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Computation of vibrational spectra of 7-methoxy-4-nitrobenzofuroxan in coordinates X_δ^0

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

In the framework of the density functional methods B3LYP 6-311++G(3df,3pd) first obtained the force field of the molecule 7-methoxy-4-nitrobenzofuroxan in coordinates X_δ^0. Found generalized force constants are calculated in the frequency (wave number) of normal vibrations and carried out their assignment to certain types of vibrations. The most intense band in the calculated spectrum of 7-methoxy-4-nitrobenzofuroxans has a value of 1344 cm^{-1}. The main contribution to this vibration makes the nitro group. However, there are the stretching vibrations of connections C=N furoxane rings and stretching vibrations of bonds C-C of benzene ring and deformation vibrations associated with the hydrogen atoms. The next band intensity has a value of 1667 cm^{-1}. This vibration involved the off-cycle bond N→furoxane rings, stretching vibrations of bonds C-N furoxane rings, stretching vibrations of bonds C-C of benzene ring and the atoms of the nitro group.

For the generalized force constants (f) of the nitro group obtained the following values: $f_{C\text{-}N}$ = 6.9219 mdyn/Å, $f_{O\text{-}N}$ = 12.5353 mdyn/Å. The greatest value of a generalized force constant of the N-O in the molecule 7-methoxy-4-nitrobenzofuroxans obtained for furoxane ring from the nitro group, which is 24.2323 mdyn/Å.

It is shown that the rearrangement of 5-methoxy-4-nitrobenzofuroxan in 7-methoxy-4-nitrobenzofuroxan (rearrangement of the Boulton-Katritzky) accompanied by increased "rigidity" C-NO_2 on 0.5622 mdyn/Å, when the N→O 0.3240 mdyn/Å, when the C-N_3 for 0.3466 mdyn/Å, when the O_2-N_3 (from the nitro group) 0.3642 mdyn/Å. Values of increasing "rigidity" of bond C-N_3 built the following series of compounds: benzofuroxan (25.8974 mdyn/Å), 5-methoxy-4-nitrobenzofuroxan (25.9473 mdyn/Å), 5-methyl-4-nitrobenzofuroxan (26.0784 mdyn/Å), 4-nitrobenzo-furoxan (26.1515 mdyn/Å), 7-methyl-4-nitrobenzofuroxan (26.1994 mdyn/Å), 5-fluoro-4-nitrobenzofuroxan (26.2838 mdyn/Å), 7-methoxy-4-nitrobenzofuroxan (26.2939 mdyn/Å).

It was mentioned that the rearrangement of the Boulton-Katritzky occurs in the connection direction in which the nitro group lies in the plane of the entire molecule. Thus there is a decrease in the calculated structure-sensitive descriptor $\nu_{cp.}'$ with 956.72 cm^{-1} to 894.65 cm^{-1}.

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