Thematic Section: Quantum-Chemical Research. **Full Paper**
Subsection: Physical Organic Chemistry. *Reference Object Identifier* – ROI: jbc-01/18-54-4-23
The Digital Object Identifier – DOI: 10.37952/ROI-jbc-01/18-54-4-23
Submitted on March 29, 2018.

The force field of 2,4-dinitrotoluene in the coordinates X_δ^0 in a saddle point

© **Alexander V. Belik**,*+ and **Maxim Yu. Pavlichev**
Faculty of Chemical Technology and Computing Chemistry. Chelyabinsk State University.
Kashyrinych Br. St., 129. Chelyabinsk, 454001. Russia.
Phone: +7 (351) 799-70-66. E-mail: belik@csu.ru

*Supervising author; +Corresponding author

Keywords: 2,4,-dinitrotoluene, the generalized force constants, coordinates X_δ^0, calculations DFT, vibration frequencies (wavenumbers).

Abstract

In the framework of the density functional method B3LYP 6-311++G(3df,3pd), for the first time a force field for 2,4-dinitrotoluene was obtained in the coordinates X_δ^0at the saddle point. Determined generalized force coefficients for the relations in the coordinate X_δ^0 calculated frequency (wave number) of normal vibrations and carried out their assignment to certain types of vibrations.

It is obtained that the most intense band in the vibrational spectrum has a value of 1367 cm^{-1}. Preferably in this vibration involves the two available atoms of the nitro groups. These are valence vibrations of C-N bonds, which move in an antiphase with respect to each other. For bonds N-O each of the nitrogroups in this vibration there are symmetrical type. However, the two nitro groups, they are in antiphase. Following the intensity band is mostly "owned" as nitrogroup. It has a value of 1581 cm^{-1}. This vibration is also involved N atoms, O atoms (of nitro group) and C atoms with the benzene ring. Asymmetric vibrations of two N-O bonds are observed in relation to the nitrogroups.The nitro group also participates in the vibrations, represented by the wave numbers: 168 cm^{-1} (asymmetric deformation vibration of the two ∠C-C-NO_2), 293 cm^{-1} (symmetric deformation of the two ∠C-C-NO_2), 349 cm^{-1} (valence vibration of C-N bond of the nitro group located at the *para*-position by –CH_3), 358 cm^{-1} (valence vibration of C-N bond of the nitro group being in *ortho*-position to –CH_3), 515 cm^{-1} (asymmetric deformation of the two vibration ∠CNO), 654 cm^{-1} (deformation vibration ∠ONO of the nitro group located at the *para*-position), 714 cm^{-1} (asymmetric deformation vibrations of the two ∠ONO), 758 cm^{-1} (out of the plane of the nitrogen atom of the nitro group at the *para*-position), 797 cm^{-1} (out of the plane of the nitrogen atom of the nitro group in *ortho*-position), 858 cm^{-1} (symmetric deformation of the two vibration ∠ONO), 932 cm^{-1}(asymmetric valence vibration for the two C-N), 1078 cm^{-1} (the stretching C-N of the nitro group in *ortho*-position), 1146 cm^{-1} (asymmetric valence vibration of the two bonds C-N), 1381 cm^{-1} (asymmetric valence vibration of the two bonds C-N symmetric and synchronous vibrations of links N-O), 1591 cm^{-1} (asymmetric vibrations of bonds N-O common mode for the two nitro groups), 1641 cm^{-1} (asymmetric vibrations of bonds N-O antiphase to two nitro groups), 1648 cm^{-1} (asymmetric vibrations of bonds N-O nitro group in the *ortho*-position).

References

[1] I.L. Knunyants. Chemical encyclopedic dictionary. *Moscow: Sov. Encyclopedia.* **1983**. 792p. (russian)
[2] A.V. Belik, M.Yu. Pavlichev, E.G. Mischinskyi. Computation of vibration spectra of *o*-nitrotoluene and *m*-nitrotoluene in the coordinates X_δ^0. *Butlerov Communications.* **2017**. Vol.51. No.9. P.57-66. DOI: 10.37952/ROI-jbc-01/17-51-9-57
[3] A.V. Belik, E.G. Mischinskyi, M.Yu. Pavlichev. Computation of vibration spectra of p-nitrotoluene and 2,4,6-trinitrotoluene in the coordinates X_δ^0. *Butlerov Communications.* **2017**. Vol.52. No.11. P.42-52. DOI: 10.37952/ROI-jbc-01/17-52-11-42
[4] W. Koch, M.C. Holthausen. A Chemist's Guide to Density Functional Theory. *Weinheim: Wiley-Vch.* **2001**. 293p.
[5] V. Kon. Electronic structure of matter – wave functions and density functionals. *Advancces in physical Sciences* (Nobel lectures in chemistry – 1998). **2002**. Vol.172. No.3. P.336-348. (russian)
[6] A.V. Belik, E.I. Fedotova. Quantum chemical study of the force field of nitromethane in coordinates of X_δ^0. *Butlerov Communications.* **2011**. Vol.25. No.5. P.60-63. ROI: jbc-02/11-25-5-60

[7] A.V. Belik. Computation of vibrational spectra of benzene and benzofuroxan molecules in coordinates X_{δ}^{0} with an estimation of a force fields in frameworks DFT. *Butlerov Communications*. **2016**. Vol.45. No.2. P.148-162. DOI: 10.37952/ROI-jbc-01/16-45-2-148
[8] A.V. Belik. Computation of vibration spectra of 4-nitro-benzofuroxan in coordinates X_{δ}^{0}. *Butlerov Communications.* **2015**. Vol.41. No.2. P.97-102. DOI: 10.37952/ROI-jbc-01/15-41-2-97
[9] A.V. Belik. Modern elements computational chemistry: monograph. *Chelyabinsk: Publ. Chelyab. State Univ.* **2013**. 161p. (Classical University). (russian)
[10] A.V. Belik. New aspects of computation chemistry: monograph. *Chelyabinsk: Polygraph – Master.* **2015**. 200p. (russian)
[11] Gaussian 09, Revision A.02. M. J. Frisch, G. W. Trucks, H. B. Schlegel [at el.]. *Wallingford: Gaussian, Inc.* **2009**.
[12] E.V. Butyrskaya. Computational chemistry: basic theory and work with programs Gaussian andGauss View. *Moscow: SOLON-PRESS.* **2011**. 224p. (russian)
[13] H. Hellmann. Quantum chemistry. *Moscow: BINOM, Knowledge laboratory*. **2012**. 533p. (russian)
[14] V.I. Baranovsky. Quantum mechanics and quantum chemistry. *Moscow: "Academy".* **2008**. 384p. (russian)
[15] V.I. Minkin, B.Ya. Simkin, R.M. Minyaev. The Theory of molecular structure. Rostov n/D: Feniks, **1997**. 560p.
[16] L.S. Mayanc. Theory and calculation of molecular vibrations. *Moscow: Publ. of Acad. Sciencec of USSR* .**1960**. 526p. (russian)
[17] E. Vil'son, Dj. Deshius, L. Kross. The theory of vibration spectra of molecules. *Moscow: Publ. «Foreign literature».* **1960**. 358p. (russian)
[18] M.V. Volkenstein, L.A. Gribov, M.A. Elyashevich, B.I. Stepanov. Vibrations of mokecules.*"Science".* **1972**. 700p. (russian)
[19] L.S. Mayants, G.B. Shaltuper. A new approach to the complete calculation of the vibrations of any molecule. *Dokl. USSR Academy of Sciences.* **1972**. No.206. P.657-660. (russian)
[20] L.S. Mayants, G.B. Shaltuper. General methods of analysing molecular vibrations. *J. Mol. Struct.***1975**. Vol.24. P.409-431.
[21] A.V. Belik. To calculate the force constants of the ammonia molecule. *Vestn. Chelyab. StateUniversity. Physics*. **2011**. No.15. Iss.10. P.60-62. (russian)
[22] A.V. Belik. The generalized force constants of NF_3 and ONF_3 molecules in X_{δ}^{0} coordinates. *Butlerov Communications.* **2014**. Vol.39. No.9. P.35-38. ROI: jbc-02/14-39-9-35
[23] A.V. Belik. Solution of a spectral problem for molecules NH_2NO_2, CH_3NO_2 and N_2O_4 in coordinates X_{δ}^{0}. *Butlerov Communications.* **2014**. Vol.40. No.11. P.84-90. ROI: jbc-02/14-40-11-84
[24] A.V. Belik. Computation of vibrational spectra of 5-methyl-4-nitrobenzofuroxan and 7-methyl-4-nitrobenzofuroxan molecules in coordinates X_{δ}^{0} with an estimation of a force fields in DFT. *Butlerov Communications.* **2016**. Vol.45. No.3. P.128-142. DOI: 10.37952/ROI-jbc-01/16-45-3-128
[25] A.V. Belik. Computation of vibrational spectra of 5-methoxy-4-nitrobenzofuroxan in coordinates X_{δ}^{0}. *Butlerov Communications.* **2016**. Vol.47. No.9. P.85-94. DOI: 10.37952/ROI-jbc-01/16-47-9-85