

# A Monte Carlo Simulation of Liquid 1,2-Dimethoxyethane

Dario Bressanini, Aldo Gamba,\* and Gabriele Morosi

*Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, Via G. Golgi 19, I-20133 Milano, Italy (Received: May 25, 1989; In Final Form: November 22, 1989)*

Monte Carlo simulations have been carried out for liquid 1,2-dimethoxyethane in the NVT ensemble at 298 K with 125 and 216 molecules. The intermolecular interactions are described as sums of Lennard-Jones and Coulomb terms. The intramolecular rotations are described by an analytical potential function fitted to MM2 energies. The heat of vaporization is found in good agreement with the experimental value. While the gas phase is a mixture of gauche and anti conformations, in the pure liquid the gauche conformation is preferred, as found experimentally. The liquid is disordered with high coordination numbers and the most evident packing effect is shown by terminal CH<sub>3</sub> groups.

## Introduction

1,2-Dimethoxyethane (DME) has a good solvent effect on proton donors and may form relatively stable complexes with alkali-metal and alkaline-earth-metal ions<sup>1</sup> and with proton donors like organolithium compounds.<sup>2</sup> It is one of the most frequently used solvents in the study of ion pairs in solutions by ESR spectroscopy.<sup>3</sup> Many conformers are possible for DME owing to the rotations around CH<sub>2</sub>—CH<sub>2</sub> and the two CH<sub>2</sub>—O bonds; owing to sterical hindrance the conformation around CH<sub>2</sub>—O is anti, while the rotational flexibility around the CH<sub>2</sub>—CH<sub>2</sub> bond allows the presence of gauche and anti conformers. From now on gauche and anti conformers refer to the CH<sub>2</sub>—CH<sub>2</sub> bond. A study by the electron diffraction method<sup>4</sup> concluded that DME exists as a mixture of several conformers in the gas phase. Using NMR spectroscopy, Viti et al.<sup>5</sup> found that the difference in energy between gauche and anti conformers is 0.42 kcal mol<sup>-1</sup> in favor of the anti form and that the population of the gauche form increases on going from gas to liquid phase. These results supported a theoretical analysis<sup>6</sup> using a semiempirical potential functions with the solvent considered as a continuous dielectric medium. Andersson and Karlström<sup>7</sup> have studied DME in the gas phase and in polar solvents; they found by ab initio calculations at the SCF level that the energy difference amounts to 0.9 kcal mol<sup>-1</sup>, and they showed that a continuous model for a polar solvent cannot explain the effect on the relative populations of gauche and anti conformers but that one must adopt a molecular description. Improvement of the basis set and introduction of the correlation energy decrease the energy difference between gauche and anti forms;<sup>8</sup> at present the best ab initio calculations suggest a difference in energy of only 0.5 kcal mol<sup>-1</sup>.

On the basis of this new potential hypersurface, in this paper we reexamine the conformational equilibria in DME in both the gas and liquid phase, simulated by a molecular model. Furthermore, the description of liquid DME is intended to be the first step of a set of simulations of ion pairs in this solvent. In the next section we will present the intermolecular and intramolecular potentials; then we will introduce the Monte Carlo simulations of the liquid, followed by thermodynamic and structural results, which will be shown to be in good agreement with available experimental data.

## Intermolecular and Intramolecular Potential Functions

The computing time in Monte Carlo simulations largely depends on the calculation of the intermolecular potential, and so it is determined by the number of interaction sites on the molecule; to reduce it, the CH<sub>2</sub> and CH<sub>3</sub> groups in DME are taken as single units centered on carbon. In the case of methanol this approximation has been shown not to hamper a correct description of the liquid.<sup>9</sup> Fixed bond lengths C—C = 1.516 Å and C—O = 1.410 Å and bond angles C—C—O = 109.47° and C—O—C = 112° are assumed, on the basis of electron diffraction data<sup>4</sup> and ab initio calculations,<sup>8</sup> while internal rotations are included in the simulation. Numbering of atoms and torsional angles is shown in Figure 1. The intermolecular potential is a sum of site-site Lennard-Jones and Coulomb terms

$$\Delta E_{ab} = \sum_i^{\text{on a}} \sum_j^{\text{on b}} \frac{A_i A_j}{r_{ij}^{12}} - \frac{B_i B_j}{r_{ij}^6} + \frac{q_i q_j}{r_{ij}}$$

For alkyl groups we used TIPS parameters;<sup>10</sup> the corresponding ones for oxygen, fitted to ethers containing only one oxygen, in a test run predicted an enthalpy of vaporization of about 9.7 kcal mol<sup>-1</sup>, with an error nearly double with respect to the results on alkyl ethers obtained by Jorgensen and Ibrahim.<sup>10</sup> We tried the parameters recommended by Mirsky<sup>11</sup> on the basis of a comparison he made among a large set of intermolecular atom-atom potentials; the agreement between theoretical and experimental heat of vaporization being improved, we decided to adopt this potential, even if we cannot claim that it is better than the TIPS potential on the basis of this single result. The charge on oxygen is adjusted so that the average dipole moment, calculated from a Boltzmann distribution for  $V(\phi_1, \phi_2, \phi_3)$  for a monomer, reproduces the experimental value of 1.71 D<sup>12</sup> at 298 K. The final value is -0.44 e; opposite charges of +0.22 e on adjacent alkyl groups balance the charge on oxygen. The value of -0.44 e is slightly less than -0.50 e suggested by Jorgensen and Ibrahim<sup>10</sup> for alkyl ethers.

Particular care was given to the definition of the intramolecular potential, owing to its influence on the relative populations of anti and gauche forms. The complete potential hypersurface as a function of the three torsional angles was calculated by the MM2 method,<sup>13</sup> optimizing all the geometrical parameters for each set of three torsional angles. As for the rotation around the central C—C bond, the minima and the lowest energy barriers are in good agreement with accurate ab initio results,<sup>8</sup> as shown in Figure 2. However, molecular mechanics predicts too high an energy for highly hindered conformations, as compared to ab initio results;

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