used for the control of the least square fit. The errors given in the tables are due mainly to the centrifugal distortion which was neglected. In Table 5 the results of the analysis of the spectrum are reported and for each group of data the corresponding correlation matrix is given.

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Table 1. Microwave Spectrum of DMNA-d_3-anti. The lines listed below the asterisk have not been used for the calculation of the rotational constants.

Transition $J_{K_-K_+} - J'_{K_-'K_+'}$	ν_{exp} (GHz)	ν_{calc} (GHz)	$\nu_{exp} - \nu_{calc}$ (kHz)
$1_{01} - 2_{02}$	13.73617	13.73626	−90
$1_{11} - 2_{12}$	12.75694	12.75734	−400
$2_{02} - 3_{03}$	20.10418	20.10453	−350
$2_{12} - 3_{13}$	19.01022	19.01056	−340
$2_{11} - 3_{12}$	22.57452	22.57431	210
$2_{21} - 3_{22}$	20.93057	20.93048	90
$2_{20} - 3_{21}$	21.75715	21.75643	720
$3_{21} - 3_{30}$	23.52308	23.52267	410
$3_{13} - 3_{22}$	18.36297	18.36362	−650
*			
$3_{31} - 4_{32}$	28.27624	28.27681	−570
$3_{30} - 4_{31}$	28.42398	28.42453	−550
$4_{41} - 5_{42}$	35.36498	35.36585	−970
$4_{40} - 5_{41}$	35.38364	35.38488	−1240
$4_{32} - 4_{41}$	33.85651	33.85704	−530
$4_{31} - 4_{40}$	33.68595	33.68655	−600
$5_{32} - 5_{41}$	33.17316	33.17396	−800
$5_{33} - 5_{42}$	33.81605	33.81713	−1080

Table 2. Microwave Spectrum of DMNA-d_3-syn. The lines listed below the asterisk have not been used for the calculation of the rotational constants.

Transition $J_{K_-K_+} - J'_{K_-'K_+'}$	ν_{exp} (GHz)	ν_{calc} (GHz)	$\nu_{exp} - \nu_{calc}$ (kHz)
$1_{01} - 2_{02}$	14.41963	14.41974	−110
$1_{11} - 2_{12}$	13.34548	13.34586	−380
$1_{10} - 2_{11}$	16.35306	16.35288	180
$2_{02} - 3_{03}$	20.74490	20.74521	−310
$2_{12} - 3_{13}$	19.77955	19.77973	−180
$2_{11} - 3_{12}$	24.21020	24.20967	530
$2_{21} - 3_{22}$	22.27420	22.27406	140
$2_{20} - 3_{21}$	23.80284	23.80291	−70
$2_{11} - 3_{22}$	31.53572	31.53504	680
$2_{12} - 3_{03}$	18.73179	18.73209	−300
$2_{12} - 3_{21}$	38.00378	38.00406	−280
$3_{22} - 3_{31}$	19.43252	19.43281	−290
*			
$3_{31} - 4_{32}$	30.36932	30.36940	−80
$3_{30} - 4_{31}$	30.82399	30.82418	−190
$4_{41} - 5_{42}$	38.07084	38.07135	−510
$4_{40} - 5_{41}$	38.16610	38.16720	−1100
$5_{33} - 5_{42}$	26.41486	26.41526	−400
$5_{32} - 5_{41}$	24.59864	24.59924	−600
$4_{32} - 4_{41}$	26.30235	26.30253	−180
$4_{31} - 4_{40}$	25.77937	25.77959	−220
$3_{12} - 4_{23}$	36.68270	36.68313	−430
$4_{04} - 5_{15}$	32.56911	32.56883	280

Table 3. Microwave Spectrum of DMNA-d_6. The lines listed below the asterisk have not been used for the calculation of the rotational constants.

Transition $J_{K_-K_+} - J'_{K_-'K_+'}$	ν_{exp} (GHz)	ν_{calc} (GHz)	$\nu_{exp} - \nu_{calc}$ (kHz)
$1_{01} - 2_{02}$	13.05414	13.05370	436
$1_{11} - 2_{12}$	12.10784	12.10771	130
$1_{10} - 2_{11}$	14.63814	14.63875	−610
$2_{02} - 3_{03}$	18.89603	18.89647	−440
$2_{12} - 3_{13}$	17.98203	17.98181	220
$2_{11} - 3_{12}$	21.72613	21.72598	150
$2_{21} - 3_{22}$	20.05995	20.05985	100
$2_{20} - 3_{21}$	21.22332	21.22322	100
$1_{10} - 2_{21}$	23.77813	23.77837	−240
$2_{21} - 3_{30}$	33.68874	38.68850	240
$2_{20} - 3_{31}$	38.31648	38.31657	−90
$2_{12} - 3_{03}$	16.79583	16.79593	−100
*			
$3_{31} - 4_{32}$	27.25839	27.25866	−270
$3_{30} - 4_{31}$	27.55816	27.55874	−580
$4_{41} - 5_{42}$	34.13879	34.13919	−400
$4_{40} - 5_{41}$	34.19279	34.19423	−1440
$4_{32} - 4_{41}$	25.31578	25.31562	160
$4_{31} - 4_{40}$	24.97039	24.97022	170
$5_{33} - 5_{42}$	25.35668	25.35712	−440
$5_{32} - 5_{41}$	24.11993	24.11986	70
$1_{11} - 2_{20}$	25.36411	25.36342	690

Table 4. Microwave Spectrum of DMNA-d_6-15-15. The lines listed below the asterisk have not been used for the calculation of the rotational constants.

Transition $J_{K_-K_+} - J'_{K_-'K_+'}$	ν_{exp} (GHz)	ν_{calc} (GHz)	$\nu_{exp} - \nu_{calc}$ (kHz)
$1_{01} - 2_{02}$	12.97607	12.97610	−30
$1_{11} - 2_{12}$	12.03422	12.03421	10
$1_{10} - 2_{11}$	14.56488	14.56469	190
$2_{02} - 3_{03}$	18.77414	18.77429	−150
$2_{12} - 3_{13}$	17.86970	17.86960	100
$2_{11} - 3_{12}$	21.61140	21.61160	−200
$2_{21} - 3_{22}$	19.94916	19.94918	−20
$2_{20} - 3_{21}$	21.12406	21.12407	−10
$1_{11} - 2_{20}$	25.15213	25.15205	80
$1_{10} - 2_{21}$	23.56362	23.56345	160
$3_{22} - 3_{31}$	18.34264	18.34277	−130
*			
$3_{30} - 4_{31}$	27.42262	27.42323	−610
$3_{31} - 4_{32}$	27.11578	27.11594	−160
$4_{40} - 5_{41}$	34.01895	34.02022	−1270
$4_{41} - 5_{42}$	33.96249	33.96309	−600
$4_{31} - 5_{32}$	34.88311	34.88388	−770
$4_{32} - 5_{33}$	33.91639	33.91700	−610
$4_{31} - 4_{40}$	24.62825	24.62866	−410
$4_{32} - 4_{41}$	24.98183	24.98231	−480
$5_{32} - 5_{41}$	23.76429	23.76500	−710
$5_{33} - 5_{42}$	25.02759	25.02839	−800

Table 5. Rotation Constants (in GHz) with correlation matrix, asymmetry parameter, moments of inertia (amu.Å^2), pseudoinertia defect. The conversion factor is 505,376 GHz.amu.Å^2. The fitting standard errors are given in parenthesis in units of the last figure.

DMNA-d_3-anti				
$A =$	8.371488 (93)	1.000		
$B =$	4.086571 (70)	0.171	1.000	
$C =$	2.890257 (63)	0.226	−0.435	1.000
$\varkappa =$	−0.563487 (70)			
$I_a =$	60.36872 (67)			
$I_b =$	123.6675 (21)			
$I_c =$	174.8550 (39)			
$\Delta =$	−9.1812 (45)			
DMNA-d_3-syn				
$A =$	7.551093 (62)	1.0000		
$B =$	4.464099 (42)	−0.107	1.000	
$C =$	2.960588 (41)	0.192	−0.447	1.000
$\varkappa =$	−0.344947 (47)			
$I_a =$	66.92753 (55)			
$I_b =$	113.2090 (10)			
$I_c =$	170.7012 (24)			
$\Delta =$	−9.4353 (27)			
DMNA-d_6				
$A =$	7.022607 (44)	1.000		
$B =$	3.976069 (55)	0.000	1.000	
$C =$	2.710547 (49)	−0.059	−0.686	1.000
$\varkappa =$	−0.413031 (57)			
$I_a =$	71.96416 (45)			
$I_b =$	127.1044 (18)			
$I_c =$	186.4480 (34)			
$\Delta =$	−12.6206 (28)			
DMNA-d_6-15-15				
$A =$	6.957073 (22)	1.000		
$B =$	3.957482 (22)	0.012	1.000	
$C =$	2.692243 (21)	0.130	−0.643	1.000
$\varkappa =$	−0.406663 (25)			
$I_a =$	72.64204 (28)			
$I_b =$	127.7014 (7)			
$I_c =$	187.7156 (15)			
$\Delta =$	−12.6279 (17)			

Discussion

The structure of DMNA with 11 atoms is determinated by $3N-6=27$ internal parameters.

This high number of parameters can be reduced assuming some constraints:

1. The frame is planar [2];
2. One of the hydrogen atoms of the methylgroup lies in this plane.

This reduces the number of structural parameters to seventeen as listed in Table 6. The molecular symmetry becomes C_s.

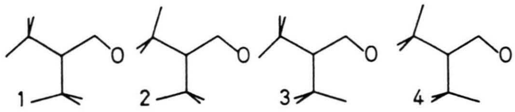

Fig. 1. Possible configurations of the methyl groups in DMNA.

As can be seen in Fig. 1 there are four configurations for the methylgroups obtained by a 60° rotation of each group.

A CNDO calculation gives the lowest energy value for the form 2 of Fig. 1 according to a preceeding evaluation of Rademacher and Stølevik [9].

A further experimental argument for the configuration 2 is given by Krebs and Mandt [10] who suggest this configuration for the anti-methylgroup in the solid DMNA at −130 °C.

r_0-structure. A large number of fitting calculations with different sets of variable parameters have been made for the four possible configurations of the methylgroups. The most reasonable results have been obtained for the cases 2 and 4 of Figure 1.

Taking into account the experimental results of Krebs and Mandt [10], and the theoretical calculations of Rademacher and Stølevik [9] and considering that a CNDO calculation, performed here, gave the best fit of the measured dipole moments for the configuration 2, we report in Table 6 only the best obtained r_0-structure refering to this configuration 2.

For this r_0-structure the value of the parameter 1, distance N-N, has been set equal to the value obtained for the r_s-structure [2] and C_{3v} symmetry for both methylgroups was assumed. Calculations in which the axis of the methylgroup was allowed to tilt, gave no reasonable results.

An examination of the data listed in Table 6 let us suspect a difference in the configuration of the methylgroups. However the large standard errors and the high value for the sum of the squared errors do not allow a reliable conclusion. This resulting structure is reported in Figure 2.

r^*-structure. Better results were obtained using a program [11] which fits the moments of inertia of the parent molecule and the differences between the moments of inertia of the parent molecule and that of the isotopic substituted molecules. Results for different types of calculations are reported in Table 6.

Table 6. List of Structures.

Parameters [a]	r_0-structure [b]	r^*-structure [c]		
		(i)	(ii)	(iii)
1. N_a-N_n	(1.3289)	1.3287 (32)	1.3180 (1)	1.344 (23)
2. N_n-O	1.243 (33)	1.2297 (59)	1.2133 (1)	1.229 (29)
3. N_a-N_n-O	113.5 (14)	113.83 (7)	113.75 (15)	114.3 (8)
4. N_a-C_c	1.442 (45)	1.4512 (17)	1.4443 (2)	1.435 (8)
5. $N_n-N_a-C_c$	122.6 (20)	121.59 (20)	121.28 (23)	120.7 (5)
6. N_a-C_t	1.441 (39)	1.4572 (23)	1.4580 (1)	1.452 (23)
7. $N_n-N_a-C_t$	115.3 (36)	115.84 (80)	116.23 (12)	114.6 (4)
8. C_c-H_i	1.081 (10)	1.1110 (67)	1.1231 (8)	1.126 (20)
9. C_c-H_o				1.119 (14)
10. $N_a-C_c-H_i$	109.1 (4)	107.44 (30)	107.63 (20)	108.4 (4)
11. $N_a-C_c-H_o$				106.9 (5)
12. $H_i-C_c-H_o$	—	(60.0)	(60.0)	58.59 (34)
13. C_t-H_i	1.076 (3)	1.0764 (80)	1.0942 (5)	1.075 (20)
14. C_t-H_o				1.077 (18)
15. $N_a-C_t-H_i$	113.2 (12)	110.22 (42)	109.55 (8)	110.8 (5)
16. $N_a-C_t-H_o$				110.0 (10)
17. $H_i-C_t-H_o$	—	(120)	(120)	119.76 (57)

[a] The meaning of the subscripts is: a → amine, n → nitroso, c → syn, t → anti, i → in plane, o → out of plane.

[b] a) The sum of the squared errors of rotational constants is 4.5204 $(\text{MHz})^2$. — b) Parameter 1 is fixed equal to the r_s-value of paper [2]. — c) C_{3v}-symmetry is assumed for both CH_3-groups.

[c] a) The sum of the squared errors of the inertia moments is: for (i) $12.886 \cdot 10^{-4}$ $(\text{amu.A}^2)^2$; for (ii) $16.730 \cdot 10^{-4}$ $(\text{amu.A}^2)^2$; for (iii) $12.626 \cdot 10^{-4}$ $(\text{amu.A}^2)^2$.
b) for (i) moments of inertia of the parent molecule and differences between the moments of inertia of the parent molecule and substituted molecules have been fitted, eleven parameters variable; for (ii) the same as (i) without parent molecule; for (iii) the same as (i) but with seventeen parameters variable.

[d] The units are Ångström (0.1 nm) for the distances and degrees for the angles. The errors are standard errors of the least square fitting procedure in units of the last figure.

A comparison among the three different sets of results shows, for the structure (iii) with 17 parameters fitted, some interesting characteristics.

From the parameters 8 to 17 an asymmetry in the structure of both methylgroups can be deduced.

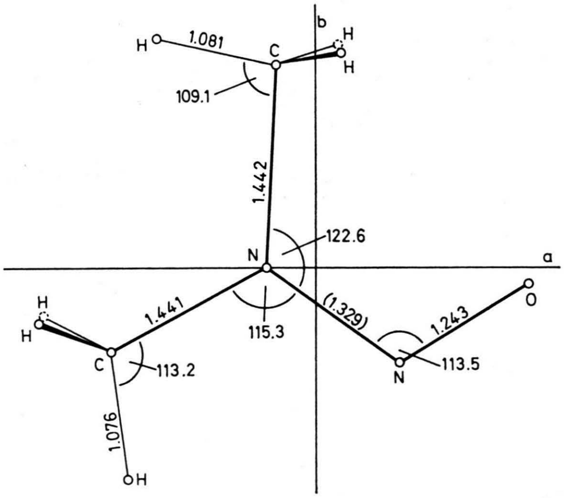

Fig. 2. r_0-structure. Distances in A; angles in degree.

The anti-methylgroup is less deformed than the syn-methylgroup as it may be expected from the smaller distance of the oxygen atom to the syn-group. So interactions seems to be stronger. However the structures (i) and (ii) are to be considered to be the most realistic according to the available experimental data. Structure (ii), which shows the smallest standard errors, is to be preferred in consequence of two reasons:

a) best fit of the pseudo-inertial defect variations [15] (amu A^2)

	(i)	(ii)	exp.
CH_3-syn	− 3.4168	− 3.4687	− 3.4575
CH_3-anti	− 3.1021	− 3.2084	− 3.2125

b) smallest total energy as results of a CNDO-calculation (6 kcal/mole smaller than (i)).

Therefore in Fig. 3 this structure is reported.

Recently V. Typke has proposed a new procedure [12] for the calculation of substitution structure (r_s-structures). His method is particularly useful in the case of simultaneous multiple substitutions as it is the case here.

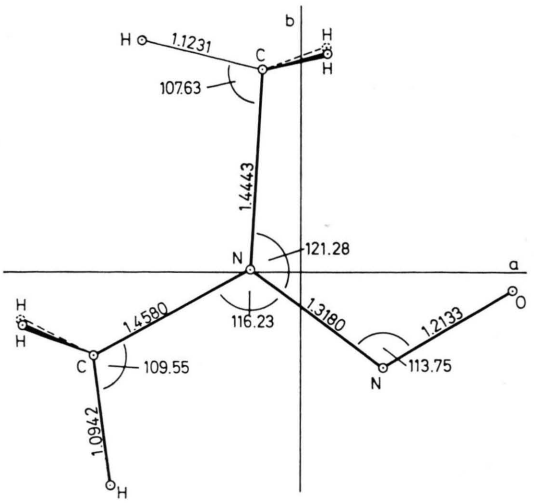

Fig. 3. r^*-structure. Distances in A; angles in degree.

However for a substitution structure (r_s-structure) as proposed by Kraitchman-Costain [13, 14], at least so many single isotopic substituted molecules as atoms in the molecule should be available. If it is not the case, the result is always an approximated r_s-structure.

We have tried to calculate the structure using the program RSSTR kindly given to us by V. Typke. Due to the incompletness of our present set of rotational constants we did not obtain convincing results. Nevertheless the same trend to a difference in the configuration of the methylgroups could be observed.

Conclusions

In this work deuterium substituted DMNA-molecules have been investigated for the first time. Differences in the configuration of the methylgroups with indication of an asymmetry have been found, an improved r^*-structure has been calculated with the consequence that the shortest intramolecular distances of N ... H and O ... H have been found in the range of 1.8–2.8 A.

Thus strong interactions are to be expected giving an argument in favour of structure differences between the methylgroups. Better informations can be obtained only by an investigation of the d-monosubstituted DMNA.

Acknowledgement

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