

Conformational stabilities from variable temperature Raman spectra, r_0 structural parameters and vibrational assignments of 1,2-diphosphinoethane

James R. Durig^{a,*}, Savitha S. Panikar^{a,1}, Shaun Sudhaunshu Purohit^{a,1}, Tain-Hen Pai^a, Victor F. Kalasinsky^b

^a Department of Chemistry, University of Missouri–Kansas City, Kansas City, MO 64110, USA

^b Division of Environmental Toxicology, Armed Forces Institute of Pathology, Washington, DC 20306, USA

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ABSTRACT

Infrared spectra (3600–500 cm^{-1}) of gas, amorphous, crystalline solid and Raman spectra (3000–200 cm^{-1}) of liquid and solid were recorded. Variable temperature Raman spectra (30 to $-38\text{ }^\circ\text{C}$) of liquid were recorded which indicates the presence of significant amounts of six conformers at ambient temperature. Rotation about C–C bond gives *Trans* (*T*) and *Gauche* (*G*) conformers and rotation around both C–P bonds gives *trans* (*t*) and *gauche* (*g*) forms. Enthalpy differences for five of the lower energy conformers w.r.t. the lowest energy *tTt* form were determined to be $272 \pm 39\text{ cm}^{-1}$, $434 \pm 40\text{ cm}^{-1}$, $443 \pm 30\text{ cm}^{-1}$, $663 \pm 60\text{ cm}^{-1}$ and $671 \pm 34\text{ cm}^{-1}$ for *g'Tt*, *g'Tg'*, *g'Tg*, *tG'g'* and *tG't* conformers, respectively, which are in the increasing order of energy. *Ab initio* calculations with various basis sets up to aug-cc-pVTZ were performed and to support the spectroscopic studies MP2(full)/6-31G(d) was used to predict Raman activities, infrared intensities, vibrational frequencies and band contours. By utilizing the previously reported microwave rotational constants along with MP2(full)/6-311+G(d,p) predictions, adjusted r_0 parameters were obtained for two *Trans* and two *Gauche* (C–C bond) conformers. The determined heavy atom structural parameters for *g'Tt* [*g'Tg'*] [*tG'g'*] [*tG't*] conformers are: distances (Å) $P_1\text{--}C_2 = 1.870(3)$ [$1.866(3)$] [$1.858(3)$] [$1.859(3)$], $C_2\text{--}C_3 = 1.535(3)$ [$1.536(3)$] [$1.534(3)$] [$1.536(3)$], $C_3\text{--}P_4 = 1.863(3)$ [$1.866(3)$] [$1.866(3)$] [$1.859(3)$], and angles ($^\circ$) $\angle P_1C_2C_3 = 110.5(5)$ [$110.4(5)$] [$117.0(5)$] [$118.5(5)$], $\angle C_2C_3P_4 = 115.5(5)$ [$110.4(5)$] [$113.7(5)$] [$118.5(5)$]. The results are discussed and compared to the corresponding properties of some similar molecules.

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1. Introduction

The 1,2-disubstituted ethane ($\text{YCH}_2\text{CH}_2\text{X}$) molecules are of interest since most of them have two conformers *trans* (*anti*) and *gauche*, present in the fluid states and their relative stabilities are believed to depend on the electronegativity and size of the substituents. For example, 1,2-difluoroethane has the *gauche* conformer lower in energy than the *trans* form by $280 \pm 30\text{ cm}^{-1}$ ($3.35 \pm 0.36\text{ kJ mol}^{-1}$) [1], whereas, 1,2-dichloroethane has the *trans* conformer lower in energy than the *gauche* form [2] by $323 \pm 7\text{ cm}^{-1}$ ($3.87 \pm 0.09\text{ kJ mol}^{-1}$) from variable temperature infrared studies of xenon solutions. When Y is a methyl group and X is a fluorine atom (1-fluoropropane) the *gauche* conformer has lower energy [3] than the *trans* form by $104 \pm 6\text{ cm}^{-1}$ ($1.24 \pm 0.07\text{ kJ mol}^{-1}$). One might expect the 1-chloro-2-fluoroethane molecule to have the *gauche* conformer with lower energy since the fluorine and chlorine

atoms are highly electronegative and the chlorine atom has a van der Waal's radius nearly the same as that of the methyl group. However, it has been reported that the 1-chloro-2-fluoroethane molecule has the *trans* form with lower energy than the *gauche* by $287 \pm 58\text{ cm}^{-1}$ ($3.43 \pm 0.69\text{ kJ mol}^{-1}$) from a determination of the enthalpy difference from the variable temperature Raman spectra of the gas [4] as well as from a variable temperature study of rare gas solutions [5]. Thus, it is clear that there are additional factors than just size and electronegativity that determines which conformer has the lowest energy.

As a continuation of our studies of 1,2-substituted ethanes, we have investigated the conformational stability of 1,2-diaminoethane (ethylenediamine) [6] and 1,2-diphosphinoethane (ethylenediphosphine) to determine whether there is a significant difference in the conformer stabilities of these two molecules since both ethylamine [7] and ethylphosphine [8] have the *trans* conformers as the lower energy forms. We were particularly interested in the phosphine molecule since some of the phosphines have been shown to have anticancer properties [9,10].

We initiated the investigation of the vibrational spectra of 1,2-diphosphinoethane with a study of the infrared spectra of the gas, amorphous and crystalline solid. Additionally, we have

* Corresponding author. Tel.: +1 816 235 6038; fax: +1 816 235 2290.

E-mail address: durigj@umkc.edu (J.R. Durig).

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investigated the Raman spectra of the liquid and solid. Variable temperature Raman spectra of the liquid have been obtained from which enthalpy differences between the various conformers were determined. Rotation about the C–C bond gives rise to *Trans* (*T*) and *Gauche* (*G*) forms which are indicated by capital letters and rotation around both of the C–P bonds also results in *trans* (*t*) and *gauche* (*g*) forms which are indicated by lower case letters. There are a total of 10 possible stable conformers that can exist for the H₂PCH₂CH₂PH₂ molecule which are shown in Fig. 1.

To support the vibrational study, we have carried out *ab initio* calculations with basis sets up to aug-cc-pVTZ as well as those with diffuse functions up to 6-311+G(2df,2pd). We have also carried out density functional theory (DFT) calculations by the B3LYP method with the same basis sets. We have calculated optimized geometries, conformational stabilities, harmonic force constants, infrared intensities and Raman activities. By utilizing the previously reported [11] microwave rotational constants along with *ab initio* MP2(full)/6-311+G(d,p) predicted structural values, adjusted r_0 parameters have been obtained for two C–C *Trans* and two C–C *Gauche* conformers. The results of these spectroscopic, structural, and theoretical studies are reported herein.

2. Experimental methods

The sample of 1,2-diphosphinoethane was purchased from Strem Chemicals, Inc., Newburyport, MA. The purity was determined by gas chromatography to be greater than 96%. The sample was subjected to trap-to-trap transfers under vacuum prior to recording spectra and stored at -78 °C.

Infrared spectra of the solid in the 3600–500 cm^{-1} region were obtained with a Perkin–Elmer 283B grating spectrophotometer and a liquid-nitrogen-cooled sampling cell with a CsI substrate. The spectra of the solids were recorded at a resolution of 2.0 cm^{-1} . Infrared spectrum of the crystalline solid was obtained by the process of annealing which was achieved by repetitive evaporation of the liquid nitrogen completely from the reservoir in the solid cell, which resulted in a gradual increase in the temperature, which was then followed by sudden freezing of the sample by the addition of liquid nitrogen. This warming process allowed the molecules to form a crystalline structure. Gaseous phase infrared

samples were contained in a 10 cm cell fitted with KBr windows, and the spectra were recorded on a Nicolet 7199 Fourier transform interferometer equipped with a Ge/KBr beamsplitter and a liquid-nitrogen-cooled MCT detector. The instrument was purged to remove the water and carbon dioxide by a commercial two column dryer with one column to remove water and the other carbon dioxide. The resolution for the spectra of the gas was 0.5 cm^{-1} at ambient pressure of the gas. The infrared spectra of the gas, amorphous and crystalline solid are shown in Fig. 2A–C, respectively.

Raman spectra were recorded from 3000 to 200 cm^{-1} on a Spex Ramalog DUV spectrometer set to use the 4880 Å line of a Spectra-Physics model 171 argon ion laser as the excitation source with a laser power of 200 mW. Liquid samples were sealed in Pyrex capillaries under vacuum, and spectra of solids and variable temperature liquids were obtained by using a cell similar to one described by Miller and Harney [12]. All of the Raman spectra were recorded at 3 cm^{-1} spectral bandwidths and frequencies are expected to be accurate to better than 2 cm^{-1} . The Raman spectra of the liquid and the solid are shown in Fig. 3A and B, respectively.

3. Theoretical methods

The *ab initio* calculations were performed with the Gaussian 03 program [13] with Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all geometric parameters by the gradient method of Pulay [14]. Several basis sets as well as the corresponding ones with diffuse functions were employed with the Møller–Plesset perturbation method [15] to the second order (MP2(full)) as well as with the density functional theory (DFT) by the B3LYP method.

In order to obtain a complete description of the molecular motions involved in the fundamental vibrations of 1,2-diphosphinoethane, normal coordinate analyses were carried out. The force field in Cartesian coordinates was obtained with the Gaussian 03 program [13] with the 6-31G(d) basis set. The internal coordinates used to calculate the G and B matrices along with the atomic numbering are shown in Fig. 4. By using the B matrix [16], the force field in Cartesian coordinates was converted to a force field in internal coordinates. Subsequently, scaling factors were applied

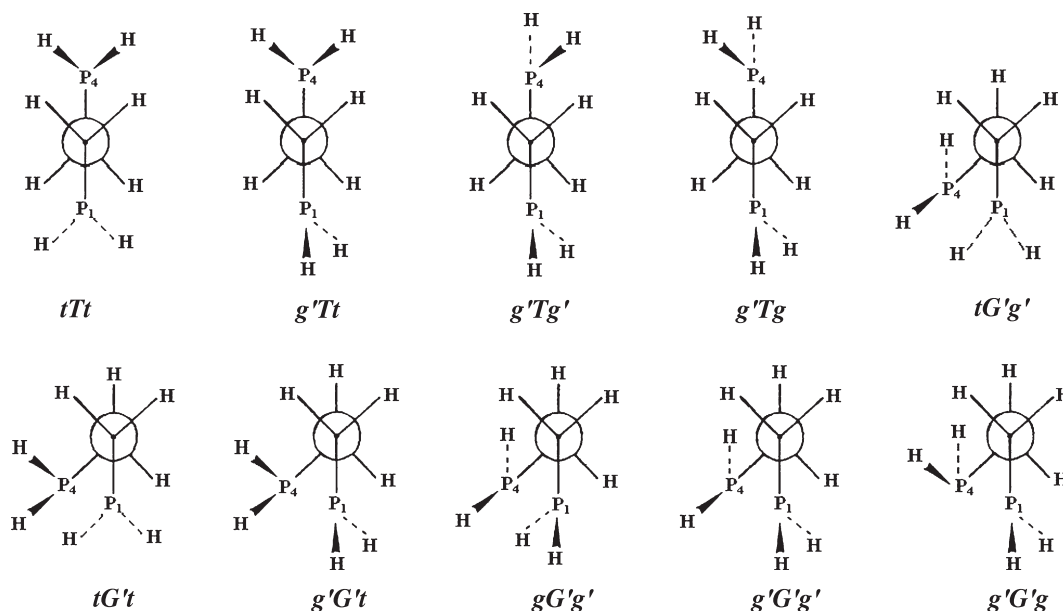


Fig. 1. Newmann projections of the 10 conformers of 1,2-diphosphinoethane.

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