Journal of Molecular Structure 921 (2009) 72–79

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Molecular structures, conformations, force fields and large amplitude motion of *cis*-3-chloro-2-propen-1-ol as studied by quantum chemical calculations and gas electron diffraction augmented with quantum chemical calculations on 2-propen-1-ol

Tor G. Strand [a,*], Snefrid Gundersen [a], Hanno Priebe [b], Svein Samdal [c,*], Ragnhild Seip [a]

[a] *Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, NO-0315 Oslo, Norway*
[b] *GE Healthcare, P.O. Box 4220 Nydalen, NO-0671 Oslo, Norway*
[c] *Center for Theoretical and Computational Chemistry (CTCC), Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, NO-0315 Oslo, Norway*

ARTICLE INFO

Article history:
Received 27 October 2008
Received in revised form 9 December 2008
Accepted 9 December 2008
Available online 24 December 2008

Keywords:
cis-3-Chloro-2-propen-1-ol
Gas electron diffraction
Conformations
Large amplitude motion
Quantum chemical calculations
2-Propen-1-ol

ABSTRACT

B3LYP and MP2(F) quantum chemical calculations have been performed for 2-propen-1-ol using the cc-pVTZ basis set. Five stable conformations are detected and related to the two conformations observed experimentally. The calculated normal frequencies are scaled for two conformers and their assignments are compared. Similar quantum chemical calculations predict three stable conformers for *cis*-3-chloro-2-propen-1-ol. Quantum chemical force field calculations reveal large amplitude motions about the C—C bond for all conformers. Least-squares refinements of the gas electron diffraction data using a mixture of two static conformers verify the presence of these two conformers. The agreement with the experimental data for this type of refinements is not satisfactory which indicates that large amplitude models should be used. Describing the torsions about the C—C bond as frame work vibrations in harmonic large amplitude angular motion of Gaussian distributions for two conformations improved the agreement with the experimental data considerably. The root-mean-square angular amplitude of the torsions for the two conformations refined to 28.6(12)° and 21.4(46)°, with dihedral angles C—C—C—O equal to −125.5(17)° and 180(fixed)°, respectively. Some r_a distances (Å) and r_α angles (degrees) obtained are: r(C—C) = 1.5044(20), r(C=C) = 1.3435(16), r(C—O) = 1.4299(14) and r(C—Cl) = 1.7366(19), <(C—C—C) = 125.60(12), <(C—C—O) = 111.0(2), <(C—C—Cl) = 123.61(10). Parenthesized values are $[\sigma_{\mathrm{lsq}}^2 + (0.001 \times r)^2]^{1/2}$ for bond distances, where σ_{lsq} is the least-squares standard deviation. For the angles σ_{lsq} is given. There is good agreement between the experimental results and the quantum chemical calculations.

1. Introduction

2-Propen-1-ol (allyl alcohol, $H_2C{=}CHCH_2OH$) has been investigated by several experimental techniques such as microwave spectroscopy(MW) [1–4], vibrational spectroscopy(infrared, IR and Raman, R) [5–11], NMR [12,13], gas electron diffraction(GED) [14] and quantum chemical methods [10,14–16] in order to determine its conformers. Surprisingly, no quantum chemical calculations have focused on the conformational properties of 2-propen-1-ol for the last two decades, and the calculations which are performed were all at a low level. Optimized geometries have been calculated for six conformations at the HF/4-21G level [14]. Aspiala et al. [10] have given energy differences between four conformations using different methods and basis sets fixed at the HF/4-21G geometry, while Kao and Katz [16] have optimized the geometry for five conformations at the HF/STO-3G level. Only one force field calculation has been found in the literature and that is for the most stable (sp, sc) conformer of 2-propen-1-ol [14]. All conformations were characterized by different dihedral angles about the C—C and C—O bonds. The most important stabilizing factors are the interaction between the hydroxyl H-atom and the π-electron system of the double bond, forming an internal H-bond, and steric hindrance. Experimentally, the existence of only two of the five conformers have been verified by IR [10], GED [14] and MW [1–4].

Our GED data of *cis*-3-chloro-2-propen-1-ol, $ClHC{=}CHCH_2OH$, were recorded in 1984, and the data have been periodically investigated in view of current available ab initio calculations. However, no really convincing agreement was obtained.

The main objects of this investigation are to study the conformational behaviour of *cis*-3-chloro-2-propen-1-ol, to obtain a best possible model for the GED investigation, to compare it with the

---

* Corresponding authors.
E-mail addresses: t.g.strand@kjemi.uio.no (T.G. Strand), svein.samdal@kjemi.uio.no (S. Samdal).

0022-2860/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2008.12.036

conformations of 2-propen-1-ol, and to determine if the Cl atom is able to form an intra molecular H-bond to the hydroxyl H-atom.

Since only low-level quantum chemical calculations are available for 2-propen-1-ol similar calculations as for *cis*-3-chloro-2-propen-1-ol has been undertaken for a better comparison between geometries and frequencies of these two molecules.

2. Quantum chemical calculations

2.1. 2-Propen-1-ol

Several calculations have been performed in this study using different methods such as HF, DFT and MP2, and basis sets such as 6-31G*, 6-311++G** and cc-pVTZ. These calculations confirm that the first five conformations given by Vanhouteghem et al. [14] are true minima while the sixth conformation is a first order transition state. All calculations are obtained using Gaussian03 [17]. Table 1 shows the calculated molecular structures for the five stable conformers obtained by the methods B3LYP and MP2(F) where F means that all electrons are included in the Møller-Plesset perturbation theory, and using the cc-pVTZ basis set. Table 2 shows the energy differences, thermodynamic quantities, dipole moments and rotational constants which should be of particular interest for MW, and for further investigations in order to detect some of the other conformers of this molecule.

Several vibrational spectroscopic investigations have been made and two of the five conformers have been assigned. In Table 3 are given both unscaled calculated frequencies obtained by B3LYP and MP2(F) using the cc-pVTZ basis set for the two assign conformers, and MP2(F) calculated frequencies which are scaled to the observed vibrational frequencies. Table S1 (Supporting information) displays unscaled calculated frequencies for all five conformers.

2.2. cis-3-Chloro-2-propen-1-ol

B3LYP/6-31G* calculations were first used to obtain the potential energy surface spanned by the dihedral angles C3—C2—C1—O7 and C2—C1—O7—H8. Three stable conformers were found. The calculated molecular structures obtained by B3LYP and MP2(F) using the cc-pVTZ basis set for the three stable conformers are given in Table 4. Table 5 shows the energy differences, thermodynamic quantities, dipole moments and rotational constants which should be of particular interest for MW. Table 6 gives unscaled calculated frequencies for the three stable conformers.

Comparing the structure parameters obtained from the B3LYP and MP2(F) calculations for the three conformers given in Table 4 reveals no pronounced differences except for the important C3—C2—C1—O7 dihedral angle for conformer 2. The B3LYP value is −154.9° while MP2(F) converges towards Cs symmetry and a dihedral angle of 179.9°. This is a surprisingly large difference. Attempts have been made to test if this difference is related to the method or to the basis set. For the B3LYP calculations a larger grid (integral = ultrafine) has been used together with the larger basis sets aug-cc-pVTZ where diffuse functions have been included, and the cc-pVQZ basis set. Dihedral C3—C2—C1—O7 angles of −155.2° and −154.9°, respectively, were obtained for the B3LYP method while the MP2(F)/cc-pVQZ gave −179.5°. These calculations indicates that the difference in the calculated C3—C2—C1—O7 dihedral angle for conformer 2 is most likely related to the method and not to the size of the grid, not to diffuse functions, and not to the size of the basis set.

3. Electron diffraction

3.1. Data reduction

cis-3-Chloro-2-propen-1-ol was prepared from *cis*-1,3-dichloropropene and aqueous sodium carbonate according to the literature [18,19] by Hanno Priebe, and the GED scattering pattern was recorded on Kodak Electron Image plates on the Oslo apparatus in November 1984. Six plates for the long camera distance data (485.21 mm) and two plates for the short camera distance data (205.21 mm) were obtained at a nozzle temperature of about 67 °C.

Table 1

Calculated and experimental geometry[a] obtained for five different conformations of 2-propen-1-ol.

	Conf. 1 = (sp, sc)[b]			Conf. 2 = (ac, −sc)[b]				Conf. 3 = (sp, ap)[b]		Conf. 4 = (ac, ap)[b]		Conf. 5 = (ac, sc)[b]	
	B3LYP	MP2(F)	GED [14]	B3LYP	MP2(F)	MW [3]	GED [14]	B3LYP	MP2(F)	B3LYP	MP2(F)	B3LYP	MP2(F)
C1—C2	1.501	1.492	1.500	1.498	1.488	1.503	1.495	1.496	1.487	1.495	1.485	1.500	1.489
C1—O7	1.417	1.410	1.425	1.428	1.421	1.423	1.432	1.419	1.413	1.428	1.421	1.429	1.422
C1—H9	1.094	1.087	1.112	1.096	1.090	1.124	1.110	1.099	1.092	1.096	1.090	1.090	1.084
C1—H10	1.099	1.092	1.108	1.092	1.085	1.095	1.106	1.099	1.092	1.098	1.091	1.098	1.091
C2═C3	1.326	1.328	1.334	1.327	1.330	1.332	1.336	1.325	1.327	1.325	1.328	1.326	1.329
C2—H6	1.086	1.079	1.103	1.086	1.078	1.098	1.101	1.086	1.079	1.085	1.078	1.087	1.080
C3—H4	1.081	1.075	1.101	1.082	1.076	1.072	1.101	1.081	1.076	1.082	1.076	1.082	1.076
C3—H5	1.082	1.076	1.102	1.084	1.078	1.099	1.103	1.081	1.075	1.084	1.078	1.084	1.078
O7—H8	0.963	0.961	1.029	0.963	0.960	0.962	1.029	0.961	0.958	0.961	0.959	0.962	0.960
C2—C1—O7	114.9	114.2	113.6	112.3	111.9	112.1	112.2	110.6	109.7	108.5	107.9	113.0	112.8
C2—C1—H9	109.5	109.5	111.3	110.1	109.6	105.2	111.9	108.8	108.8	110.0	109.4	110.1	109.6
C2—C1—H10	109.0	109.1	111.7	110.3	110.5	108.0	112.1	108.8	108.8	109.1	109.3	109.9	110.1
O7—C1—H9	105.8	105.9	112.0	111.3	111.6	114.6	112.3	111.0	111.2	111.3	111.6	105.8	105.9
O7—C1—H10	111.1	111.3	106.5	105.0	105.1	107.4	105.8	111.0	111.2	110.1	110.5	110.3	110.6
H9—C1—H10	106.1	106.6		107.6	107.9			106.6	107.1	107.7	108.1	107.5	107.7
C1—C2—C3	125.4	124.4	124.7	124.4	123.5	124.5	125.3	125.4	124.4	124.5	123.7	124.7	123.9
C1—C2—H6	114.7	115.8		115.5	116.3			114.3	115.4	115.1	115.9	115.8	116.7
C3—C2—H6	119.9	119.9	119.0	120.2	120.2	120.4	118.9	120.3	120.2	120.3	120.3	119.5	119.5
C2—C3—H4	121.4	121.1	119.8	121.9	121.7	123.2	119.9	121.1	120.8	121.7	121.5	121.9	121.7
C2—C3—H5	121.4	120.8	119.0	121.4	120.7	119.3	119.9	121.2	120.6	121.6	120.9	121.4	120.7
H4—C3—H5	117.2	118.1		116.7	117.6			117.7	118.7	116.8	117.7	116.7	117.7
C1—O7—H8	108.2	107.0	102.8	107.9	106.7	107.2	102.8	108.5	107.6	108.5	107.7	108.6	107.6
C3—C2—C1—O7	5.1	5.2		123.5	120.6	122.0	122.0	0.0	0.0	128.4	125.4	120.5	118.2
C2—C1—O7—H8	62.1	60.3		−57.2	−58.0	−56.3	−62.0	180.0	180.0	168.8	169.5	65.8	64.6

[a] Distances in Å and angles in degrees. Basis set is cc-pVTZ.

[b] sp = syn-periplanar(−30° to +30°), +sc = syn-clinal(+30° to +90°), +ac = anti-clinal(+90° to +150°), +ap = anti-periplanar(+150° to +210°), −ac = −anti-clinal(+210° to +270° or −90° to −150°) and −sc = −syn-clinal(+270° to +330° or −30° to −90°). Changing the sign gives mirror image which is identical from a GED point of view.