N-propyl nitrate vibrational spectrum analysis using DFT B3LYP quantum-chemical method

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Abstract. Calculation of a molecular structure, conformation and related vibrational spectra of the n-propyl nitrate C₃H₇NO₃ was carried out by means of density functional theory (DFT) by employing the Gaussian 03 package. The molecular geometries were fully optimized by using the Becker's three-parameter hybrid exchange functional combined with the Lee–Yang–Parr correlation functional (B3LYP) and using the 6-31G(d) basis set. By scanning the dihedral angles around C-O and C-C bonds, five energetically most favorable conformers of n-propyl nitrate - TG, TT, GT, GG and G`G forms were found. Vibrational spectra of the most energetically favorable conformers were calculated. The comparative analysis of calculated and experimental spectra is carried out, the spectral features of the conformational state of n-propyl nitrate and the spectral effects of formation of intramolecular hydrogen bonds are established.

1. Introduction

Aliphatic nitrate esters (O-nitrocompounds), forming high energy compounds were studied in many works [1-6]; however, the data of the molecular structure and vibrational spectra correlation are limited. With respect to study of physico-chemical properties of high-energy substances, such as molecular-structural (including conformational) heterogeneity in the reaction process of synthesis of high-molecular nitroesters, their use and thermal decomposition, a particular attention is paid to the simplest representatives of this compounds class, particularly n-propyl nitrate. In this direction, valuable information can be obtained from spectroscopic analysis methods in combination with quantum-chemical calculations [4,5]. The study of the vibrational spectrum, the establishment of frequencies and forms of normal vibrations, detecting spectral characteristics of the conformational state of n-propyl nitrate are a relevant objective.

This paper presents the results of IR-spectroscopic and theoretical investigations of the n-propyl nitrate structural features, the analysis of its various conformations obtained by scanning the dihedral angles of the CC and the CO-bonds and energy optimization is presented. Conformational sensitive vibrations are investigated, and special attention is paid to low-frequency oscillations, which were not studied previously, due to the complexity of interpretation.
For calculations the authors used the currently widely applied method of the density functional theory DFT B3LYP with the 6-31G(d)-basis, allowing one to achieve high accuracy of calculations of thermodynamic functions and spectral characteristics [4].

2. Calculations

All calculations in the framework of the density functional theory (DFT) were performed using the software package Gaussian 03 [7]. For DFT, Becker’s three parameter exchange functional was used in combination with the Lee-Yang-Parr correlation functional (B3LYP) [8,9]. The standard 6-31G (d) basis was applied. The agreement obtained stationary points and minimum potential energy is checked by calculating the Hessian matrices and analysis of the absence of imaginary frequencies. To correct systematic errors due to the limited size of the basis set of functions, force constants were multiplied by the correction scaling factors: $F_{scale} = (s_is_j)^{1/2} F_{ij}$. Here, $F_{ij}$ are force constants in the dependent internal coordinates. Conversion of force constants calculated in Cartesian coordinates to internal coordinates and its scaling were performed using the program [10]. The comparison of the experimental results [5,6] and calculated frequencies allowed one to add a scaling factors of force constants $v$ (CH, N=O), $\delta$ (HCH), equal to 0.9, $\tau$ (NO), equal to 1.1; all others were kept unchanged.

3. Study of the n-propyl nitrate conformational state using the B3LYP/6-31G(d) calculation method

Search of the n-propyl nitrate stable conformations was conducted by calculating of the two-dimensional potential energy surface as a function of the values of the two torsion angles CC-ON ($\phi_1$) and CC-CO ($\phi_2$) by the B3LYP/6-31G(d) method. The scan step was 60°. The deepest minimum on the surface corresponds to the TG-form of the n-propyl nitrate molecule (Figure 1). The relative energy values of the other stable conformers TT, GT, GG and G’G and their corresponding dihedral angles are presented in table 1. In addition, table 1 shows the distance between the proton and the oxygen of nitrate group r (H…O), the values of which are important for the qualitative assessment of energy and for possibility of the intramolecular hydrogen bonds formation.

Table 1. Optimized B3LYP/6-31G(d) n-propyl nitrate conformers

| Conformers | Energy, kcal / mol (relatively the minimum) | $\phi_1$ | $\phi_2$ | $\rho$ (H…O), Å |
|------------|-----------------------------------------------|--------|--------|---------------|
| TG (1)     | 0.038                                         | -180.0 | -82.15 | 2.53          |
| TT (2)     | 0.016                                         | -180.0 | -82.15 | 2.53          |
| GT (3)     | 0.187                                         | -180.0 | -82.15 | 2.53          |
| GG (4)     | 1.179                                         | -180.0 | -82.15 | 2.53          |
| G’G (5)    |                                               | -180.0 | -82.15 | 2.53          |

4. The spectral effects determination of the conformation n-propyl nitrate state

For each n-propyl nitrate conformation, a vibrational spectrum was calculated using the B3LYP/6-31-G(d)-method. The experimental [6] and calculated frequencies, the assignment of vibrations are presented in table 2.

In the frequency range of 3000-3200 cm$^{-1}$ ($\nu_{30} - \nu_{36}$) medium and low-intensity absorption bands are observed typical for the symmetric and antisymmetric stretching vibrations of $\nu$ CH of the CH$_3$ and CH$_2$ fragments. According to the data from table 2, the conformational state of n-propyl nitrate has the most noticeable effect on the oscillation frequency of $v_s$ and $v_a$, CH group C3H$_2$: values differ by 20-30 cm$^{-1}$. In the spectra of TG and TT - forms the absorption bands $v_s$ CH and $v_a$ CH are evident at ~3129
(2969) cm\(^{-1}\), and 3074(2916) cm\(^{-1}\), respectively. Changing the dihedral angle of C – O-bond, i.e. as a result of the transition to GT, GG and G’G-forms, the frequency of \(\nu\) CH increases to CH \(\sim\)3159 (2997) cm\(^{-1}\) and \(\nu_{as}\) CH to 3094 (2935) cm\(^{-1}\). The values of the frequencies \(\nu\) CH at atoms C1 and C2 differ less: 5-10 cm\(^{-1}\).

According to the quantum chemical calculations for C3 atom in the case of \textit{trans}-orientation of ONO2-group a smaller electronegativity \(q\) is customary: if TG and TT \(q = -0.033\) and -0.027, respectively, so GT, GG and G’G \(q = -0.047\), are -0.055 -0.067, respectively. According to the known Gordy ratio [11], for stretching vibrations localized on a particular group of atoms, in particular, \(\nu\) C3H2, an increase of electronegativity of the heaviest carbon atom leads to an increase in the force constant of the bond, and, as a consequence, to the increase of the frequency oscillations.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{spectrum.png}
\caption{Theoretical spectrum of TG-form of n-propyl nitrate. Marked ranges of 30-600, 1000-1300 and 1400-1600cm\(^{-1}\) additionally 10 times enhanced relatively the original spectrum}
\end{figure}

Table 1 presents the calculated distances \(r\) (H…O) between the proton of C3H2 and oxygen of NO2 -groups. The values of \(r\) lie in the interval of 2.19-2.53 Å, which is less than the sum of van-der-Waals radii of these atoms. As a result, a short contact between these groups is formed, therefore, the formation of intramolecular hydrogen bonds (IHB) is possible. The values of the frequencies \(\nu\) CH correlate well with distance \(r\) (H…O), hence, with the energy of force [12]. That is, for TG and TT-forms weaker forces (IHB) and lower \(\nu\) CH frequencies are typical as compared to GT, GG and G’G-forms.

In the calculated spectra a high absorption intensity can also be noted (relative units) \(\nu_{as}\) C3H for TG (0.10), and TT (0.17)-forms, compared to GT (0.05), GG (0.03) and G’G (0.02)-forms. In previously obtained experimental spectra [6] a high-intensity absorption band \(\nu\) CH was typical for the n-propyl nitrate in the crystalline state. So, according to the calculations and experiments, the conformers with the \textit{trans}-location of ONO2 and C3H7 fragments relatively to the C - O connection, i.e. TG and TT-forms, are really implemented in the crystal.

\textit{In the frequency range of} \(1650-1800\ \text{cm}^{-1}\) (\(\nu_{as}\) N=O) \textit{an intensive absorption of stretching vibrations \(\nu_{as}\) N=O is observed. The conformational state of the PNA has a weak influence on the frequency of \(\nu_{as}\) N=O.}
However, these vibrations are sensitive to the phase state of the sample, in particular, in the spectra of the crystals the lower frequency value \(39 \text{ cm}^{-1}\) are marked, compared to the spectra of the n-propyl nitrate gases (table 2).

**In the frequency range of 1360-1580 cm\(^{-1}\) \((\nu_{32}-\nu_{35})\) the low intensity absorption bands of planar deformation vibrations – \(\delta(\text{CH}_3)\) and \(\delta_{s}(\text{CH}_3)\), scissoring \(\delta(\text{CH}_2)\) are observed, as well as \(\omega(\text{CH}_2)\) outside the planar wagging oscillations. The scissor vibrations \(\delta(\text{C3H}_2)\) deserve a special attention. For TG and TT-forms the frequency of these fluctuations is \(\sim 35 \text{ cm}^{-1}\) higher as compared to GT, GG and G’G-forms. As noted above, for the n-propyl nitrate forms with the trans-orientation of ONO_2 group the Table 2. Experimental and calculated B3LYP/6-31-G(d) frequencies and the assignment of vibrations of n-propyl nitrate

| Calculation | \(\nu\), cm\(^{-1}\)[6] | Experiment \(\nu\), cm\(^{-1}\) [6] |
|-------------|-----------------|------------------|
| Assignment \(^{(a)}\) | TG | TT | GT | GG | G’G | gas | fluid | solid state |
| v 36 \(\nu_{as}\) CH\(_3\) | 3137(2976) | 3128 | 3127 | 3132 | 3129 | 2984 | 2963 | 2970 |
| v 35 \(\nu_{as}\) C3H\(_2\) | 3129(2969) | 3131 | 3147 | 3150 | 3159 | 2979 | 2943 | 2943 |
| v 34 \(\nu_{as}\) CH\(_3\) | 3119(2960) | 3114 | 3118 | 3120 | 3126 | 2979 | 2943 | 2943 |
| v 33 \(\nu_{as}\) C2H\(_2\) | 3089(2930) | 3092 | 3097 | 3098 | 3080 | 2900 | 2913 | 2913 |
| v 32 \(\nu_{as}\) C3H\(_2\) | 3074(2916) | 3073 | 3089 | 3086 | 3094 | 2883 | 2883 | 2883 |
| v 31 \(\nu_{s}\) CH\(_3\) | 3054(2897) | 3050 | 3048 | 3052 | 3058 | 1569 | 1636 | 1620 |
| v 30 \(\nu_{s}\) C2H\(_2\) | 3051(2894) | 3060 | 3062 | 3049 | 3042 | 1465 | 1473,1465 | 1466(1455) |
| v 29 \(\nu_{as}\) NO\(_2\) | 1751(1668) | 1751 | 1752 | 1752 | 1753 | 1659 | 1448 | 1443 |
| v 28 \(\delta_{s}(\text{C3H}_2) - \delta(\text{HCH})\) | 1539(1478) | 1547 | 1505 | 1501 | 1506 | 1465 | 1473,1465 | 1466(1455) |
| v 27 \(\delta_{as}(\text{CH}_3) - \delta(\text{HCH})\) | 1538(1469) | 1533 | 1531 | 1537 | 1529 | 1448 | 1444 | 1443 |
| v 26 \(\delta_{as}(\text{CH}_3), \delta_{s}(\text{C3H}_2), \rho(\text{CH}_3)\) | 1525(1457) | 1530 | 1524 | 1530 | 1538 | 1509 | 1509 | 1509 |
| v 25 \(\delta(\text{C2H}_2)\) | 1447(1419) | 1445 | 1444 | 1448 | 1448 | 1388 | 1378 | 1378(1390) |
| v 24 \(\delta_{s}(\text{CH}_3)\) | 1424(1409) | 1436 | 1434 | 1421 | 1424 | 1348 | 1348 | 1348 |
| v 23 \(\omega(\text{C3H}_2) - \delta(\text{CCH}), \delta(\text{HCH})\) | 1399(1386) | 1361 | 1363 | 1401 | 1404 | 1312 | 1312 | 1312 |
| v 22 \(\omega(\text{C2H}_2) - \delta(\text{CCH}), \delta(\text{HCH})\) | 1335(1318) | 1328 | 1331 | 1340 | 1338 | 1286 | 1283 | 1288(1280) |
| v 21 \(\nu_{s}\) NO\(_2\) | 1320(1281) | 1332 | 1345 | 1322 | 1318 | 1243 | 1243 | 1243 |
| v 20 \(\tau(\text{CH}_2)\) | 1275(1273) | 1277 | 1299 | 1300 | 1305 | 1118 | 1118 | 1111 |
| v 19 \(\tau(\text{C3H}_2) - \delta(\text{OCH}), \delta(\text{CCH})\) | 1183(1181) | 1196 | 1200 | 1183 | 1189 | 1118 | 1118 | 1111 |
| v 18 \(\tau(\text{C3H}_2) - \delta(\text{OCH}), \delta(\text{CCH})\) | 1142(1139) | 1053 | 1049 | 1123 | 1120 | 1054* | 1051 | 1052 |
| v 17 \(\nu(\text{C1-C2})\) | 1071(1071) | 1157 | 1141 | 1066 | 1070 | 998* | 981 | 983 |
| v 16 \(\nu(\text{C2-C3})\) | 982(980) | 1017 | 1014 | 984 | 978 | 967 | 953 | 952 |
| v 15 \(\nu(\text{C-O})\) | 935(934) | 912 | 900 | 911 | 930 | 892 | 919 | 920 |
| v 14 \(\tau(\text{CH}_2), \tau(\text{CH}_3)\) | 897(896) | 930 | 907 | 876 | 855 | 887(884) | 885 | 870 | 874 |
| v 13 \(\nu(\text{C1-C2}), \nu(\text{C2-C3}), \omega(\text{CH}_2)\) | 785(785) | 778 | 767 | 787 | 790 | 759 | 759 | 762 |
| v 12 \(\nu(\text{N-O}), \delta(\text{O=O}=\text{N}=\text{O})\) | 765(765) | 762 | 763 | 761 | 756 | 576 | 569 | 567 |
| v 11 \(\nu(\text{CH}_2), \delta_{as}(\text{CH}_3)\) | 706(705) | 701 | 666 | 658 | 645 | 695* | 699 | 708 |
| v 10 \(\gamma(\text{NO}_2)\) | 570(569) | 610 | 616 | 579 | 585 | 574* | 567 | 569 |
| v 9 \(\delta(\text{CON}), \delta(\text{O=N}=\text{O}), \tau(\text{CH}_2)\) | 447(447) | 343 | 402 | 458 | 451 | 341 | 348 | 353 |
| v 8 \(\delta(\text{O=N}=\text{O})\) | 306(306) | 354 | 279 | 267 | 279 | 451 | 450* | 404 | 453 |
| v 7 \(\delta(\text{COC})\) | 264(264) | 148 | 344 | 390 | 378 | 307 | 310 | 320 |
| v 6 \(\delta(\text{CCC})\) | 182(182) | 240 | 236 | 228 | 239 | 266 | 270 | 284 | 273 |
\[ \nu \text{ C-H stretching; } \delta \text{ - bending; } \delta' \text{ - scissoring; } \tau \text{ - rocking; } \tau w \text{ - twisting; } \omega \text{ - wagging; } \tau \text{ - torsion; } \text{as} \text{ – asymmetric; } s \text{ – symmetric} \]

\[ \text{calculated frequencies (scaled frequencies in brackets, because their changes in accuracy repeat the calculated frequencies changes, the authors show them only for one conformer)} \]

\[ \text{weak IHB is typical, i.e., the } \delta \text{C-H frequency correlates with the energy of IHB. Frequencies of}\]

\[ \text{wagging oscillations } \omega \text{C-H have lower values (~38 cm}^{-1}\text{) in the case of the } \text{trans-orientation of the}\]

\[ \text{CH}_2\text{ONO}_2 \text{fragment, possibly due to the steric effects.}\]

\[ \text{It is important to note high intensity absorption band } \omega \text{C-H for the TT and GT-forms of n-propyl nitrate.}\]

\[ \text{In the frequency range of } 900-1360 \text{ cm}^{-1} (\nu_{14} - \nu_{12}) \text{ a high intensity absorption is observed at}\]

\[ 1335(1318) \text{ cm}^{-1}, \text{ customary for } \nu \text{ N=O stretching vibrations (above experimental values). The}\]

\[ \text{frequency rate of this vibration for different forms of n-propyl nitrate differs by } ~5-9 \text{ cm}^{-1}, \text{i.e. explicit}\]

\[ \text{conformational sensitivity } \nu \text{ N=O is not observed.}\]

\[ \text{The weak intensity bands at 1320(1281), 1275(1273) cm}^{-1}\text{, observed in the spectrum of TG-forms,}\]

\[ \text{are typical for of twisting vibrations } \tau w \text{C-H at the C2 and C3 atoms, respectively. Moreover, if the}\]

\[ \text{frequency } \tau w \text{C-H is sensitive to rotation around the C-C bond: it is increased by } 12-25 \text{ cm}^{-1}\text{, for}\]

\[ \text{TT and GT-forms, so the frequency } \tau w \text{C-H is sensitive to rotation around the C-O bond: it is } ~25 \text{ cm}^{-1}\]

\[ \text{lower for TG and TT-forms, i.e. with the } \text{trans-orientation ONO}_2 \text{ and C3H7 groups relatively to C-O-}\]

\[ \text{bond. As noted above, TG and TT-forms have a weaker force IMB, i.e. the fluctuations in } \tau w \text{C-H}\]

\[ \text{"feel" the force IMB.}\]

\[ \text{A low-intensity absorption band at } 1183(1181) \text{ cm}^{-1}\text{ in the TG-spectrum is determined by the}\]

\[ \text{rocking oscillations } \tau \text{C3H2. For TT and GT-forms the frequency value is } 13-17 \text{ cm}^{-1}\text{ higher.}\]

\[ \text{In the considered spectral range, along with the deformation vibrations, the average intensity}\]

\[ \text{absorption bands of stretching vibrations } \nu \text{ C-C and } \nu \text{ C-O (table.2) are also observed. Conformational}\]

\[ \text{sensitivity of stretching vibrations is more pronounced than that of deformation oscillations: up to } ~90 \text{ cm}^{-1}\]

\[ \text{below the frequency } \nu \text{ C1-C2 in the spectrum of TT and GT-forms, while the frequency of } \nu \text{ C2-C3}\]

\[ \text{and } \nu \text{ C-O in these forms is } ~80 \text{ and } ~40 \text{ cm}^{-1}\text{ higher, respectively. I.e. these fluctuations are}\]

\[ \text{sensitive to internal rotation relative to the C-C bond.}\]

\[ \text{The intensive absorption bands observed in the frequency range of } 600-900 \text{ cm}^{-1} (\nu_{9} - \nu_{11}) \text{ are}\]

\[ \text{customary for vibrations involving ONO}_2 \text{ group. In particular, for TG and TT-forms, i.e. in } \text{trans-}\]

\[ \text{orientation of ONO}_2 \text{ and C3H7 fragments concerning the C-O bond the oscillations of } \nu \text{ NO}\]

\[ \delta \text{ O=N=O have frequencies } ~885 \text{ cm}^{-1}, \text{ fluctuations } \delta \text{ CON - } 706-701 \text{ cm}^{-1}.\]

\[ \text{In gauche-orientation of these fragments the frequencies } \nu \text{ NO and } \delta \text{ O=N=O are } ~15 \text{ cm}^{-1}\text{ lower, } \delta \]

\[ \text{O=N=O are } 40-60 \text{ cm}^{-1}\text{ lower. A similar trend was noted in the experiment (Table.2). It is possible to}\]

\[ \text{see a good correlation of frequencies of these oscillations with distance } r (\text{H ... O}), \text{ and, consequently,}\]

\[ \text{with the energy of force IMB: energetically stronger IMB have lower frequency vibrations with participation of atoms CONO}_2\text{-fragments.}\]

\[ \text{In this range there are also low intensity absorption bands of the rocking deformation vibrations } \tau \]

\[ \text{C3H2 mixed with the twisting vibrations } \tau w \text{C3H2. For this reason, they are difficult to interpret.}\]

\[ \text{Absorption band at 765 cm}^{-1}\text{ due to the out-of-plane vibrations } \gamma \text{ NO}_2\text{, is very typical and does not}\]

\[ \text{depend on the molecular shape of n-propyl nitrate.}\]

\[ \text{In the low-frequency spectral range of } 50-600 \text{ cm}^{-1} (\nu_{1} - \nu_{5}) \text{ weak intensity absorption bands are}\]

\[ \text{observed of the deformation vibrations } \delta \text{ CCC, } \delta \text{ CCO, } \delta \text{ CON and torsion oscillations } \tau \text{ C-O, } \tau \text{ NO}_2, \tau \]

\[ \text{CH}_3, \tau \text{ C2-C3. Conformers with the } \text{trans-orientation of ONO}_2\text{ and C3H7 groups relatively to the C-O-}\]

\[ \text{bond, i.e., TG and TT, have frequencies of oscillation } \delta \text{ CCC } 20-80 \text{ cm}^{-1}\text{ higher as compared to the}\]

\[ \text{other conformers. Here there is a correlation with the energy of hydrogen bond: as noted above, TG}\]

\[ \text{and TT forms – weak IBM and for GT, GG and GG`- forms – stronger forces IBM are typical.}\]
Deformation $\delta$ CCO and torsion $\tau$ C2-C3 oscillations were sensitive to internal rotation around the C- C-bond: with the trans-orientation of the CH$_4$ONO$_2$ and C$_2$H$_5$ fragment relatively C-C-bond (TT and GT-forms) the frequency of these oscillations are ~ 50-90 cm$^{-1}$ lower. Perhaps, there is the influence of steric effects. In the low frequency region of the spectrum high frequency value $\tau$ NO$_2$ of TT-forms and $\tau$ CO of GT -form can also be noted, which may be a spectral characteristic of the n-propyl nitrate conformation. The influence of the phase state of the sample on the torsion oscillations was found in the experimental spectra [6], the conformational sensitivity was not observed.

5. Conclusion

During the quantum chemical calculations using the $B3LYP/6-31-G(d)$ method with the scanning of the dihedral CC-ON and CC-CO-angles, energetically most favorable geometric structures-conformations of n-propyl nitrate - TG, GT, TT, GG and G`G were found. The values of their energy, geometrical parameters were calculated.

With the $B3LYP/6-31-G(d)$-method, vibrational spectra of the obtained conformations were calculated. Analysis of the vibrational spectra allowed identifying two main types of conformational sensitivity of oscillations:

a) oscillations that are sensitive to the orientation ONO$_2$ and C$_3$H$_7$ fragments relatively to the C - O bond; they are $\nu$ C3H$_2$, $\delta$C3H$_2$, $\tau w$ C3H$_2$, $\nu$ N-O, $\delta$ CON, $\delta$ O=N=O, $\delta$ CCC, $\delta$ CCO.

b) oscillations that are sensitive to the orientation of CH$_4$ONO$_2$ and C$_2$H$_5$ fragments relative to the C - C bond; they are $\delta$C2H$_5$, $\delta$ CH$_3$, $r$ C3H$_2$, $\nu$ CC, $\nu$ CO, $\tau$ C-C.

A correlation was established between the change in the frequency of oscillations sensitive to rotation around the C-O bond with the distance between the proton C3H$_2$ and oxygen NO$_2$ of group $r$ (H…O), i.e. with the energy of force IMB.

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