Nuclear Quadrupole Hyperfine Structure and Methyl Torsional Fine Structure in the Rotational Spectra of N,N-Dimethylformamide and N-Nitrosodimethylamine

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Dedicated to Prof. Dr. A. Klemm on the occasion of his eightieth birthday

The complicated nuclear quadrupole hyperfine structure and methyl torsional fine structure in the rotational spectra of N,N-dimethylformamide and N-nitrosodimethylamine have been studied using microwave Fourier transform spectroscopy. It has been found that both molecules are rather similar in terms of their parameters of methyl group internal rotation as well as in terms of their amino nitrogen quadrupole coupling constants.

Introduction

The first microwave studies on dimethylformamide (DMF), $(CH_3)_2NCHO$, and N-nitrosodimethylamine, or dimethylnitrosamine (DMNA), $(CH_3)_2NNO$, have been reported in 1973 by Elzaro et al. [1] and in 1972 by Scappini et al. [2], respectively. In the former work, the authors came to the conclusion that DMF has a planar heavy atom geometry and an intermediate barrier of about 1 kcal/mol to internal rotation of the *cis* methyl group. No nuclear quadrupole hyperfine structures in the spectra had been resolved.

The latter work on DMNA, and subsequent studies on several isotopomers by the same group [3, 4], showed that this molecule also has a planar skeleton, but high barriers to internal rotation of the methyl groups, as there was no resolvable torsional fine structure; on the other hand, for this molecule the quadrupole coupling constants for both of the nitrogen nuclei have been determined from analyses of the spectra of the mono-^{15}N substituted isotopomers.

Microwave Fourier transform (MWFT) spectroscopy offers the advantages of both superior resolving power and potentially higher sensitivity compared to conventional Stark spectroscopy. The present study was undertaken with the initial goal to exploit these advantages to fully resolve nuclear quadrupole hyperfine structures, in order to obtain coupling constants of high precision. It turned out later that the torsional fine structures also showed very interesting features, and that it was possible to obtain all the barriers to internal rotation of the methyl groups, i.e. for both methyl groups in both molecules.

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Experimental Methods

Both DMF and DMNA are rather common chemicals. We used commercial samples without further purification.

The static gas experiments were performed at temperatures of about -30 °C, and at pressures of about 0.1 Pa (0.8 mTorr). For the molecular beam experiments, the vapor above liquid DMNA at room temperature was diluted with argon at about 1 bar stagnation pressure.

The rotational spectra of both DMF and DMNA are dominated by numerous ^aQ-branch transitions. On the other hand, the highest ^aR-branch transitions within the range of our spectrometers (4–40 GHz) were the ones with $J, K_a = 5, 3-4, 3$. Only very few *b*-type transitions have been recorded because the ratio of the dipole moment components μ_b/μ_a is rather small in both molecules. In the molecular beam experiments on DMNA (see below), only the lowest R-branch transitions have been recorded.

The experimental work was carried out in three stages:

Initially, a fairly large number of ^aQ-branch transitions and the transitions $J, K_a, K_c = 1_{0,1}-0_{0,0}$ and

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Table 1. Observed frequencies of hyperfine structure components of rotational transitions of dimethylformamide, torsional species $\sigma_1\,\sigma_2 = 0\,0$. ν = observed frequencies (in MHz), $\Delta\nu$ = offsets from hyperfine free centre frequencies (in MHz), $\delta\Delta\nu$ = observed−calculated offsets (in kHz).

$J'\ K_a'\ K_c'$	$J''\ K_a''\ K_c''$	F'	F''	ν	$\Delta\nu$	$\delta\Delta\nu$
R-branch transitions:						
1 0 1	0 0 0	2	1	7 168.441	−0.103	0
		1	1	7 169.060	0.516	1
		0	1	7 167.513	−1.031	0
4 2 3	3 2 2	5	4	28 506.524	−0.089	1
		4	3	28 506.861	0.248	−1
		3	2	28 506.436	−0.177	1
5 1 5	4 1 3	6	5	32 019.782	−0.066	0
		5	4	32 020.033	0.095	0
		4	3	32 019.940	0.002	−1
Q-branch transitions:						
3 1 2	3 1 3	4	4	7 411.774	0.552	1
		3	3	7 409.569	−1.653	−1
		2	2	7 412.544	1.322	0
7 1 6	7 1 7	8	8	30 739.845	0.500	1
		7	7	30 738.134	−1.211	2
		6	6	30 740.089	0.744	−2
5 2 3	5 2 4	6	6	5 973.605	0.327	0
		5	5	5 972.429	−0.849	−1
		4	4	5 973.845	0.567	1
9 2 7	9 2 8	10	10	29 581.822	0.427	0
		9	9	29 580.397	−0.998	−1
		8	8	29 581.982	0.587	1
8 3 5	8 3 6	9	9	7 497.059	0.257	1
		8	8	7 496.196	−0.607	1
		7	7	7 497.167	0.364	−1
9 3 6	9 3 7	10	10	12 473.657	0.311	−1
		9	9	12 472.618	−0.728	1
		8	8	12 473.775	0.429	0

$2_{1,1}-1_{1,0}$ of DMNA were recorded using waveguide MWFT spectrometers in the frequency range 5.3–26.4 GHz [5–8]. The analysis of these transitions yielded relatively precise coupling constants and also torsional parameters for one of the methyl groups of DMNA, since most of the higher-K_a ^{a}Q-branch transitions clearly showed doublet splittings of all hyperfine components. It was at first not clear, which methyl group (*cis* or *trans* with respect to oxygen) was responsible for these splittings; in either case, the barrier to internal rotation had to be on the order of 2 kcal/mol.

To shed some light on this problem, in the second stage we studied the spectrum of DMF in more detail than had previously [1] been possible. Here, a *cis* methyl group torsional barrier of only about 1 kcal/mol had been determined by Elzaro et al. [1]. Our work in the frequency ranges 5.3–18 GHz [5–7] and 26.4–40 GHz [9] clearly revealed the hyperfine structures and the smaller *trans* methyl group torsional splittings. The measured transitions are given in Tables 1 and 2, the determined parameters (see next section) in Tables 3 and 4.

Quantum chemical ab initio calculations at the 4-31 G* level (program Gaussian 86 [10]) confirmed that the *cis* torsional barrier in DMNA should also be considerably lower than the *trans* barrier. These findings, together with the somewhat anomalous inertial defects in DMNA-h_6 and *trans* DMNA-d_3 found by Guarnieri and Nicolaisen [4], led us to the suspicion that DMNA might have a *rather low cis* methyl group torsional barrier, even lower than the corresponding barrier in DMF. In this case, the torsional fine structure splittings might have been so wide that the corresponding lines had eluded detection.

In the third stage, we therefore concentrated on the lowest R-branch transitions of DMNA and used our molecular beam (MB-) MWFT spectrometer [11, 12] to locate the missing torsional satellites. Because of the geometrical situation, a low barrier to internal rotation of the *cis* methyl group should mainly influence the effective B rotational constant; thus, the position of the transition $1_{1,1}-0_{0,0}$ (the frequency of which does not depend on B, and which had not been studied previously) should not be affected too much. Indeed, we found a pattern made up of the expected seven hyperfine components, each split into five torsional satellites (intensity ratio approx. 2:2:1:2:1). Subsequently, we also found torsional satellites for the low J ^{a}R-branch transitions. Here, the torsional splittings were between 40 and 90 MHz (Table 6)! The hyperfine patterns for the $J = 2$-1 transitions were very complicated (Table 5), each showing about a dozen identifiable hyperfine components, each of these in turn split into doublets ($\sigma_1 = 0$, $\sigma_2 = 0$, ± 1) plus triplets ($\sigma_1 = \pm 1$, $\sigma_2 = 0$, ± 1, ∓ 1); here, σ denotes the torsional sublevels [13]. The hyperfine patterns were in all cases virtually identical for all torsional sublevels.

Because these results were already sufficient to determine the *cis* methyl group torsional barrier (assuming reasonable values for the internal rotor's moment of inertia, and the angle between the internal rotation axis and the principal axis, from structural arguments), we decided not to reinvestigate the ^{a}Q-branch spectrum; for the expected huge splittings, model errors are likely to make the analysis of these lines unreliable.

Table 2. Hyperfine free centre frequencies of torsional fine structure components of rotational transitions of dimethylformamide. ν = centre frequencies of $\sigma_1\sigma_2 = 0\,0$ components (in MHz), $\delta\nu$ = deviations from frequencies calculated with constants from Table 3 (in kHz), $\Delta\nu$ = torsional splittings referred to $\sigma_1\sigma_2 = 0\,0$ components (in MHz), $\delta\Delta\nu$ = observed−calculated splittings (in kHz; primed: fit II, double primed: fit I).

J'	K'_a	K'_c	J''	K''_a	K''_c	σ_1	σ_2	ν	$\delta\nu$	$\Delta\nu$	$\delta\Delta\nu'$	$\delta\Delta\nu''$
1	0	1	0	0	0	0	0	7 168.544	−1			
						1	0			−0.763	−51	
2	1	1	1	1	0	0	0	15 576.159	0			
						1	0			−2.160	−26	
4	1	3	3	1	2	0	0	30 648.877	−11			
						1	0			−3.731	−138	
4	2	3	3	2	2	0	0	28 506.613	−16			
						1	0			−2.696	−59	
4	3	2	3	3	1	0	0	20 039.366	17			
						0	0			0.044		−10
						1	0			−2.808		−1
						1	1			−2.445		3
						1	−1			−3.097		−3
4	3	1	3	3	0	0	1	29 176.0909	10			
						0	0			−0.069		9
						1	0			−4.062		1
						1	1			−4.447		−2
						1	−1			−3.796		3
5	0	5	5	0	4	0	0	32 716.020	−15			
						1	0			−0.707	−27	
5	1	5	4	1	4	0	0	32 019.938	−18			
						1	0			−1.063	−49	
5	3	3	4	3	2	0	0	36 363.931	−9			
						1	0			−4.044	−58	
5	3	2	4	3	1	0	0	36 824.401	65			
						1	0			−5.008	−91	
5	0	5	4	1	4	0	0	31 193.928	−23			
						1	0			−2.121	−95	
3	1	2	3	1	3	0	0	7 411.222	−3			
						1	0			−4.214	−5	
4	1	3	4	1	4	0	0	12 230.036	7			
						0	1			−0.033		0
						1	0			−6.874	−77	
						1	±1			−6.909	−78	
5	2	3	5	2	4	0	0	5 973.278	8			
						1	0			−5.819	−58	
7	1	6	7	1	7	0	0	30 739.445	−79			
						0	1			−0.100		3
						1	0			−13.701	−126	
						1	±1			−13.802	−122	
7	2	6	7	0	7	0	0	34 508.149	30			
						0	1			−0.152		4
						0	1			−8.753	80	
						1	±1			−8.903	89	
7	2	5	7	2	6	0	0	15 978.785	−9			
						1	1			−13.092	−133	
9	2	7	9	2	8	0	0	29 581.455	−21			
						0	1			−0.060		−2
						1	0			−19.435	−237	
						1	±1			−19.495	−237	
8	3	5	8	3	6	0	0	7 496.803	27			
						1	0			−10.278	58	
9	3	6	9	3	7	0	0	12 473.346	28			
						1	0			−15.223	8	
12	3	9	12	3	10	0	0	33 869.485	16			
						1	0			−28.015	−323	
12	4	8	12	4	9	0	0	13 901.423	13			
						0	1			0.048		−5
						1	0			−21.452	42	
						1	±1			−21.389	52	
14	4	10	14	4	11	0	0	28 656.184	49			
						1	0			−33.414	−177	
15	5	10	15	5	11	0	0	14 810.234	0			
						0	1			0.084		−5
						1	0			−27.487	115	
						1	±1			−27.400	113	
17	5	12	17	5	13	0	0	30 306.055	31			
						0	1			0.086		−7
						1	0			−42.135	−7	
						1	±1			−42.049	−13	
18	6	12	18	6	13	0	0	15 299.120	−42			
						0	1			0.130		6
						1	0			−32.887	249	
						1	±1			−32.760	253	
20	6	14	20	6	15	0	0	31 926.558	6			
						0	1			0.155		9
						1	0			−50.469	–	
						1	±1			−50.304	–	
23	7	16	23	7	17	0	0	32 701.385	−41			
						0	1			0.203		6
						1	0			−57.870	–	
						1	±1			−57.680	–	
26	8	18	26	8	19	0	0	32 993.922	−44			
						0	1			0.240		−3
						1	0			−63.972	–	
						1	±1			−63.725	–	
29	9	20	29	9	21	0	0	32 865.773	44			
						0	1			0.278		−4
						1	0			−68.407	–	
						1	±1			−68.128	–	

Analysis

General

Nuclear hyperfine structures were analysed using a first order hamiltonian of the form $H = H_R + H_Q$ [14]. In the case of DMNA we used the "parallel" coupling scheme $I_1 + I_2 = I$, $I + J = F$. The coupling energies being very small compared to the rotational energies, the neglect of matrix elements of H_Q off-diagonal in the quantum number J was justified.

The torsional splittings in the spectrum of DMF, and the smaller splittings in the spectrum of DMNA, were analysed using a perturbational approach based on the high barrier approximation. The programs used (AC3IAM/FC3IAM) [15]) are based on the internal axis method and able to fit the parameters

Table 3. Effective rotational, quartic centrifugal distortion (Watson's A-reduction), and nitrogen quadrupole coupling constants of the $\sigma_1\sigma_2 = 0\,0$ torsional species of dimethylformamide.

A'	8925.516(19)	MHz [a]
B'	4203.8368(57)	MHz
C'	2964.7107(54)	MHz
Δ_J	0.68(12)	kHz
Δ_{JK}	5.27(26)	kHz
Δ_K	3.51(114)	kHz
δ_J	0.190(11)	kHz
δ_K	3.31(27)	kHz
χ_{aa} [b]	2.0614(16)	MHz
χ_- [b]	6.6673(19)	MHz
χ_{bb}	2.303(2)	MHz [c]
χ_{cc}	−4.364(2)	MHz [c]

[a] Numbers in parentheses are single standard deviations in units of the last significant digits.
[b] $\chi_- \equiv \chi_{bb} - \chi_{cc}$.
[c] derived parameters.

Table 4. Results of fine structure analyses of dimethylformamide. w_1 = Fourier coefficient in 10^{-4}, θ = angle between internal rotor axis and a principal inertial axis in degrees, I_α = moment of inertia of internal rotor in amuÅ^2, s = reduced potential barrier, V_3 = effective threefold potential barrier in cal/mol, σ = standard deviation of the fit, $\Delta\nu$ = mean torsional splitting.

Parameter	Fit I		Fit II
	trans	*cis*	*cis*
w_1	−0.1307(12)	−8.543(6)	−8.384(7)
θ	31.99(11)	87.75(6)	87.69(10)
I_α	3.2 [a]	3.2 [a]	3.2 [a]
s	61.96(58)	30.029(21)	30.209(25)
V_3	2207.(21)	1045.86(73)	1052.14(88)
σ	6 kHz		111 kHz
$\Delta\nu$	1.117 MHz		11.21 MHz

[a] assumed value.

(moment of inertia I_α, angle to principal axes θ, and first Fourier coefficient w_1 of the Mathieu eigenvalues) of two inequivalent internal rotors to the torsional splittings. Because of the approximative nature of this treatment, the splittings are usually reproduced with a precision of only about 1% of their value.

The torsionally perturbed low-J lines of DMNA were analysed using a more elaborate procedure, which included off-diagonal matrix elements in the torsional quantum number v via a Van Vleck-perturbational approach (program VC3IAM [16]). In this case, the rotational constants and torsional parameters were fitted simultaneously to the observed frequencies of Table 6. In all other cases, the centre frequencies of the nuclear quadrupole patterns of the lines belonging to the totally symmetric species, $\sigma_1\sigma_2 = 0\,0$ (Tables 2 and 8) were subjected to a fit of

Table 5. Frequencies of hyperfine structure components of rotational transitions of N-nitrosodimethylamine ($\sigma_1\sigma_2 = 0\,0$ torsional species), observed in a molecular beam. ν = observed frequencies (in MHz), $\Delta\nu$ = offsets from hyperfine free centre frequencies (in MHz), $\delta\Delta\nu$ = observed − calculated offsets (in kHz).

J'	K_a'	K_c'	J''	K_a''	K_c''	I'	F'	I''	F''	ν	$\Delta\nu$	$\delta\Delta\nu$
1	0	1	0	0	0	2	3	–	– [a]	7 784.106	−0.197	0
						2	2	–	–	7 784.989	0.686	−1
						2	1	–	–	7 783.013	−1.290	−2
						1	2	–	–	7 784.402	0.099	1
						1	1	–	–	7 783.814	−0.489	1
						1	0	–	–	7 785.287	0.984	3
						0	1	–	–	7 784.904	0.601	2
1	1	1	0	0	0	2	2	–	– [a]	12 222.219	−1.340	−1
						2	1	–	–	12 226.343	2.784	−2
						1	2	–	–	12 224.242	0.683	2
						1	1	–	–	12 221.715	−1.844	1
						1	0	–	–	12 222.733	−0.826	−5
2	1	2	1	1	1	2	4	2	3	14 124.889	−0.212	−1
						2	3	2	3	14 125.637	0.536	0
						2	2	2	2	12 127.513	2.412	3
						2	2	2	1	14 123.385	−1.716	0
						2	1	1	1	14 125.281	0.180	−5
						2	1	1	0	14 124.264	−0.837	2
						1	3	2	3	14 123.826	−1.275	−7
						1	3	2	2	14 125.340	0.239	4
						1	2	1	2	14 123.301	−1.800	−2
						1	2	1	1	14 125.830	0.729	1
						1	1	2	1	14 123.975	−1.126	2
						0	2	0	1	14 125.056	−0.045	−1
2	1	1	1	1	0	2	4	2	3	17 011.710	−0.265	2
						2	3	2	3	17 013.383	1.408	−9
						2	3	1	2	17 012.490	0.515	−3
						2	2	2	2	17 014.236	2.261	−2
						2	2	1	2	17 010.857	−1.118	3
						2	1	1	1	17 012.422	0.447	−2
						2	1	1	0	17 010.451	−1.524	−1
						1	3	2	3	17 011.076	−0.899	−4
						1	3	2	2	17 012.172	0.197	0
						1	2	1	2	17 009.701	−2.274	−2
						1	2	1	1	17 012.769	0.794	2
						1	1	2	1	17 011.333	−0.642	0
						1	1	1	0	17 013.818	1.843	−1
						0	2	0	1	17 011.874	−0.101	−3

[a] all sublevels are degenerate in 1st order.

effective rotational and quartic centrifugal distortion constants.

DMF

The different models which were used to analyse the data are of varying quality. Therefore we first determined the nitrogen quadrupole coupling constants using the lines of the totally symmetric torsional species ($\sigma_1, \sigma_2 = 0, 0$). In this fit, the hypothetical centre frequencies of the lines were treated as fit parameters.

J'	K_a'	K_c'	J''	K_a''	K_c''	$\sigma_1\sigma_2$	ν	$\delta\nu$	$\sigma_1\sigma_2$	ν	$\delta\nu$
1	1	1	0	0	0	0 0	12 223.559	−0.017	1 0	12 223.322	−0.014
1	0	1	0	0	0	0 0	7 784.303	0.118	1 0	7 715.865	0.458
2	0	2	1	0	1	0 0	15 270.090	0.401	1 0	15 188.800	0.170
2	1	2	1	1	1	0 0	14 125.102	0.711	1 0	14 087.900	−1.236
2	1	1	1	1	0	0 0	17 011.975	−0.173	1 0	16 952.340	−0.146

Table 6. Hyperfine free centre frequencies of fine structure components $\sigma_1\sigma_2 = 0\,0$ and $1\,0$ of rotational transitions of N-nitrosodimethylamine, ν = hyperfine free centre frequencies (in MHz), $\delta\nu$ = observed−calculated frequencies (in MHz).

Table 7. Hyperfine free centre frequencies of torsional fine structure components $\sigma_1\sigma_2 = 0\,0$ and splittings between components $\sigma_1\sigma_2 = 0\,0$ and $0\,1$ of rotational transitions of N-nitrosodimethylamine. − ν = centre frequencies (in MHz), $\Delta\nu$ = splittings referred to $\sigma_1\sigma_2 = 0\,0$ component (in MHz), $\delta\Delta\nu$ = observed−calculated splittings (in kHz).

J'	K_a'	K_c'	J''	K_a''	K_c''	ν	$\Delta\nu$	$\delta\Delta\nu$
5	1	4	5	1	5	20 625.34	−0.080	0
11	4	7	11	4	8	13 871.45	0.125	18
11	4	7	11	3	8	26 268.25	−0.200	−16
14	5	9	14	5	10	16 622.10	0.220	42
15	6	9	15	6	10	6 673.18	0.150	13
18	7	11	18	7	12	7 873.73	0.210	23
19	7	12	19	7	13	13 696.92	0.293	24
22	8	14	22	8	15	15 388.39	0.339	3
23	8	15	23	8	16	24 054.77	0.420	1
23	9	14	23	9	15	5 563.10	0.130	−51
25	9	16	25	9	17	16 997.32	0.435	36
26	10	16	26	10	17	6 250.74	0.210	−3
28	10	18	28	10	19	18 524.20	0.450	−6
29	11	18	29	11	19	6 908.76	0.230	−11

Table 8. Hyperfine free centre frequencies of torsional fine structure components $\sigma_1\sigma_2 = 0\,0$ of rotational transitions of N-nitrosodimethylamine. − ν = hyperfine free centre frequencies (in MHz), $\delta\nu$ = observed−calculated frequencies (in MHz) (see Table 10).

J'	K_a'	K_c'	J''	K_a''	K_c''	ν	$\delta\nu$
2	1	2	1	0	1	18 564.34 [a]	−0.47
2	2	0	2	1	1	13 615.73 [a]	−2.00
4	4	1	4	3	2	35 692.80 [a]	−2.11
4	4	0	4	3	1	35 427.84 [a]	−1.51
4	3	2	3	3	1	31 633.17 [a]	−0.12
4	3	1	3	3	0	31 863.18 [a]	−0.43
5	4	2	4	4	1	39 580.64 [a]	−0.43
5	4	1	4	4	0	39 614.10 [a]	−0.96
1	1	1	0	0	0	12 223.559	−0.521
5	1	4	5	0	5	21 186.500	−1.242
6	2	4	6	1	5	17 339.570	−0.797
11	4	7	11	3	8	26 268.250	0.284
1	0	1	0	0	0	7 784.303	0.068
2	0	2	1	0	1	15 270.090	0.069
2	1	2	1	1	1	14 125.101	0.135
2	1	1	1	1	0	17 011.975	0.036
3	2	2	2	2	1	23 352.630	−0.008
3	2	1	2	2	0	24 470.730	0.033
5	1	4	5	1	5	20 625.34	−0.080
6	2	4	6	2	5	13 233.010	0.057
7	2	5	7	2	6	19 868.735	−0.229
11	4	7	11	4	8	13 871.450	1.010
14	5	9	14	5	10	16 622.100	0.918
15	5	10	15	5	11	24 905.300	0.920
15	6	9	15	6	10	6 673.180	0.478
18	7	11	18	7	12	7 873.730	−0.018
19	7	12	19	7	13	13 696.920	−0.239
22	8	14	22	8	15	15 388.390	−0.989
23	8	15	23	8	16	24 054.770	−0.763
23	9	14	23	9	15	5 563.100	−0.565
25	9	16	25	9	17	16 997.320	−1.059
26	9	17	26	9	18	26 288.700	0.142
26	10	16	26	10	17	6 250.740	−0.454
28	10	18	28	10	19	18 524.200	0.976
29	11	18	29	11	19	6 908.760	0.969

[a] from [2].

These centre frequencies were then used to determine the rotational and quartic centrifugal distortion constants. These, and the coupling constants, are presented in Table 3.

The torsional splittings were evaluated from corresponding isolated hyperfine structure components. Because small (< 100 kHz) and large (> 50 MHz) torsional splittings occur (see Table 2), a fit of four torsional parameters (w_1 and θ for both methyl groups) to all measured splittings produced unreliable results for the parameters of the *trans* methyl group (which has a relatively high hindering potential and therefore produces small splittings on the order of the overall root mean square deviation of the torsional fit). We therefore used only the fully resolved R-branch transitions J, $K_a = 4, 3-3, 3$ and the splittings between the components $\sigma_1, \sigma_2 = 0, 0$ and $0, 1$ of a number of Q-branch transitions to determine the torsional parameters w_1 and θ of both methyl groups. The moments of inertia of both methyl groups were indeterminable and had to be fixed at assumed values. In a second fit, we included the remaining torsional splittings up to 50 MHz but kept the torsional parameters w_1 and θ of the *trans* methyl group fixed at the values from the first fit. The results for the potential barrier are significantly different in the two fits (Table 4); the remaining deviations in the second fit are, however, clearly systematic (see second last column of Table 2) and therefore less reliable than the results of the first fit.

Table 9. Spectroscopic parameters[a] of N-nitrosodimethylamine. s = reduced potential barrier, w_1 = first Fourier coefficient, (1) = amino nitrogen, (2) = nitroso nitrogen atom, $\chi_- \equiv \chi_{bb} - \chi_{cc}$. See also Table 4 for definitions of parameters.

A	9053.13(49) MHz[b]		
B	4596.93(18) MHz		
C	3170.39(17) MHz		
V_3(cis)	416.6 (7) cal/mol		
θ(cis)[c]	89.0°	$\chi_{aa}(1)$	2.0210(25) MHz
I_α(cis)[c]	3.16 amuÅ^2	$\chi_-(1)$	6.2783(56) MHz
s(cis)[d]	11.78(2)	$\chi_{bb}(1)$[d]	2.1287(31) MHz
w_1(trans)	−0.00001863(35)	$\chi_{cc}(1)$[d]	−4.1497(31) MHz
θ(trans)	29.7(13)°	$\chi_{aa}(2)$	1.9054(25) MHz
I_α(trans)[c]	3.16 amuÅ^2	$\chi_-(2)$	−8.9182(48) MHz
V_3(trans)[d]	2107. (38) cal/mol	$\chi_{bb}(2)$[d]	−5.4118(27) MHz
s(trans)[d]	58.4(11)	$\chi_{cc}(2)$[d]	3.5064(27) MHz

[a] The rotational constants in this table have been evaluated accounting for the torsional effects of the *cis*-methyl group, using the frequencies of Table 6.
[b] Numbers in parentheses are single standard deviations in units of the last digits.
[c] These parameters were held fixed in the fit.
[d] Derived parameter.

Table 10. Effective[a] rotational and centrifugal distortion constants (Watson's A-reduction) of the torsional species $\sigma_1\,\sigma_2 = 0\,0$ of N-nitrosodimethylamine.

	This work	Ref. [2]
A'	9053.74(15) MHz[b]	9052.89(8) MHz
B'	4613.91(11) MHz	4613.77(4) MHz
C'	3170.33(11) MHz	3170.46(3) MHz
Δ_J	0.7(71) kHz	–
Δ_{JK}	0.[c]	–
Δ_K	21.7(22) kHz	–
δ_J	1.086(26) kHz	–
δ_K	14.8(11) kHz	–

[a] Obtained using frequencies from Table 8.
[b] Numbers in parentheses are single deviations in units of the last significant digits.
[c] Parameter held fixed during the fit.

DMNA

In the case of DMNA, the problems mentioned above concerning the accuracy of the torsional model are even more severe. This is partly because the torsional effects, and also the model deficiencies, are greater for the *cis* methyl group of DMNA, and partly because some frequencies have been obtained with higher precision through the use of the molecular beam technique. Only these latter recordings were finally used to obtain the nitrogen quadrupole coupling constants for both nitrogen nuclei (Table 9), and the hypothetical centre frequencies of the quadrupole patterns of the torsional species σ_1, $\sigma_2 = 0, 0$ and $1, 0$ of the five lowest rotational transitions (Table 6). All Q-branch transitions, measured with the waveguide spectrometers, were only used to evaluate the torsional splittings between the components σ_1, $\sigma_2 = 0, 0$ and $1, 0$ and the centre frequencies of the σ_1, $\sigma_2 = 0, 0$-species. Nevertheless, because the torsional splitting of the b-type transition $1_{1,1} - 0_{0,0}$ was smaller than the residual root mean square deviation of a fit of the rotational constants plus two torsional parameters (V_3 and θ) to the centre frequencies obtained with the molecular beam instrument, we fixed one of the torsional parameters (θ) at the only value which reproduced the pattern of this crucial transition. This procedure, although statistically equivalent to the use of widely different weighting coefficients for data of comparable precision, is justifiable in this case since the deviations are largely introduced through model deficiencies, and probably proportional to the size of the torsional effects.

Results and Discussion

The most noteworthy result of this work is the resolution of an apparent dissimilarity between the two isoelectronic molecules DMF and DMNA: the potential barriers hindering internal rotation of the methyl groups are, contrary to earlier results, of comparable magnitude. For the *trans* methyl group, the reduced potential barriers are $s = 62.0(6)$ for DMF and 58.4(11) for DMNA; for the *cis* methyl group, these values are 30.03(3) for DMF and 11.78(2) for DMNA. The relatively low barriers for the *cis* methyl groups are probably caused by a cancellation effect: the leading terms in the contributions of the *trans* methyl group and the formyl/nitroso group to the hindering potential have opposite phases (because they are geometrically opposite to each other), so that only their difference is effective. The same is true for the *trans* methyl groups; however, here one of the two contributions is apparently dominant. The angles between the internal rotor axes and the principal inertial axes are in all cases in accordance with plausible structures; as there are as yet no reliable structural analyses, these angles can only be used unambiguously to identify the methyl groups (*cis* or *trans*).

A comparison of the two molecules can also be made in terms of the nitrogen quadrupole coupling

constants, in particular of the components χ_{cc} of the amino nitrogen atom. The values are $\chi_{cc} = -4.364(2)$ MHz for DMF, and $\chi_{cc} = -4.150(3)$ MHz for DMNA. Both values are considerably more positive than in trimethylamine ($\chi_{cc} = -5.39$ MHz [17]), and indicate significant delocalization of the electron pair towards the oxygen atom in the respective functional group. This effect appears to be even more pronounced in DMNA than in DMF, as indicated by the more positive value of χ_{cc}.

Finally, it is interesting to compare the inertial defects $\Delta = I_{aa} + I_{bb} - I_{cc}$ of the two molecules. Using the effective rotational constants of Tables 3 and 10, the values obtained are 6.38 amuÅ^2 for DMF, and 5.94 amuÅ^2 for DMNA (using the conversion factor 505 379 MHz amuÅ^2). The discrepancy is obvious, since in both cases two pairs of methyl protons are not coplanar with the heavy atoms. If one uses instead the rotational constants of DMNA from Table 9, which were obtained accounting for the torsional effects of the *cis* methyl group, the value of Δ is 6.36 amuÅ^2. This is much closer to the corresponding number for DMF. (There are also torsional effects on the rotational constants from both methyl groups in DMF, and from the *trans*-methyl groups in DMNA; these are, however, much smaller.) This shows that one has to account properly for torsional effects if structural conclusions are to be drawn. Therefore, the substitution structure of DMNA of [3, 4] needs a correction. It is possible that the heavy atom coordinates are not affected too much by the neglect of the torsional effects; the hydrogen coordinates, however, must be the subject of a further investigation.

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