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Vibrational spectra and conformations of bis(*N*-ethyl)nitramine molecule ☆

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Abstract

The Raman (50–3200 cm^{-1}) and infrared (50–3200 cm^{-1}) spectra of bis(*N*-ethyl)nitramine, $(CH_3CH_2)_2NNO_2$, in the liquid and crystal states have been recorded. Optimized geometries and conformational stabilities have been obtained from ab initio calculations utilizing the RHF/6-31G** level. This compound was shown to have two stable conformations with a planar nitramine fragment and the CH_3 groups orthogonal to it and located either on the same or on the different sides of it. The computed energy difference between two conformers is 0.57 kcal/mol. $(CH_3CH_2)_2NNO_2$ exists as a mixture of the two conformations in the liquid state, while only the most stable one, with the CH_3 groups located on the different sides of the nitramine fragment, remains in crystal state. The vibrational frequencies have been calculated using ab initio scaled force fields, and the vibrational spectra have been interpreted in detail. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Vibrational spectra; Electron scattering; IR spectrum

1. Introduction

The nitramines are widely used in applied chemistry. These compounds are interesting from a theoretical point of view as well. The problem of bond configuration of nitrogen amine atom and molecular conformations is important and discussed for the last years in detail (Refs. [1–3] (and references therein)).

Recent gas electron diffraction studies of (*N*-chloromethyl-*N*-methyl)- [1] and bis(*N*-chloromethyl)- [2] nitramines showed that the most stable conformers have the C–Cl bonds which are practically orthogonal to the plane C_2NNO_2. In bis(*N*-chloromethyl)nitramine [2] two C–Cl bonds are placed on the opposite sides of the frame plane. It is possible to explain the found orthogonal conformers by the repulsive interactions of the negatively charged chlorine atoms and oxygen of the nitrogroup. Anomeric effect can be the alternative reason of the found conformation using the concept of the intramolecular interaction of the nitrogen lone pair electrons and antibonding σ^* orbital of C–Cl bonds.

☆ In honour of Professor Peter Klæboe on the occasion of his 70th birthday.

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