Physical Chemistry

Structure and vibrational spectra of mononitroalkanes

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Structures and force fields for several mononitroalkane molecules were determined by *ab initio* quantum-chemical methods. The data obtained were used for calculation of the frequencies and modes of normal vibrations. Potentialities of different methods (RHF, MP2, and B3LYP) and basis sets for estimation of the structures and spectra were studied.

Key words: mononitroalkanes, quantum chemistry, molecular structure, force fields, vibrational spectra.

Although many researchers studied the structure of aliphatic nitro compounds, few experimental data[1—4] on the molecular structure of such compounds in the gas phase have been collected to date. The results of determination of the structure of molecules in the gas phase by two main methods, *viz.*, microwave spectroscopy (MW) and gas electron diffraction (ED), differ strongly in some cases.[1—4] * Only nitromethane[5] and trinitromethane[6] have been studied in the condensed state among relatively simple compounds of this class.

At the same time, a great body of experimental spectra is available in the literature. However, their interpretation is often far from unambiguity. Explanation of spectral features is often based on analogies and researcher´s intuition. As a result, data on only several reliably assigned frequencies of the whole massive of experimental results is used in practice. For nitro compounds, these are usually frequencies of antisymmetrical $\nu_{as}(NO_2)$ and symmetrical $\nu_s(NO_2)$ stretching vibrations of the nitro group.

Experimental data are usually insufficient and ambiguous, which impedes substantiated conclusions about specific features of individual structures and general structural and spectral regularities in the series of aliphatic nitro compounds in general and mononitroalkanes in particular. Therefore, studies of the structure and prop-

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[†] Deceased.

* The use of different experimental methods allows one to determine structural parameters with different physical senses. However, quantitative differences in bond lengths and angles, as a rule, are insignificant.

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erties of these compounds by quantum-chemical methods, which provide reliable information, are of considerable interest. For example, it has recently been shown that the results of calculations of the structural parameters and spectral frequencies for nitromethane almost coincide with experimental data.[7] Therefore, we can expect that the application of the theory to other nitro compounds would be justified. This assumption needed verification, which became one of the tasks of this work. Another task was to reveal the general structural and spectral regularities in the mononitroalkane molecules in the framework of a single approach.

In this work, we performed a series of quantum-chemical calculations for relatively simple mononitroalkane molecules, first of all, for those for which experimental data are available.

Calculation methods

Main calculations by the RHF, MP2, and B3LYP methods in different basis sets were carried out on an SGI Power Challenge computer using the GAUSSIAN-94 program package[8] at the Center for Computation of Chemical Research of the Division of General and Technical Chemistry, Russian Academy of Sciences, at the Institute of Organic Chemistry, RAS. All stationary points found for the nitroalkanes were characterized by the Hesse matrix.

Results and Discussion

Molecular structure. The results of quantum-chemical studies of the nitromethane molecule have been discussed in detail.[7] In this work, we present only our calculation data for the $MeNO_2$ structure by the B3LYP method in different basis sets. The task of these calculations was to reveal the influence of the basis on the determination accuracy of structural parameters.

The data in Table 1 show that this effect becomes small beginning from the 6-31G(d) basis set. For bond lengths (Å), changes are usually in the third decimal place, whereas for angles they are ≤1°. Thus, the geometry of molecules of aliphatic mononitro compounds can presumably be estimated satisfactorily in the 6-31G(d) basis set.

The nitroethane molecule was the next object to be studied. The experimental MW [10] and ED [11] data for this molecule and the corresponding values calculated by different methods are presented in Table 2.

As can be seen in Table 2, the structural parameters of nitroethane obtained by the MW and ED methods somewhat differ. The greatest difference is observed for the C—N bond length, namely, 0.04 Å. The results of the B3LYP, RHF, and MP2 calculations in the 6-311++G(d,p) basis set also differ, although this difference is lower (0.024 Å). The results of RHF calculations are nearest to the experimental values (MW) followed by the MP2 and then B3LYP data. Comparison of the calculation with the ED results exhibits the qualitatively analogous situation, and only the difference between the theory and experiment is greater.

The calculated C—C bond length is the same for all three methods and differs from experiment (MW) by 0.026 Å. The N—O bond length, according to the B3LYP data, virtually coincides with experiment but it is some-

Table 1. Structure of the nitromethane molecule*

Parameter	B3LYP calculation in different basis sets							Experiment[9]
	6-31 G(d)	6-311 G(d,p)	cc-pvtz	6-311++ G(d,p)	6-311++ G(3df,3dp)	6-311++ G(df,p)	6-311++ G(2dp)	
Bond length/Å								
C—H(1)	1.091	1.090	1.088	1.090	1.087	1.090	1.089	1.089
C—H(2)	1.088	1.086	1.084	1.086	1.084	1.086	1.085	1.089
C—H(3)	1.091	1.086	1.084	1.086	1.084	1.086	1.085	1.089
C—N	1.500	1.503	1.499	1.503	1.498	1.501	1.498	1.489
N—O(1)	1.226	1.220	1.218	1.221	1.218	1.220	1.221	1.224
N—O(2)	1.227	1.220	1.218	1.221	1.218	1.220	1.221	1.224
Angle/deg								
C—N—O	117.7	117.0	117.1	117.2	117.1	117.2	117.2	117.4
O—N—O	126.0	126.0	125.8	117.2	125.7	125.6	125.7	125.3
H—C—N	108.4	106.7	106.7	106.5	106.5	106.6	106.5	107.5
H—C—N	107.2	108.0	108.1	108.0	108.1	108.1	108.1	107.5
H—C—N	107.1	108.0	108.1	108.0	108.1	108.1	108.1	107.5
H—C—H	112.2	112.9	112.9	113.0	113.0	112.9	113.0	107.5
H—C—H	112.0	110.6	110.4	110.5	110.4	110.5	110.4	107.5
H—C—H	109.7	110.5	110.4	110.5	110.4	110.5	110.4	107.5

* In the equilibrium conformation, one of the CHN planes is perpendicular to the CNO_2 plane.

Table 2. Structure of the nitroethane molecule*

Parameter	Experiment		Calculation in 6-311++G(d,p) basis set		
	MW [10]	ED [11]	B3LYP	RHF	MP2
Bond length/Å					
C—C	1.540	—	1.514	1.514	1.514
C—N	1.500	1.46±0.02	1.523	1.499	1.507
N—O(1)	1.220	1.21±0.02	1.220	1.184	1.230
N—O(2)	1.220	1.21±0.02	1.222	1.188	1.230
Angle/deg					
C—N—O(1)	116.5	—	118.6	118.8	118.6
C—N—O(2)	116.5	—	116.0	115.9	115.9
O—N—O	127.0	127.5	125.5	125.3	125.5
C—C—N	—	—	107.7	113.6	112.9
Symmetry group of molecule	C_s	C_s	C_s	C_1	C_1

* Here and in Tables 3 and 4 we did not include the data on the C—H bond lengths and H—C—H angles.

what overestimated in MP2 and strongly underestimated in RHF. The O—N—O angle is the same being determined from the MW and ED data, and the values calculated by different methods are close. The difference between the theory and experiment is ~1.5°. For the other angles, it is difficult to compare the theory and experiment because the ED data are insufficient.

For the Pr^iNO_2 molecule, the bond lengths obtained by the MW [12] and ED [13] methods also somewhat differ (Table 3). The maximum difference for the C—C bond is 0.015 Å. The difference is somewhat smaller for the C—N bond and minimum (0.008 Å) for the N—O bond. The scatter of calculated values for the C—C and C—N bonds is small and close by the order of magnitude to similar data for nitroethane. The situation is somewhat worse for the N—O bond length, which is noticeably underestimated in the RHF method. The experimental and calculated angles are, as a whole, in good accordance.

Table 3. Structure of the 2-nitropropane molecule

Parameter	Experiment		Calculation in 6-311++G(d,p) basis set		
	MW [12]	ED [13]	B3LYP	RHF	MP2
Bond length/Å					
C(1)—C(2)	1.533±0.006	1.518(10)	1.525	1.523	1.522
C—N	1.508±0.018	1.518(10)	1.532	1.506	1.507
N—O	1.218±0.015	1.226(2)	1.222	1.187	1.233
Angle/deg					
C—N—O	116.8±1.5	117.3(0.2)	117.4	117.4	117.3
O—N—O	—	125.4(0.3)	125.2	125.1	125.3
C—C—N	108.9±1.7	109.2(0.9)	108.5	108.6	108.4
C—C—C	—	113.5(1.7)	113.7	113.8	113.1
N—C—H	—	106.4(6.1)	103.3	—	—
Symmetry group of molecule	C_s	C_1	C_s	C_s	C_s

Table 4. Structure of the 2-methyl-2-nitropropane molecule

Parameter	Experiment, ED [13]	Calculation in 6-311++G(d,p) basis set		
		B3LYP	RHF	MP2
Bond length/Å				
C(1)—C(2)	1.533(15) [1.530±0.02]*	1.533	1.530	1.526
C—N	1.533(15)	1.561	1.529	1.521
N—O(1)	1.240(2)	1.222	1.188	1.243
N—O(2)	1.240(2)	1.220	1.186	1.243
Angle/deg				
C—N—O(1)	—	116.6	116.7	116.5
C—N—O(2)	—	118.6	118.9	119.0
O—N—O	122.2(0.6)	124.7	124.5	124.5
C—C—N(1)	—	106.0	106.3	106.3
C—C—N(2)	—	108.9	109.3	109.1
C—C—C(1)	110.9(1.1)	111.9	111.5	111.7
C—C—C(2)	110.9(1.1)	111.7	111.7	111.4
Symmetry group of molecule	C_1	C_s	C_s	C_s

* MW.[14]

The MW experimental data for the 2-methyl-2-nitropropane are incomplete.[14,15] Therefore, we compared the ED results and calculation (Table 4). As can be seen, the C—C and C—N bond lengths are most successfully reflected by the RHF calculation, and the MP2 method is optimum for N—O. These methods give approximately the same description for bond angles.

Consideration of all obtained values (including the parameters of the $MeNO_2$ molecule) suggests that the accuracy of calculation of the geometric parameters of the mononitroalkane molecules by the modern quantum-chemical methods is close to that of the experimental determination. Thus, experimental data can be supplemented by calculation results.

Moreover, different experimental methods give structural parameters with different physical senses. Therefore, calculation methods for determination of the equilibrium structure have certain advantages in analysis of the structural regularities.

We also calculated the molecular structures of several nitro compounds for which experimental data are lacking, namely, Pr^nNO_2 and Bu^nNO_2 (Table 5). The latter molecules required rotamerism to be taken into account. *trans*-Isomers turned out to be more stable. The main structural parameters are either the same as those for the previously studied molecules or differ insignificantly.

All calculation data for the molecular structures were considered together. Figure 1 illustrates the general regu-

Table 5. Calculations of the structures of the *n*-nitropropane and *n*-nitrobutane molecules by the B3LYP [6-31G(d)] method

Parameter	*trans*-Pr^nNO_2	*trans*-Bu^nNO_2
Bond length/Å		
N—O	1.227	1.227
N—O	1.227	1.227
C—N	1.515	1.516
C—C(1)	1.521	1.520
C—C(2)	1.534	1.537
C—C(3)	—	1.532
Angle/deg		
C—N—O(1)	118.5	118.5
C—N—O(2)	116.0	115.9
O—N—O	125.5	125.5
C—C—N	113.8	113.9
C—C—C(1)	111.0	111.3
C—C—C(2)	—	112.4

larities in the mononitroalkane structures by the C—N, C—C (C—C is the closest to the nitro group), and N—O bond lengths. The diagrams show (see Fig. 1) that changes in the bond lengths in the mononitroalkane series are small. The maximum of changes is in the C—N bond, being of at most 0.06 Å, mainly in the case of the strongly sterically hindered Bu^tNO_2 molecule. We assume that the C—N bond elongation is due to the steric effect.

The bond angles of molecules in the considered series of compounds change insignificantly.

Based on this consideration, we conclude that the structural parameters of the nitro groups and their nearest environment in the mononitroalkane molecules are to some extent conservative. Thus, the structures of other compounds of this class can be predicted with a high probability. The main structural differences are determined by the conformational peculiarities of internal rotation barriers about the C—N and C—C bonds. Experiments and additional calculations should be performed to reveal these questions.

Spectra of molecules. The authors of a recent work used nitromethane as example to show the advantages of the B3LYP method in vibrational spectroscopy over other quantum-chemical methods. The B3LYP method predicts frequencies in the vibrational spectrum with an average error of ~2% without the use of any scaling factors of the force fields.[7]

In continuation of quantum-chemical studies, we first considered the methodological aspects of various calculation approaches to determination of frequencies in vibrational spectra of aliphatic nitro compounds.*

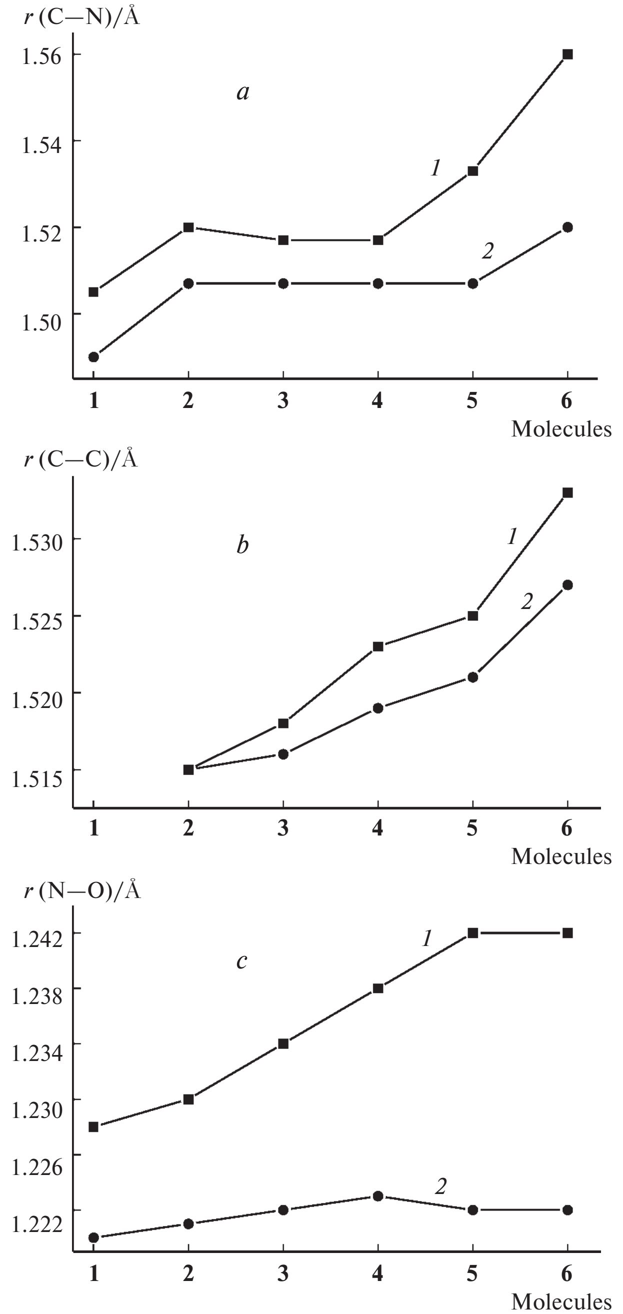

Fig. 1. Diagram for changing C—N (*a*), C—C (*b*), and N—O (*c*) bond lengths in the molecules of aliphatic nitro compounds $MeNO_2$ (**1**), $EtNO_2$ (**2**), Pr^nNO_2 (**3**), Bu^nNO_2 (**4**), Pr^iNO_2 (**5**), and Bu^tNO_2 (**6**): calculations by B3LYP (*1*) in the 6-311++G(d,p) (**1**, **2**, **5**, **6**) and 6-31G(d) (**3**, **4**) basis sets and MP2/6-311++G(d,p) (*2*) method.

The main objects of the study were $MeNO_2$, $EtNO_2$, Pr^iNO_2, and Bu^tNO_2. These compounds were chosen because they have been characterized by the sufficient structural and spectral data.

Nitromethane. Using the nitromethane molecule, we continued the methodological studies, namely, revealed

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* We have previously[15—18] shown that nitramines and nitrobenzene require the introduction of scaling factors to be calculated by the RHF and MP2 methods.

Table 6. Average ($\Delta\nu_{av}$) and maximum ($\Delta\nu_{max}$) errors of calculations of the frequencies for nitromethane in different basis sets (B3LYP)*

Basis	$\Delta\nu_{av}$	$\Delta\nu_{max}$
	%	
6-311++G(2dp)	1.84	3.70
6-311++G(df,p)	2.02	3.99
6-311++G(d,p)	2.15	4.00
6-311++G(3df,3dp)	2.35	4.02
cc-pvt2	2.20	3.85
6-311G(d,p)	2.34	4.22
6-31G(d)	3.14	6.21

* From 14 frequencies ignoring the torsion vibration.

the influence of the basis set on the accuracy of determination of spectral frequencies. The main method used was B3LYP.

Some results of calculations are presented in Table 6, *viz.*, average ($\Delta\nu_{av}$) and maximum ($\Delta\nu_{max}$) errors of calculation of the nitromethane frequencies by the B3LYP method in different basis sets.

As follows from Table 6, since some step extension of the basis set looses efficiency. The best result was obtained in the 6-311++G(2dp) basis set: $\Delta\nu_{av}$ = 1.84%, $\Delta\nu_{max}$ = 3.7%. The last value concerns the frequencies of stretching C—H vibrations. The error in the frequency of the stretching antisymemtrical vibration $\nu_{as}(NO_2)$ is also significant.

The frequencies obtained in each particular variant of calculation somewhat differ. The differences are due to slight differences in the force constants. For example, the diagonal force constant of the N—O bond (F_{NO}) is 10.309 and 10.892 in the (6-311++G(2dp)) and 6-31G(d) basis sets, respectively. It was found that such differences virtually have no effect on the vibration mode, and the 6-31G(d) basis set suffice to make spectral assignments.

The $\nu_{as}(NO_2)$ frequency can serve as a tentative criterion of goodness for spectra of the nitro compounds (Fig. 2). This frequency smoothly changes with the basis set change. In experiment for $MeNO_2$ $\nu_{as}(NO_2)$ = 1584 cm^{-1}, and in calculations it varies from ~1607 to 1689 cm^{-1}. Such a regularity is not observed for other frequencies, especially for the frequency of the torsion vibration of the C—NO_2 group (τ_{NO_2}). Note that in the $MeNO_2$ molecule the rotation about the C—N bond is virtually free, the barrier is ~6 cal mol^{-1}, and τ should be lower than 5 cm^{-1}. It is overestimated in all variants of calculation.

Nitroethane. The problem of interpretation of the spectrum was primary for nitroethane, unlike nitromethane. Quantum-chemical studies of this nitroalkane have not been performed to date. The experimental spectra of $EtNO_2$ were studied several times (see, *e.g.*, Refs. 19—21), including those for its isotopomers. The positions of intense bands in the spectra of the $EtNO_2$ and $MeNO_2$ molecules are close. Some distinctions were found for medium and weak bands. The available experimental data and analogies to the spectra of nitromethane were used for the assignment of vibrational frequencies of the $EtNO_2$ molecule. Based on calculation of the frequencies and modes of normal vibrations, the authors[19] proposed the quantitative interpretation of this spectrum. However, although this interpretation reflects the apparent similarity of the spectra of $MeNO_2$ and $EtNO_2$, it cannot be considered rigid and reliable. In this work, we used alternative methods to prove the interpretation of the spectra.

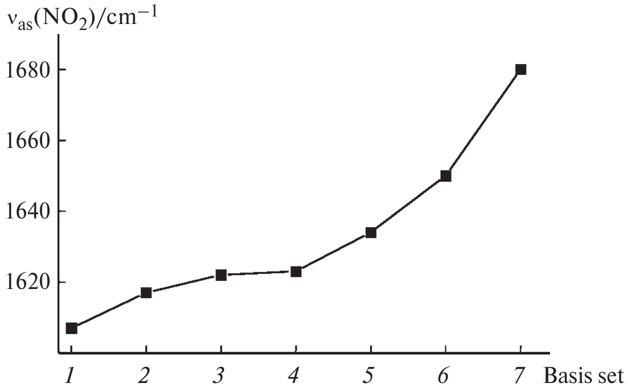

Fig. 2. Diagram for the change in the frequency of the stretching asymmetrical vibration $\nu_{as}(NO_2)$ for nitromethane calculated (B3LYP method) in different basis sets: 6-311++G(2dp) (*1*), 6-311++G(df,p) (*2*), 6-311++G(d,p) (*3*), 6-311++G(3df,3dp) (*4*), cc-pvtz (*5*), 6-311G(d,p) (*6*), and 6-31G(d) (*7*).

We determined the force fields of the nitroethane molecule by the RHF, MP2, and B3LYP methods. The frequencies and modes of vibrations for $EtNO_2$, $CD_3CH_2NO_2$, and $C_2D_5NO_2$ were calculated using the quantum-chemical force fields and structural data. As expected, B3LYP [6-311++G(d,p)] gives a good agreement between the theory and experiment for the spectra of nitroethane and its isotopomers. Some data obtained are presented in Table 7. The average deviation of the theory from experiment ($\Delta\nu_{av}$) is ~2%. The MP2 and RHF methods exhibit worse results on frequencies and require the use of scaling factors. The frequencies of nitroethane were assigned from analysis of the vibration modes and potential energy distribution (PED) over vibrations, which were obtained using the quantum-chemical force fields. Despite the differences between these fields (RHF, MP2, and B3LYP in the same basis), the modes of the corresponding vibrations differ insignificantly.

The use of calculated intensities for the assignment of spectral frequencies is of doubtful value. A small set of

Table 7. Spectra of $C_2H_5NO_2$ and $C_2D_5NO_2$*

$C_2H_5NO_2$				$C_2D_5NO_2$		
Experiment (gas)		Calculation**		Experiment, IR (gas)	Calculation**	
IR	Raman	ν	PED		ν	PED
1576 v.w	1556 dp	1619	91 NO	1568 v.s	1612	94 NO
1471 m	1463 dp	1500		1379 s	1412	74 NO, 12 CN
1448 m	1437 dp	1485		1188 m	1211	46 CC
1448 m		1477		1080 v.w	1092	
1396 s	1394 p	1430	27 NO	1060 m	1080	
1367 s	1366 p	1402	57 NO	1051	1069	
1328 w	1329 p	1353		1048***	1066	
1264 w	1264 dp	1297		935 w	980	
1136 m	1130 dp	1148		918 w	969	25 ρNO_2
1102 m	1100 p	1120	49 CC	880 m	940	14 CN
995 m	994 dp	1002	44 CC, 17 CN	784 m	891	33 CN, 30 ONO
876 s	876 p	883	31 CN, 29 ONO	629	777	19 CN
805 w		815	11 ρ NO_2	581	637	26 ρNO_2
616 m	615 p	636	49 CN, 22 CNO, 12 ONO, 18 CCN		583	52 CN, 10 CNO
583		586	69 ρNO_2	476	504	37 ρNO_2
497 w	494 dp	508	49 CNO, 14 CN, 11 CCN	260 w	481	54 CNO, 13 CN, 11 CCN
285 w	295 dp	289	62 CCN, 36 CNO		263	53 CCN, 28 CNO
221 w		219			160	
		18	55 τNO_2, 29 ρNO_2		14	53 τNO_2, 20 ρNO_2

* Hereafter frequencies in cm^{-1}, PED in %; s is strong, m is medium, w is weak band, v is very, p is polarized, dp is depolarized line. Stretching vibrations of C—H and C—D are not considered. Only the contributions from the C—NO_2 group and C—C bond are presented.

** B3LYP/6-311++G(d,p).

*** For the liquid state.

experimental intensities for several bands in the IR spectra of nitroethane solutions was available. Comparison of the theory (B3LYP) and experiment shows that these sets of magnitudes change in parallel (Table 8), although intensities for vapors and solutions, of course, can noticeably differ. For the RHF and MP2 methods, the agreement between the theory and experiment for the intensities of the same bands of nitroethane is still worse.

Table 8. Integral intensities (*A*) of some bands in the IR spectra of nitroethane*

Band	Experiment[19]		Calculation (B3LYP/6-311++G(d,p))	
	ν	*A**	ν	*A*
1	1568	100	1619	100
2	1410	19	1430	24
3	1382	17	1402	18
4	882	7	883	3
5	617	2	636	8
6	499	6	508	3

* Integral intensities were measured in solutions: bands *1*, *2*, and *3*, in CH_2Cl_2; *4*, in $CHBr_3$; *5* and *6*, in MeCN.

For simplification of the spectra interpretation and convenience of analysis, we separated from the whole set of fundamental bands of nitroethane the bands that involve, to a great extent, the parameters of the C—NO_2 group and C—C bond (see Table 7). Comparison of the separated frequencies of the nitro group in nitroethane with those in nitromethane[7] shows their close analogy.

However, a closeness in positions of the bands of the nitro groups in nitromethane and nitroethane does not imply their analogy in shape. Analysis of changes in the shapes and PED of vibrations of the $MeNO_2$ and $EtNO_2$ molecules showed more or less regularity for all stretching vibrations of the C—NO_2 group, although the characters of vibrations of C—N in the $MeNO_2$ and $EtNO_2$ molecules somewhat differ. For example, for the $EtNO_2$ molecule two frequencies, *viz.*, 883 and 636 cm^{-1}, can formally be assigned to ν(CN). According to PED, the contribution of the C—N coordinate to ν = 636 cm^{-1} is greater than that to ν = 883 cm^{-1} in the $EtNO_2$ molecule, whereas for $MeNO_2$ this contribution to similar vibrations is the same. Within the same interpretation of the spectra, we assign the frequency at 883 cm^{-1} to the stretching C—N vibration, and 636 cm^{-1} can be attributed to the bending CNO vibration in the $\mathrm{EtNO_2}$ molecule. The stretching C—C vibration can be assigned for the $\mathrm{EtNO_2}$ molecule, its identification for $\mathrm{MeCD_2NO_2}$ is less reliable, and it is not identified at all for $\mathrm{C_2D_5NO_2}$. In the latter case, this vibration is distributed over different coordinates.

The assignment of bending vibrations of the C—$\mathrm{NO_2}$ groups is complicated. Unlike $\mathrm{MeNO_2}$, in $\mathrm{EtNO_2}$ deformation of these angles participate efficiently in many vibrations (Fig. 3). Thus, some bending vibrations of the nitromethane and nitroethane molecules substantially differ in both the modes and PEDs.

***n*-Nitropropane and *n*-nitrobutane.** No detailed spectral data for the nitropropane and nitrobutane molecules in the gas phase were available. Therefore, we restricted our calculations by the 6-31G(d) B3LYP basis set and examined only the frequencies with the maximum participation of the parameters of the nitro group.

The calculation results showed that the frequencies of stretching vibrations are somewhat overestimated. Among the stretching C—N vibrations, two bands for each nitroalkane, which were difficult to distinguish, were assigned. For $\mathrm{PrNO_2}$ $\nu = 941$ cm^{-1}, PED is 28% CN and 911 cm^{-1}, PED is 25% CN. A similar situation is observed for $\mathrm{BuNO_2}$.

Bending vibrations of the nitro groups of the $\mathrm{PrNO_2}$ and $\mathrm{BuNO_2}$ molecules are in the standard region for nitroalkanes and somewhat differ in frequencies from those of nitroethane. For example, for the first molecule these values are 738, 642, 471, and 18 cm^{-1}, whereas for the second molecule they are 732, 638, 488, and 17 cm^{-1}.

2-Nitropropane and 2-methylnitropropane. We also studied the molecules of branched nitroalkanes. Their spectra have previously been studied.[12,15] However, their complete interpretation is very complicated and barely possible even when good experiment and the results of classical calculations of frequencies and modes of normal vibrations are available. Therefore, in this work we performed quantum-chemical calculations of the force fields. The frequencies of vibrational spectra of the $\mathrm{Pr^iNO_2}$ and $\mathrm{Bu^tNO_2}$ molecules were calculated using the calculated force fields.

The calculations were performed by the RHF, MP2, and B3LYP methods in the 6-311++G(d,p) basis set. As follows from analysis of the results, The B3LYP method gives the best agreement of the theory and experiment for these molecules. The average deviation of the calculated frequencies from experiment ($\Delta\nu_{\mathrm{av}}$) is ~2.5%. The use of results obtained by the RHF and MP2 methods without force field scaling is inefficient. A great number of frequencies (some of which are close to each other) of relatively large molecules $\mathrm{Pr^iNO_2}$ and $\mathrm{Bu^tNO_2}$ impede the comparison of the theory and experiment. This conclusion is clearly illustrated by the data in Tables 9 and 10 containing the results of frequency calculations using the RHF and B3LYP methods for the $\mathrm{Pr^iNO_2}$ molecule

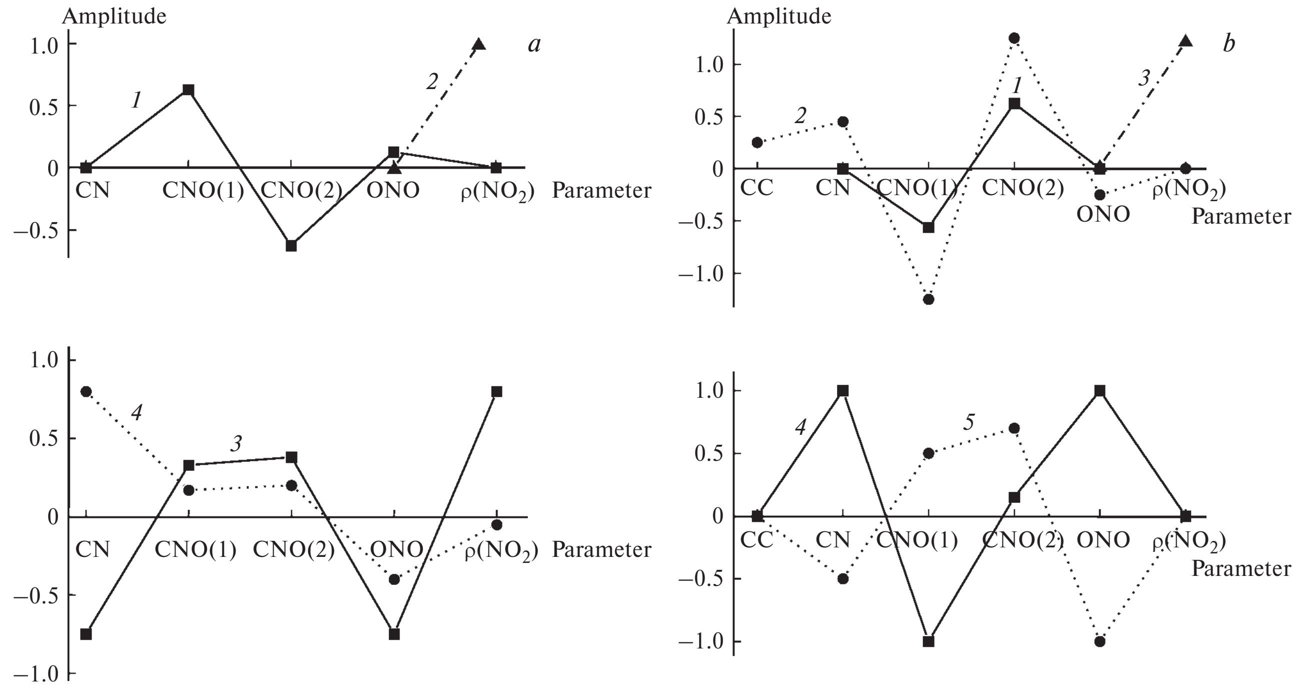

Fig. 3. Diagram of some vibration modes for the $\mathrm{MeNO_2}$ (*a*) and $\mathrm{EtNO_2}$ (*b*) molecules; contributions of natural coordinates to vibrations of the frequencies: *a*, 482 (*1*), 612 (*2*), 662 (*3*), and 925 cm^{-1} (*4*); *b*, 289 (*1*), 508 (*2*), 586 (*3*), 636 (*4*), and 883 cm^{-1} (*5*).

Table 9. Spectra of Pr^{i}NO$_2$

Experiment^{12} (gas)		Calculation in 6-311++G(d,p) basis		
IR	Raman	RHF	B3LYP	
		ν	ν	PED
1571 v.s	1555 w	1816	1617	86 NO
1478 s	1477 s	1668	1514	
1466 s	1466* w	1627	1498	
1456 s	1454 m	1615	1490	
1444* m	1445 w	1607	1484	
1402 s	1402 w	1601	1437	26 NO, 6 CNO
1378 s	1394 s	1546	1403	
1361 s	1361 m	1535	1395	43 NO, 10 CNO, 5 CN
1325* w	1320 w	1482	1361	
1306 m	1306 m	1468	1328	
1183 w	1184 w	1304	1201	
1140 m	1134* m	1243	1148	
1106 m	1107 s	1230	1122	12 CCN, 6 CN
	957 w	1035	962	
941 v.w	941* w	1025	951	
906 w	902 v.w	1015	906	21 CN, 15 CNO
851 s	851 s	936	861	46 CNO, 24 CC
724 v.w		841	743	71 ρNO$_2$
621 m	620 v.w	706	633	31 CCN, 24 CN, 21 CNO
528 m	524 s	579	526	39 CNO, 22 CN
313 w		361	339	14 CNO
270 w	272* w	326	302	54 CCN, 21 CNO, 7 CN
264 w		289	264	64 CCN, 21 ρNO$_2$
	250 v.w	269	250	
238 w	233 v.w	231	218	
		43	35	63 τNO$_2$

* Spectra for the liquid state.

Table 10. Spectra of the Bu^{t}NO$_2$ molecule

Experiment^{15} (gas)		Calculation in 6-311++G(d,p) basis set		
IR	Raman	MP2	B3LYP	PED
1563 v.s	1553 w	1784	1605	93 NO
1502* m		1581	1522	
1485 m		1560	1501	
1467 s		1559	1497	
1457* m		1550	1491	
1446* m	1452** m	1543	1484	
1423* w		1535	1472	
1408 m	1408 w, p	1488	1444	20 NO, 2 CN, 2 CC
1377 s	1373** s, p	1458	1407	8 CC, 7 NO
1364* m	1362* w	1449	1401	10 CC
1360 s	1350 m, p	1396	1386	70 NO
1266*		1337	1281	49 CC
1254		1315	1257	50 CC
1200		1273	1205	12 CN, 4 CC
1035		1091	1054	10 CC
	1038*	1088	1053	9 CC
	965*	1003	977	
935	938**	981	940	41 CC
		981	939	52 CC
862	863	895	866	44 CNO, 30 CN
800	803	822	799	81 CC
731*		746	739	18 CC
571	570	597	555	59 CC
	523*	546	525	32 CNO, 22 CN
376	777	395	384	
361*		391	367	38 CN
306*		370	355	30 CNO
286	285**	312	286	38 CNO, 4 CN
280*	273*	304	286	
270*	260*	286	257	
229*	223*	279	256	
223*	218*	222	198	
		42	40	75 τNO$_2$

* Spectra for the crystalline state.

** Spectra for the liquid state.

and MP2 and B3LYP for Bu^{t}NO$_2$. Based on analysis of the vibration modes and PED, we assigned all fundamental vibrational frequencies for the 2-nitropropane and 2-methylnitropropane molecules. The results obtained for frequencies of the nitro groups are presented in Tables 9 and 10.*

Comparison of the calculation results for the Pr^{i}NO$_2$ and Bu^{t}NO$_2$ molecules to analogous data for MeNO$_2$ and EtNO$_2$ showed that the character of the stretching N—O vibrations changed slightly in this series of compounds. The situation for the stretching C—N vibrations is worse because the involvement of the C—N coordinate in various vibrations, including the stretching C—N vibration itself, noticeably changes. For example, the band at 523 cm^{-1} in the spectrum of Bu^{t}NO$_2$ can formally be assigned to the stretching C—N vibration because the C—N bond, along with the C—N—O angles, contributes considerably to this frequency. The frequencies of bending vibrations change rather significantly in the spectra of the series of mononitroalkane molecules.

For example, the frequency of the nonplanar bending vibration of the nitro group (ρ(NO$_2$)) increases by at least 100 cm^{-1} on going from linear to branched molecules. The frequencies of other bending vibrations exhibit smaller changes but the modes change significantly on going from these to other molecules.

Note the change in the frequency of the torsional vibration on going from nonbranched to branched molecules. In this case, we have to use mainly calculated data not confirmed by experiment.

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* The data on the vibration modes are cumbersome and, hence, not presented.

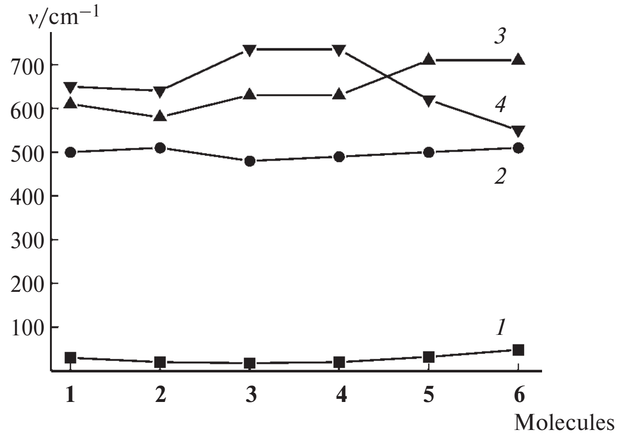

Fig. 4. Diagram for the change in the frequencies of bending vibrations for the C—NO$_2$ group τ (*1*), δ_{as}(ONO) (*2*), ρ(NO$_2$) (*3*), and δ_s(CNO) (*4*) in the series of molecules of aliphatic nitro compounds **1—6**, B3LYP calculations in the 6-311++G(d,p) (**1**, **2**, **5**, **6**) and 6-31G(d) (**3**, **4**) basis sets.

The general character of changes in the frequencies of bending vibrations of the C—NO$_2$ group in the series of mononitroalkane molecules is demonstrated in Fig. 4.

In conclusion let us summarize the results of analysis of the quantum-chemical calculations compared to experiment. This study allowed us to examine in detail the spectra of mononitroalkanes. The apparent similarity observed in the spectra of different related compounds, *e.g.*, closeness of frequencies, does not always prove the similarity of their modes. Each particular case needs reliable calculations.

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