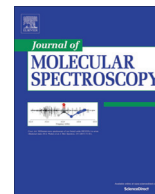




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Microwave spectrum, molecular structure, dipole moment, and quantum chemical calculations of *s-trans*-(*E*)-2-methyl-2-propenal oxime

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ABSTRACT

The spectroscopic constants of *s-trans*-(*E*)-2-methyl-2-propenal oxime (methacryl-aldehyde oxime) of normal, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{—CH}=\text{NOH}$, and its deuterated species, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{—CH}=\text{NOD}$, were determined by observing their microwave spectra in the frequency range of 8 to 40 GHz in the ground vibrational state. The rotational constants were $A = 8321.38(82)$, $B = 2076.09(1)$, and $C = 1678.60(1)$ MHz for normal species and $A = 8283.7(16)$, $B = 1998.63(2)$, and $C = 1626.21(2)$ MHz for deuterated species, respectively. The inertial defects ($\Delta I = I_c - I_a - I_b$) of normal and deuterated species were determined to be $-3.09(2)$ and $-3.10(3)$ $\text{u}\text{\AA}^2$, respectively. The dipole moments were determined as $\mu_a = 0.53(2)$, $\mu_b = 0.27(2)$, and $\mu_{\text{total}} = 0.60(5)$ D. The ^{14}N nuclear quadrupole coupling constants were determined as $\chi_{aa} = 3.62(12)$, $\chi_{bb} = -5.1(14)$, and $\chi_{cc} = 1.48(26)$ MHz. The comparison of the observed spectroscopic parameters with the calculated ones led to the conclusion that the assigned spectrum was due to *s-trans*-(*E*) form. The r_s coordinates of the hydrogen atom in a hydroxyl group were determined and the OH bond was found to be at the *trans* position with respect to the C=N double bond. The structural parameters of $r(\text{C}_2\text{—C}_3)$, $r(\text{C}_2\text{—C}_6)$, $\angle\text{C}_2\text{C}_3\text{N}$ and $\angle\text{C}_6\text{C}_2\text{C}_3$, for *s-trans-syn* form were adjusted to the four observed rotational constants (B and C). The observed rotational constants for *s-trans*-(*E*) form were in good agreement with those calculated using the MP2/6-31 G (d,p) level of theory.

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1. Introduction

We have previously reported the molecular conformations of two oximes with an unsaturated C=C bond by microwave spectroscopy; those are 2-propenal oxime (acrylaldehyde oxime, $\text{CH}_2=\text{CH—CH}=\text{NOH}$) (Fig. 1a) [1], and 2-butenal oxime (crotonaldehyde oxime, $\text{CH}_3\text{—CH}=\text{CH—CH}=\text{NOH}$) (Fig. 1b) [2], which are the related compounds of acetaldehyde oxime [3]. Two conformers of these oximes were found as *s-trans*-(*E*) and *s-trans*-(*Z*) forms. According to the MP2/6-31G(d,p) calculation, *s-trans*-(*E*) form were more stable by 4.3 and 1.31 kJ/mol than *s-trans*-(*Z*) form of 2-propenal oxime [1] and 2-butenal oxime [2], respectively.

On the other hand, we have studied propanal oxime (propionaldehyde oxime, $\text{CH}_3\text{—CH}_2\text{—CH}=\text{NOH}$) (Fig. 1c) [4,5], in which the vinyl group of 2-propenal oxime is replaced by an ethyl group. We have determined two rotational conformers of propanal oxime: (*E*)-*ac* (*anticlinal*: $\varphi: \angle\text{C}_1\text{C}_2\text{C}_3\text{N} = 120^\circ$) [4] and (*Z*)-*ap* (*antiperiplanar*: $\varphi = 180^\circ$) by microwave spectroscopy [5]. Third rotational isomer (*E*)-*sp* (*synperiplanar*: $\varphi = 0^\circ$) of propanal oxime was found by gas electron diffraction [6]. Ab initio calculations reproduced the

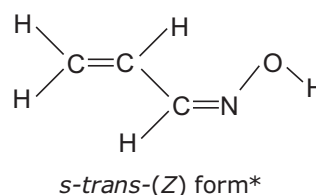
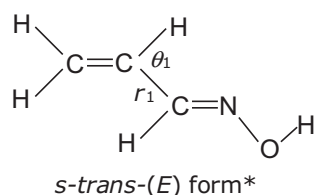
experimental data about conformational stability [7]. We found that the (*E*)-*ac* form was most stable and the energy difference between (*E*)-*ac* and (*E*)-*sp* was ca. 0.38 kJ/mol and that between (*E*)-*ac* (*Z*)-*ap* was ca. 1.19 kJ/mol.

Conformation of 2-methyl-2-propenal oxime ($\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{—CH}=\text{NOH}$) which is the title compound of this paper is interesting in terms of a conjugated molecular frame like 1,3-butadiene and 2-methyl-2-propenal (methacrylaldehyde, $\text{CH}_2=\text{C}(\text{CH}_3)\text{—CH}=\text{O}$) [8]. However, there are no experimental investigations of detailed and precise structural data for 2-methyl-2-propenal oxime although few experimental and theoretical studies were reported about the molecular conformation. The *syn* geometrical isomer ((*E*)-isomer) of this compound has been reported by ^1H NMR spectroscopy [9]. Then, *s-trans* form of the (*E*)-isomer of this compound was identified by ^{13}C NMR and ^1H NMR spectroscopy [10,11]. The dipole moment of *s-trans*-(*E*) form has also been found to be 0.79 D in carbon tetrachloride solution [12]. The electronic spectrum of *s-trans*-(*E*) form has been observed to be a $\pi\text{—}\pi^*$ transition at 222 nm in *n*-heptane solution [13]. Conformations of some oximes including 2-methyl-2-propenal oxime were studied by MINDO/3 calculations [14] for the interpretation of the electronic spectra of these compounds. The ab initio MO calculations at the RHF/6-31G(d) level of theory were performed in some oximes

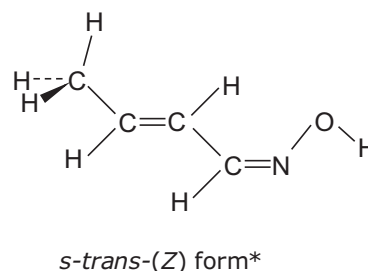
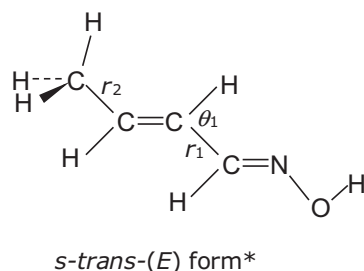
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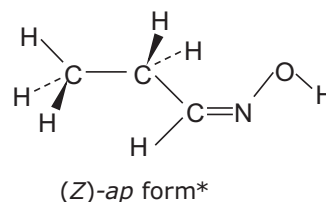
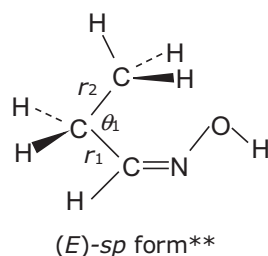
(a) 2-propenal oxime



(b) 2-butenal oxime



(c) propanal oxime



(d) 2-methyl-2-propenal oxime

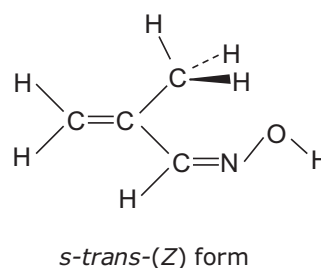
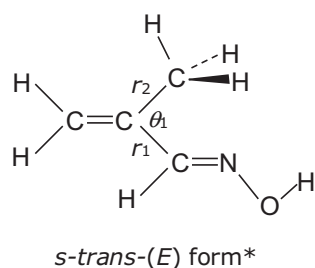


Fig. 1. Molecular structures of (a) 2-propenal oxime, (b) 2-butenal oxime, (c) propanal oxime and (d) 2-methyl-2-propenal oxime. The molecules marked with an asterisk determined by microwave spectroscopy. The molecule marked with double asterisks determined by gas electron diffraction.

including the (*E*)-isomer of 2-methyl-2-propenal oxime [15]; the relative conformational energies as a function of dihedral angle φ ($C=C-C=N$) were roughly calculated, so that their data points were insufficient and the feature of the potential curve was not elucidated.

As seen in these previous studies on 2-methyl-2-propenal oxime, experimental and theoretical information about the molecular structure and conformation of this compound is not sufficient. Rotational spectroscopy is a powerful experimental method to elucidate these properties precisely. In this work, we determined the rotational constants of normal and deuterated species, dipole moment, ^{14}N nuclear quadrupole coupling constants, and four structural parameters of *s-trans-(E)* form of 2-methyl-2-propenal oxime by microwave spectroscopy. We also discuss these

properties with the results of the theoretical calculations and the related compounds..

2. Experimental section

2-methyl-2-propenal oxime was prepared by adding 25 mL of 2-methyl-2-propenal into the solution of hydroxyl amine hydrochloride (20 g) and K_2CO_3 (20 g) in 60 mL water under 283 K with continuous stirring over 30 minutes. After separating and extracting the organic liquid, the sample was purified by the vacuum distillation. The deuterated species was produced by stirring the mixture of heavy water and 2-methyl-2-propenal oxime at 70 °C for 24 h, and extracted with ether as a solvent. The final

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