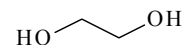


304 C₂H₆O₂ED, MW, *ab initio*
calculations**1,2-Ethanediol**

Ethylene glycol

C₁ (*g⁻Ga*)**C₂ (*g⁻Gg*)****C_{2h} (*aAa*)**

| r_a^0 | $\text{\AA}^a)$ | | |
|-----------------------------|------------------------|------------------------|---------------------|
| | <i>g⁻Ga</i> | <i>g⁻Gg</i> | <i>aAa</i> |
| O–H ^{b) c)} | 0.961(8) | 0.962(8) | 0.960(8) |
| C–H ^{b) c)} | 1.118(6) | 1.117(6) | 1.118(6) |
| C–O ^{b) c)} | 1.424(1) | 1.424(1) | 1.424(1) |
| C–C | 1.517(5) | 1.521(5) | 1.517(5) |
| θ_a^0 | deg ^{a)} | | |
| | <i>g⁻Ga</i> | <i>g⁻Gg</i> | <i>aAa</i> |
| C–C–O ^{b)} | 109.3(4) | 111.2(7) | 110.5(30) |
| Δ_1 ^{d)} | 5.6(34) | 0.5(21) | 0.0 ^{e)} |
| C–O–H ^{b)} | 105.8(27) | 108.2(21) | 109.6(21) |
| R–C–H ^{b) f)} | 109.1(10) | 108.0(11) | 110.5(21) |
| Δ_2 ^{f) g)} | 2.0(41) | 0.0(19) | 0.0 ^{e)} |
| τ_1 ^{h)} | –54.0(21) | –45.6(21) | 180.0 ^{e)} |
| τ_2 ⁱ⁾ | 60.7(18) | 57.5(30) | 180.0 ^{e)} |
| τ_3 ^{j)} | –169.7(20) | 76.0(21) | 180.0 ^{e)} |



ED data were supplemented by ground state rotational constants for eight isotopic species taken from the literature. The system model consisted of three conformers, *g⁻Ga*, *g⁻Gg* and *aAa*, which were found to provide a good representation of the 10 possible different conformations. *A* (*anti*) and *G* (*gauche*) designate the heavy atom conformations; lower case letters describe the orientations of the H atoms in the OH groups with respect to the C–C bond. The ratio of conformers *g⁻Ga*:*g⁻Gg*:*aAa* was found to be 58(7):34(7):8(7) at 376 K. The internal energy difference ΔE° of 1.4(5) kcal mol^{–1} for the reaction *G* → *A* estimated by *ab initio* (HF/6-31G*) method may be taken as a rough value for the energy of the O–H...O internal hydrogen bond.

The experimental data were obtained at nozzle temperatures of 376 K and 733 K. The data are presented here for 376 K.

^{a)} Twice the estimated standard errors.

^{b)} Average value within each conformer.

^{c)} Bond lengths of different conformers were refined as groups with differences between them assumed at the value from HF/6-31G* calculations.

^{d)} [C–C(1)–O] – [C–C(2)–O].

^{e)} Assumed.

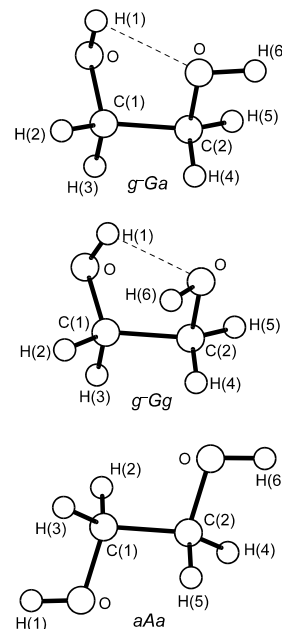
^{f)} R = C or O. O–C–H and C–C–H assumed to be equal.

^{g)} [R–C(1)–H] – [R–C(2)–H].

^{h)} C–C–O–H(1) torsional angle from the *syn* position.

ⁱ⁾ O–C–C–O torsional angle from the *syn* position.

^{j)} C–C–O–H(6) torsional angle from the *syn* position.



Kazerouni, M.R., Hedberg, L., Hedberg, K.: J. Am. Chem. Soc. **119** (1997) 8324.

Structure Data of Free Polyatomic Molecules

MW

| r_0 | \AA^a | | θ_0 | deg^a | |
|-----------|---------------------|---------------------|------------------|---------------------|---------------------|
| | g^-Ga | g^-Gg | | g^-Ga | g^-Gg |
| C(1)–C(2) | 1.5124 ^b | 1.5159 ^b | O–C(2)–C(1) | 108.08(50) | 112.21(50) |
| C(2)–O | 1.4385(50) | 1.4388(50) | O–C(1)–C(2) | 110.64 ^b | 110.47 ^b |
| C(1)–O | 1.4138(50) | 1.4126(50) | H(3)–C(1)–C(2) | 110.10 ^b | 110.59 ^b |
| C(1)–H(3) | 1.0923 ^b | 1.0930 ^b | H(2)–C(1)–C(2) | 108.75 ^b | 109.08 ^b |
| C(1)–H(2) | 1.0987 ^b | 1.1021 ^b | H(4)–C(2)–C(1) | 110.57 ^b | 111.09 ^b |
| C(2)–H(4) | 1.0977 ^b | 1.0975 ^b | H(5)–C(2)–C(1) | 108.68 ^b | 109.39 ^b |
| C(2)–H(5) | 1.0964 ^b | 1.0911 ^b | H(6)–O–C(2) | 106.40(50) | 105.41(50) |
| O–H(6) | 0.9579 ^b | 0.9604 ^b | H(1)–O–C(1) | 103.98 ^b | 104.29 ^b |
| O–H(1) | 0.9617 ^b | 0.9622 ^b | O–C(1)–C(2)–O | 60.80(50) | 56.88(50) |
| | | | H(3)–C(1)–C(2)–O | 179.47 ^b | 175.99 ^b |
| | | | H(4)–C(2)–C(1)–O | 181.76 ^b | 181.25 ^b |
| | | | H(2)–C(1)–C(2)–O | –61.76 ^b | –65.50 ^b |
| | | | H(5)–C(2)–C(1)–O | –58.21 ^b | –58.45 ^b |
| | | | H(6)–O–C(2)–C(1) | 196.57(50) | 67.97(50) |
| | | | H(1)–O–C(1)–C(2) | 295.57(50) | 302.39(50) |

The microwave spectrum of an energetically unfavored g^-Gg conformer was observed. This spectrum is dominated by an interconversion geared-type large-amplitude motion, during which each OH group in turn forms the intramolecular hydrogen bond. The observed spectrum was analyzed with the help of a Watson-type Hamiltonian plus a 1.4-GHz tunneling splitting. The rotational dependence of this splitting was examined using an IAM approach and this yielded qualitative information on the tunneling path the molecule uses to interconvert between its two most stable conformers. Unexpectedly, but in agreement with *ab initio* calculations, when tunneling occurs between the energetically equivalent g^-Gg and gGg^- conformers, the OH groups are rotated stepwise through 240° in the sense of a flip-flop rather than a concerted rotation and the molecule goes through the more stable g^-Ga and aGg^- forms.

^a) Uncertainties were not estimated in the original paper.

^b) Assumed.

Christen, D., Coudert, L.H., Larsson, J.A., Cremer, D.: J. Mol. Spectrosc. **205** (2001) 185.

Replaces [II/25B\(3, 896\)](#)