Vibrational spectra and structure of *N,N*-dinitromethylamine

V. G. Avakyan,[a]★ ***V. A. Shlyapochnikov,***[b]★ ***B. S. Fedorov,***[c] ***V. N. Margolin,***[d] ***and V. V. Volkova***[a]

[a]*A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,*
29 Leninsky prosp., 117912 Moscow, Russian Federation.
Fax: +7 (095) 230 2224
[b]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328
[c]*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588
[d]*Scientific Research Institute of Plant Protection Chemicals,*
31 ul. Ugreshskaya, 109088 Moscow, Russian Federation

The vibrational (IR and Raman) spectra of *N,N*-dinitromethylamine were studied. The assignments of the bands were carried out using a comparison of spectra obtained in different aggregate states, invoking the results of normal coordinate analysis. The most probable symmetry of the molecule was shown to be C_s with a planar configuration of the $N(NO_2)_2$ moiety.

Key words: nitramines, vibrational spectra, *N,N*-dinitromethylamine.

The present work is devoted to the investigation of vibrational (IR and Raman) spectra of *N,N*-dinitromethylamine in different aggregate states. The normal coordinate analysis was performed for the purpose of assigning experimental vibrational frequencies and estimating the symmetry and structure of the molecule.

Experimental

N,N-Dinitromethylamine (DNMA) was synthesized according to the known procedure[1] and was purified by vacuum distillation, b.p. 33 °C (14 Torr), n_D^{20} 1.4470.

The Raman spectra were recorded on a Coderg T-800 laser Raman spectrometer using the Ar^+ laser line λ = 514.5 nm for excitation of the spectrum. The accuracy of $\Delta\nu$ measurement was within 2 cm^{-1}. The measurements of the depolarization ratio of the Raman lines were carried out with a 1/2 λ plate. A sealed glass capillary with a 2 mm diameter was used as a measuring cell for obtaining the Raman spectrum of the pure liquid. For recording the Raman spectrum of a crystalline DNMA sample, a small transparent Dewar flask was mounted in the cell compartment of the instrument, and a capillary with the substance was attached directly under the surface of liquid nitrogen.

The IR spectrum of crystalline DNMA in the 3600—400 cm^{-1} region was recorded on a Unicam SP-800 spectrometer with a resolution of ~1 cm^{-1}. The substance was depos-

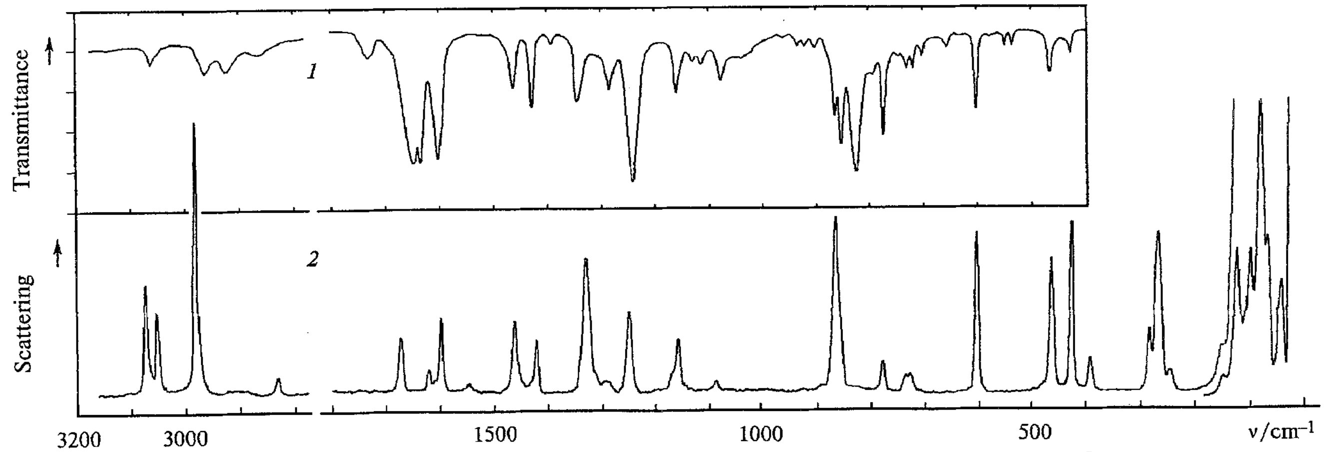


Fig. 1. IR (*1*) and Raman (*2*) spectra of crystalline *N,N*-dinitromethylamine at the temperature of liquid N_2.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1503—1507, August, 1995.

Table 1. Vibrational frequencies (ν/cm^{-1}) of *N,N*-dinitromethylamine

Vibration	IR			Raman			Calculation
	Crystal*	Glass**	Vapor	Liquid	Depolarization ratio	Crystal**	
ν_{16}	3060 w			3058 w	0.63	3074 m	3044
ν_1				3042 w	0.47	3048 m	3042
ν_2	2958 w	2940 vw		2968 vs	0.05	2975 vs	2965
$2\nu_4$	2922 w		2860 vw	2886 vw	p		
$\nu_4+\nu_5$						2829 w	
$2\nu_5$				2822 vw	p		
ν_{17}	1645 vs	1650 vs	1655 R vs 1650 P vs	1646 w			1646
	1634 vs		1630 s b			1622 w 1619 w sh	
ν_3	1604 vs	1604 vs		1608 w		1598 m	1610
$2\nu_{23}$				1548 w			
ν_4	1465 m	1460 m	1462 R sh	1452 m	0.77	1463 m	1475
ν_{18}			1455 Q ? w				1453
ν_5	1428 m	1426 m	1422 Q w 1416 P sh	1418 m	0.24	1420 m	1427
						1376 vw	
ν_6	1345 m	1340 m		1327 vs	0.09	1330 vs	1321
			1320 m			1311 sh	
	1290 w					1285 w b	
ν_{19}	1243 vs b	1250 vs	1258 vs	1255 w	0.85	1251 s	1273
ν_{20}	1174 m	1175 m	1168 R 1160 Q w 1155 P	1142 w		1166 sh 1156 m	1156
ν_7		1135 w	—	—		—	1071
ν_8	1082 w	1080 w	1084 R 1080 Q vw 1077 P	1080 vw		1086 w b	998
ν_{21}	922 w						970
ν_9	866 m 852 s	866 m 850 sh		859 vs	0.08	863 m	878
ν_{10}	825 vs b 795 vw	826 vs b 795 sh	825 vs b	825 vw sh			820
ν_{22}	784 s	780 s		779 w 744 vw		774 w	789
ν_{23}	731 w b 721 w	729 w				730 sh 725 w	729
	702 w	702 w		704 w			
ν_{11}	603 m	600 m		597 w	0.23	599 s	643
ν_{24}	467 m			466 w b		464 m	485
ν_{12}	428 w			433 s	0.28	427 m 395 w	459
ν_{25}				346 vw	0.75		332
ν_{13}						283 w	320
ν_{14}				250 m	0.48	264 s	194

Table 1. *(continued)*

Vibration	IR			Raman			Calculation
	Crystal*	Glass**	Vapor	Liquid	Depolarization ratio	Crystal**	
ν_{26}						245 w b 153 w	190
ν_{27}						124 m 108 sh 99 m	101
ν_{15}						89 s 77 s 65 w 44 m	93

* $T = -145$ °C. ** $T = 77$ K.

ited from the gas phase onto a KBr plate cooled by liquid nitrogen down to 77 K and placed in a vacuum cryostat. After the appearance of sufficiently intense bands of DNMA, the sample was annealed. The observed narrowing and splitting of IR bands indicated the conversion of the glass-like phase into the crystalline phase.

The IR spectrum of the gas phase of DNMA in the 4000—400 cm^{-1} region was recorded on a Specord M-82 spectrophotometer in a standard gas cell (l = 10 cm, KBr window) with a resolution of 0.2 cm^{-1}. The spectrogram representing the IR and Raman spectra of a crystalline DNMA sample obtained at a low temperature is shown in Fig. 1.

A normal coordinate analysis was carried out using a program set.[2] The structural parameters of the molecule were chosen in accordance with data of an electron diffraction study: R(NO) = 1.231, R(NN) = 1.48, R(CN) = 1.494, R(CH) = 1.09 Å (earlier,[3] a value of 1.121 Å was taken), angles NNN, ONO, NCH, and HCH are equal to 117.0, 132.0, 107.5, and 109.47°, respectively, γ = 42.2°, τ = 0° (earlier,[3] the value of τ was determined to be 0.12°). For comparison of the force constants of DNMA and other nitramines, a calculation was performed assuming equality of force constants of all four NO bonds. To achieve a better agreement between the calculated and experimental frequencies, the force constants of the initial approximation, as a basis for which we used the force constants of *N*-nitromethylamine,[4] were refined by the variation method. The assignment of frequencies is shown in Table 2.

Results and Discussion

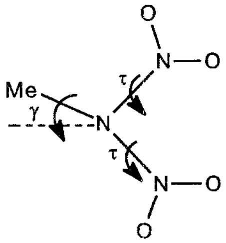
The maximum possible symmetry of a DNMA molecule is C_s with a planar or nonplanar configuration of the $\mathrm{N(NO_2)_2}$ group. With an asymmetric turn of the $\mathrm{NO_2}$ groups relative to the NNN plane, the symmetry is reduced to C_1. It is this structure that was considered[3] as initial during the electron diffraction study of DNMA. From the results of the investigation, it appears that the nitramine moiety is practically planar.

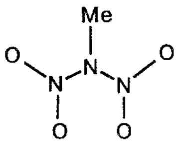
We have tried to deduce the symmetry of the molecule from a number of polarized lines in the Raman spectrum by comparing it to a prediction based on selection rules for the point group of C_1 and C_s symmetry. If the molecule belongs to the C_1 group, all lines must be polarized since they are assigned to the totally symmetric class. If the C_s symmetry is realized, then 27 normal vibrations are divided on irreducible representations of this group as follows: Γ = 15 A'+12 A". Then, according to the selection rules, all vibrations of the

Table 2. Assignment of frequencies of *N,N*-dinitromethylamine

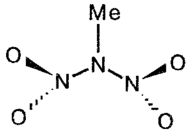
Symmetry species	Frequency No.	Vibration mode
A'	1	$\nu(\mathrm{CH_2})$, s
	2	ν(CH)
	3	$\nu(\mathrm{NO_2})$, as, in-phase
	4	$\alpha(\mathrm{CH_3})$, s
	5	$\alpha(\mathrm{CH_3})$
	6	$\nu(\mathrm{NO_2})$, s, in-phase
	7	β $\mathrm{CH_3}$, s
	8	ν(NN), s
	9	ν(CN)
	10	$\rho(\mathrm{NO_2})$, in-phase
	11	$\angle$NNO, s, in-phase
	12	$\angle$NNO, as, in-phase
	13	$\angle$CNN, s
	14	$\angle$NNN
	15	$\tau(\mathrm{NO_2})$, out-of-phase
A"	16	$\nu(\mathrm{CH_2})$, as
	17	$\nu(\mathrm{NO_2})$, as, out-of-phase
	18	$\alpha(\mathrm{CH_3})$, as
	19	$\nu(\mathrm{NO_2})$, s, out-of-phase
	20	$\beta(\mathrm{CH_3})$, as
	21	ν(NN), as
	22	$\rho(\mathrm{NO_2})$, out-of- phase
	23	$\angle$NNO, s, out-of-phase
	24	$\angle$NNO, as, out-of-phase
	25	$\angle$CNN, as
	26	$\tau(\mathrm{NO_2})$, in-phase
	27	$\tau(\mathrm{CH_3})$

Note. Abbreviations used: ν is stretching vibrations, α is deformation vibrations of HCH, β is deformation vibrations of NCH; ρ is out-of-plane vibrations of the $\mathrm{NO_2}$ group, τ is twisting vibrations, s — symmetric vibrations of the atomic group, as — antisymmetric vibrations of the atomic group.

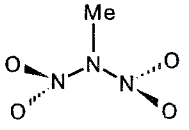




C_s-planar



C_s-nonplanar



C_1

molecule should be active in both the IR and Raman spectra, and only 15 lines assigned to the completely symmetric class A' should be the most intense and polarized in the Raman spectrum of liquid DNMA.

In the experimental Raman spectrum (see Table 1), ten polarized lines are observed, eight of which are assigned to the fundamentals and two of which correspond to overtones. Five lines appear to be completely depolarized. The fact that the number of polarized lines is greater than the number of depolarized lines indicates that the molecule belongs to the C_s symmetry group. Therefore, even if nitro groups in DNMA are turned by some angle, this angle provides the retention of the symmetry plane in the molecule passing through the CN bond and the bisector of the NNN angle.

For experimental assignment of the frequencies, the analysis of vibrational-rotational contours was carried out for the IR spectrum of gaseous DNMA. The application of the above geometry parameters for the calculation of rotational constants leads to the following values: $A = 0.123$, $B = 0.064$, $C = 0.044$ cm^{-1}. Calculation by known formulas[5] of the frequency separations of the P- and R-branches (Δ(PR)) necessary for identification of the vibrational-rotational band envelopes in the IR spectra of vapor DNMA gave Δ(PR) values equal to 12, 9, and 18 cm^{-1} for types A, B, and C bands, respectively. According to the orientation of the inertia moment axes in the molecule, the bands in the IR spectrum of vapor assigned to vibrations of A' class symmetry should have type A and C contours, whereas A" class vibrations should give rise to a B type contour.

Analysis of the IR spectrum of DNMA vapor showed that a pronounced splitting under three branches R, Q, and P (see Table 1) is observed for only two bands (1160 and 1080 cm^{-1}). However, the Δ(PR) values for them are significantly lower than those calculated by the Seth-Paul and Dijkstra formulas[5] (13 and 7 cm^{-1}, respectively). We assumed that the band at 1160 cm^{-1} should be assigned to the C type, having a higher Δ(PR) value and a more intense Q-branch, and the 1080 cm^{-1} band, having lower Δ(PR) values, is assigned to the A type. The band at 1650 cm^{-1} in the spectra of NMA and NDMA was assigned to the B type, because there is a minimum in the center of its contour and the observable Δ(PR) value amounts to 5 cm^{-1}, which, as should be expected, is less than the Δ(PR) value for type A and C bands.

The appreciable difference between the calculated Δ(PR) values and the observed values can be explained either by the fact that the real magnitudes of the rotational constants, whose function is Δ(PR), differ significantly from the constants calculated from the electron diffraction data, or by the possibility that the above-mentioned formulas give rise to overestimated Δ(PR) values. Since the average Δ(PR) separation, equal to 8.3 cm^{-1} and calculated by the formula $\Delta(PR) = [(A + B + C)T]^{1/2}$, where A, B, and C are the rotational constants of the molecule, T is the absolute temperature (see Ref. 6), are close to the observed magnitude in experiments, the latter assumption is more probable.

The interpretation of vibrational spectra suggested below is based on a comparison of the relative intensities of IR bands and Raman lines, results of measurements of Raman line depolarization ratios, analysis of IR band envelopes in spectra of vapor, reference data on the frequency assignments of nitramines,[4,7] as well as on the results of normal coordinate analysis of DNMA.

The major interest is in the frequencies of stretching vibrations of the nitramine group, which contains information on the character of intramolecular interactions.

From the formal viewpoint, the DNMA molecule has two pairs of nonequivalent NO bonds: axial bonds oriented parallel to the bisector of the NNN angle and angular bonds oriented at an acute angle to the bisector. According to this view, four vibrations of NO bonds are expected to be revealed in the spectra. In the present work we shall follow the tradition of considering vibrations of the nitro group as a whole, dividing them into symmetric and antisymmetric modes.

Comparison of IR and Raman spectra shows that a pair of bands is observed in the IR spectrum in the region of symmetric vibrations of the nitro groups (1350—1250 cm^{-1}). In the IR spectrum of crystalline DNMA, the band at 1250 cm^{-1} is more intense than the band at 1345 cm^{-1}. In the Raman spectrum of the crystal, the lines at 1251 and 1330 cm^{-1} correspond to the above IR bands, the former line being less intense than the latter. In the Raman spectrum of liquid DNMA, the 1327 cm^{-1} line is strongly polarized, but the 1251 cm^{-1} line is completely depolarized. These data allow one to assume that the higher frequency vibration should be assigned to the in-phase symmetric stretch of the NO_2 group and the low frequency vibration likely corresponds to out-of-phase vibrations.

In the range of antisymmetric vibrations of the NO_2 groups (above 1600 cm^{-1}), a pair of bands is also observed in the IR and Raman spectra. In the IR spectrum of gaseous DNMA, a very intense band at 1650 cm^{-1} with the B type contour and a weaker band at 1630 cm^{-1} are revealed. In the IR spectrum of crystalline DNMA, the 1645—1634 cm^{-1} doublet is also more intense in comparison with the second band at 1604 cm^{-1}. In contrast, the lower frequency line at 1608 cm^{-1} is revealed to be stronger than the doublet at 1627—1624 cm^{-1} in the

Raman spectrum. These data allow us to assume that the out-of-phase antisymmetric stretching mode of the $N(NO_2)_2$ group has a higher frequency, whereas a lower frequency conforms to an in-phase vibration of the same type.

However, consideration of the Raman spectrum of the liquid casts some doubt on the correctness of this conclusion, because the high frequency line at 1646 cm^{-1} has a higher intensity in comparison with the lower frequency line at 1608 cm^{-1}, the former line being somewhat more polarized than the latter. These characteristics permit us to assign the 1646 cm^{-1} line to in-phase vibrations and the 1608 cm^{-1} line to out-of-phase vibrations of the $N(NO_2)_2$ group. Hence, the assignment of the pair of antisymmetric modes appears to be contradictory, although we are inclined to the first assignment, in favour of which there are more experimental facts and literature data.[7]

The question of the complete assignment of the frequencies to the stretching vibrations of the NN and CN bonds (one CN and two NN bonds) remains open until the synthesis of labeled derivatives of DNMA because these vibrations are usually uncharacteristic due to the proximity of the atomic masses of carbon and nitrogen. But it is already clear that the most intense and polarized line at 859 cm^{-1} observed in the Raman spectrum of liquid DNMA, to which corresponds the very strong line at 860 cm^{-1} in the Raman spectrum of the crystal and the weak band at 866 cm^{-1} in the IR spectrum should be assigned to the totally symmetric stretch of the molecule as a whole with maximum contribution of the CN and NN coordinates.

In the IR spectrum of vapor, absorption is missing in this range, whereas the very strong band at 825 cm^{-1} is likely to be assigned to the out-of-plane deformation mode of the NO_2 group. Since data on the spectra of labeled derivatives of molecules are unavailable, it is difficult to identify the bands of the torsional vibrations of NO_2 groups, which is important for an estimation of the NN bond order.

The calculation of normal vibrations permitted us to more or less reliably carry out assignments of the rest of the DNMA vibrations. However, the uncertainty in the assignment of the in-phase and out-of-phase antisymmetric modes of the NO_2 groups has remained, because it has been ascertained that the opposite order of in-phase and out-of-phase ν_{as} (NO_2) and ν_s (NO_2) observed in experiments may be achieved only if the off-diagonal element describing the interaction of a pair of axial NO bonds enter into the force constant matrix. Without this element, the frequencies of the in-phase ν_{as} (NO_2) and ν_s (NO_2) are higher than the corresponding out-of-phase vibrations. Meanwhile, the availability of a nonnull element describing an interaction of stretching bond coordinates of "through-two-bonds" type is inherent in groups with a high degree of electron density delocalization.[8]

It may seem that this conclusion contradicts structure of DNMA, in the molecule of which an amine nitrogen atom has a significantly nonplanar configuration, which should result in lowering the degree of lone electron pair conjugation of the nitrogen atom with nitro groups. A decrease in the conjugation should cause an extension of the NN bonds. Indeed, in comparison, for instance, with a molecule of *N*-nitrodimethylamine (NDMA) (R(NN) = 1.382 Å),[3] which has a planar configuration of the amine moiety, the NN bond in DNMA is longer by almost 0.1 Å (R(NN) = 1.48 Å). However, the acceptor ability of the two nitro groups in DNMA remains high enough to promote the preservation of the planar configuration of the $N(NO_2)_2$ moiety, due to increase in the NN bond order as a consequence of electron density withdrawal from the amino group, followed by an appreciable delocalization of electron density within this moiety.*

At the same time, comparison of the force constants of the NN and NO bonds in molecules of NMA and NDMA[4] ($K(NN) = 9.8 \cdot 10^6$, $K(NO) = 10.8 \cdot 10^6$ cm^{-2}) and DNMA ($K(NN) = 9.85 \cdot 10^6$, $K(NO) = 12.6 \cdot 10^6$ cm^{-2}) shows that replacement of a hydrogen atom in NMA or a methyl group in NDMA with a nitro group is followed by a noticeable increase in the force constants of the NO bonds with practically invariable K(NN). This fact supports the assumption that the conjugation of a nitro group with a lone electron pair of the nitrogen atom in DNMA is, indeed, realized to a lesser degree than in molecules of NMA and NDMA. This results in an increase in the double bond character of the N and O atoms and, consequently, in an increase in K(NO) force constants.

---

* It is noteworthy that configurations of the $C(NO_2)_n$ moieties are nonplanar in the molecules of aliphatic *C*-di- and -trinitro compounds.

References

1. E. B. Hamel, G. Heights, and E. Olsen, US Pat. 3,428,667, 1969.
2. L. A. Gribov and V. A. Dement'ev, *Metody i algoritmy vychislenii v teorii kolebatel'nykh spektrov molekul* [*Methods and Algorithms of Calculations in the Theory of Vibrational Spectra of Molecules*], Nauka, Moscow, 1981 (in Russian).
3. N. A. Tarasenko, L. V. Vilkov, G. E. Slepnev, and Yu. A. Pankrushev, *Zh. Strukt. Khim.*, 1977, **18**, 953 [*J. Struct. Chem.*, 1977, **18** (Engl. Transl.)].
4. V. G. Avakyan, *Kolebatel'nye spektry i stroenie nitraminov* [*Vibrational Spectra and Structure of Nitramines*], Ph. D. (Chem.) Thesis, Moscow, 1971.
5. W. A. Seth Paul and G. Dijkstra, *Spectr. Acta*, 1967, **23A**, 2861.
6. T. Ueda and T. Shimanouchi, *J. Mol. Spectr.*, 1968, **28**, 350.
7. V. A. Shlyapochnikov, *Kolebatel'nye spektry alifaticheskikh nitrosoedinenii* [*Vibrational Spectra of Aliphatic Nitro Compounds*], Nauka, Moscow, 1989 (in Russian).
8. L. A. Gribov, V. A. Dement'ev, and A. T. Todorovskii, *Interpretirovannye kolebatel'nye spektry alkanov, alkenov i proizvodnykh benzola* [*Interpreted Vibrational Spektra of Alkanes, Alkenes, and Benzene Derivatives*], Nauka, Moscow, 1986 (in Russian).

Received December 26, 1994