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ScienceDirect
Journal of Molecular Structure 878 (2008) 26–31
Journal of MOLECULAR STRUCTURE
www.elsevier.com/locate/molstruc

Geometric and electronic structures of benzoyl nitrite and benzoyl nitrate

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Received 19 March 2007; received in revised form 24 July 2007; accepted 26 July 2007
Available online 6 August 2007

Abstract

The electronic structures of benzoyl nitrite ($C_6H_5C(O)ONO$) and benzoyl nitrate ($C_6H_5C(O)ONO_2$) have been studied by HeI photoelectron spectroscopy (PES) and quantum chemical calculations. The photoelectron spectra are assigned with the help of the outer valence Green's function (OVGF) calculations. The first vertical ionization energies of $C_6H_5C(O)ONO$ and $C_6H_5C(O)ONO_2$ are determined to be 9.20 and 9.54 eV, respectively. According to the results of theoretical calculations, it can be concluded that a planar C—C(O)—O—N—O skeleton in $C_6H_5C(O)ONO$ and a planar C—C(O)—O—N skeleton in $C_6H_5C(O)ONO_2$ are the stable structures in the gas phase.

Keywords: HeI photoelectron spectroscopy; Ionization energy; Benzoyl nitrite; Benzoyl nitrate

1. Introduction

Compounds containing the moiety of —ONO or $-ONO_2$ attract much attention because of their important role in atmospheric chemistry. For example, the molecule of FC(O)ONO, which may be regarded as the NO adduct of the FC(O)O radical, is postulated to be an intermediate in the atmospheric degradation of chlorofluorocarbons [1]. Chlorine and bromine nitrates ($ClONO_2$, $BrONO_2$) can participate in the halogen and NO cycles of ozone depletion in the stratosphere [2,3]. Peroxynitric acid ($HOONO_2$) and peroxynitrates ($ROONO_2$) act as reservoir and transport species for NO_2 in atmospheric chemistry [4].

As for the structure of nitrites and nitrates, the bonding properties are of great interest. Recently, Oberhammer reviewed the N—O bond property in covalent nitrates and nitrites [5]. Because of the chemical instability of nitrites, a small number of gas phase structural studies of covalent nitrites have been performed [5]. The N—O bond length of HONO (1.397(6) Å) is the shortest among known nitrites (RONO) [6]. Organic nitrites RONO with R = methyl [7,8], ethyl [9], isopropyl [10], *t*-butyl [11], are thermally stable and their structures have been studied by microwave spectroscopy. Our group has reported longer N—O bond length of $CM_3C(O)ONO$ (M = H (1.560 Å), Cl (1.660 Å), F (1.675 Å)) by theoretical calculations (B3LYP/6-311+G(d,p)) [12].

The number of stable nitrates is larger than that of nitrites because of their chemical stability. The N—O single bond length in gaseous nitrates $RONO_2$ depends strongly on the substituent R. These compounds possess predominately covalent character with some polarity of the O—R bond. In covalent nitrates, the NO_3 moiety adopts C_s symmetry in comparison to the D_{3h} symmetry for NO_3 radical [13]. Among all the known nitrates, the shortest O—N single bond is in Me_3SiONO_2 (1.383(5) Å) [14], and the longest is in $CF_3C(O)ONO_2$ (1.604 Å, derived at the B3LYP/6-311+G(d,p) level) [12].

The study of electronic structures of carboxylic acids and their derivatives reveals the interactions between carbonyl oxygen lone pair (n_O) and the approximately non-

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doi:10.1016/j.molstruc.2007.07.037

bonding anti-symmetric π_2 orbital [15]. Photoelectron spectroscopy has been proved to be an effective method for studying the electronic structures of nitrites and nitrates [12,13]. No work has been reported when the substituent R of RONO and $RONO_2$ is a conjugated aryl group. In the present study, we report the photoelectron spectra of benzoyl nitrite and benzoyl nitrate. The molecular structures have been investigated by quantum chemical calculations. Their electronic structures are also analyzed according to the experimental and theoretical results.

2. Experimental and computational methods

Benzoyl nitrite ($C_6H_5C(O)ONO$) and benzoyl nitrate ($C_6H_5C(O)ONO_2$) were generated at room temperature of 20 °C through gas–solid reactions by passing ClNO or $ClNO_2$ vapor over finely powdered $C_6H_5C(O)OAg$, and in situ photoelectron spectra of the gas phase products were recorded. This procedure is similar to the description in Ref. [12] in detail. The reaction route is illustrated as follows:

$$ClNO(g) + C_6H_5C(O)OAg(s) \rightarrow C_6H_5C(O)ONO(g) + AgCl(s)$$

$$ClNO_2(g) + C_6H_5C(O)OAg(s) \rightarrow C_6H_5C(O)ONO_2(g) + AgCl(s)$$

ClNO and $ClNO_2$ were prepared according to Ref. [16], and the photoelectron spectra of both compounds were the same as that in Refs. [17,18]. $C_6H_5C(O)OAg$ were purchased from Alfa Aesar, and had been dried in vacuum (1×10^{-4} Torr) for 3 h at 60 °C before use.

Photoelectron spectrum was recorded on a double-chamber UPS-II instrument [19], which was specially designed for detecting unstable species. The spectral resolution of HeI spectra is about 30 meV, when measured as the full width at half-maximum (FWHM) of the $3p^{-1}\ ^2P_{2/3}$ $Ar^+ \leftarrow Ar\ (^1S_0)$ line. During the experiments, small amount of Ar gas and CH_3I was added to the sample flow to calibrate the experimental vertical ionization potentials.

Gaussian 03 programs [20] were used for the theoretical calculations of the two molecules, $C_6H_5C(O)ONO$ and $C_6H_5C(O)ONO_2$. These two molecules were optimized with three different methods MP2/6-311++G(d,p), B3PW91/6-311++G(d,p), and B3LYP/6-311++G(d,p), respectively. The vertical ionization energies were calculated at the ab initio level according to Cederbaum's outer valence Green's function (OVGF) [21] method. Compared with the experimental determined structures of covalent nitrates and nitrites, the B3LYP method reproduces all bond lengths very well [5]. So the structures derived from B3LYP/6-311++G(d,p) are used for OVGF calculations.

3. Results and discussion

3.1. Molecular structures

According to Ref. [12], benzoyl nitrites and nitrates may exist in the gas phase of two conformers with the C═O bond *syn* or *anti* with respect to the O—N bond (Chart 1). Furthermore, benzoyl nitrites may adopt a *syn*- or *anti*periplanar conformation between the benzoyl moiety and the N═O bond (Chart 2) [5]. So all the four possible conformers of $C_6H_5C(O)ONO$ and two possible conformers of $C_6H_5C(O)ONO_2$ were optimized. However, only the two conformers with C═O bond *syn* with respect to the O—N bond (*syn* structure in Chart 1) were found to be stable conformers after vibrational analysis. As for $C_6H_5C(O)ONO$, the conformer with benzoyl moiety *anti* to the N═O bond (*anti* structure in Chart 2) is the stable one. The other conformers are not local minima by vibrational analysis. The spatial interactions between the benzoyl group and the ONO or ONO_2 moiety decrease the stability of the other conformers.

In order to search for other possible conformers with different dihedral angle of δ_{CCON}, relax scans of the potential energy surface were performed by rotating the torsional angle δ_{CCON} in steps of 10° with HF/6-31G(d) and B3LYP/6-31G(d) approximation. The potential curves for $C_6H_5C(O)ONO$ and $C_6H_5C(O)ONO_2$ are shown in Figs. 1 and 2, respectively. At both levels, there are three minima

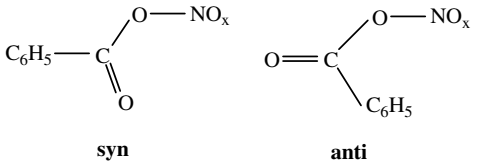

Chart 1. Possible conformers of $C_6H_5C(O)ONO_x$.

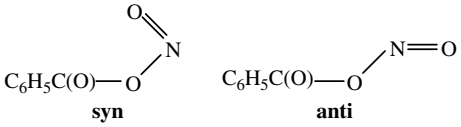

Chart 2. Possible conformers of $C_6H_5C(O)ONO$.

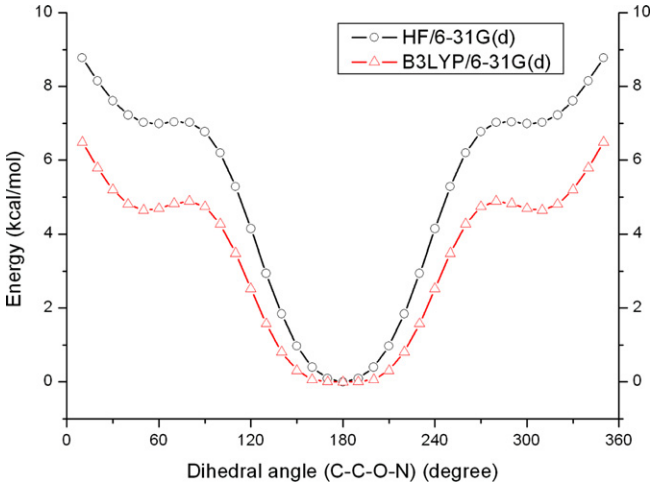

Fig. 1. Calculated potential curves for internal rotation around the C—O bond in $C_6H_5C(O)ONO$ at the HF/6-31G(d) and B3LYP/6-31G(d) levels.