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Theoretical study of malonamide and nitromalonamide in vacuum and in water solution☆

Giuseppe Buemi*, Felice Zuccarello

Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria nr. 6, 95125 Catania, Italy

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Abstract

The molecular geometries of the most stable conformations of malonamide and nitromalonamide have been studied at DFT B3LYP/6-311++G(d,p) level, in gas phase and in aqueous solution. For each compound the strength of the hydrogen bridges as well as the internal rotation barriers of the hydroxyl and nitro groups were also calculated. The vibration frequencies of the most important stretching modes calculated taking into account the anharmonicity of the system are discussed and compared with those obtained in water solution. The specific solvent effect is discussed too.

Keywords: Malonaldehyde; Malonamide; Nitromalonamide; Intramolecular hydrogen bond; IR spectra; Solvent effect

1. Introduction

In a previous paper [1], the hydrogen bond strengths and the harmonic OH stretching frequencies of amino- and nitro-malonaldehyde, malonamide and nitromalonamide in gas phase were studied at DFT B3LYP/6-31G** level. The obtained results were in line with the experimental findings, where available [2–8], and it was found that the hydrogen bond strengths (E_{HB}) correlate sufficiently well with the ν_{OH} calculated under the harmonic approach as well as with the resonance energy variation inside the chelate ring, evaluated according to the procedure suggested by Grabowski [9].

It is, however, known that the OH stretching mode is highly anharmonic and recent studies have shown that in the parent malonaldehyde the anharmonicity effect in gas phase is in the range of 500 cm^{-1} [10,11]. Use of a scale factor is only a rough approach to improve the agreement between theoretical and experimental findings since the frequencies overestimation is not homogeneous for all transitions. Further calculations are therefore necessary to better understand the IR spectra, especially in molecules as malonamide and nitromalonamide, characterized by intramolecular hydrogen bridges stronger than in the parent malonaldehyde. Moreover, the hydrogen bond strengths (E_{HB}) are highly sensitive to the solvent effect, which, in turn, depends on the polarity and dielectric constant, ε, of the solvent as well as on the polarity of the solute. The present paper is mainly devoted to a deeper investigation of malonamide and nitromalonamide in vacuum and water solution by means of a basis set (6-311++G(d,p)) more extended than the 6-31G** one previously used, in order to obtain additional informations on the cited arguments and to know which geometry changes and which frequency shifts occur in a highly polar solvent as water ($\varepsilon = 78.4$). Literature informations in this solvent are scarce because the most common solvents used in IR spectroscopy are characterized by low ε and also because in some cases water can induce formation of various oligomers, as occurs, e.g. for formaldehyde [12].

2. Calculations

All calculations were carried out by means of the G03W computation package [13], installed on a Pentium IV with

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* Corresponding author. Tel.: +39 095 7385081; fax: +39 095 580138.
E-mail address: gbuemi@dipchi.unict.it (G. Buemi).

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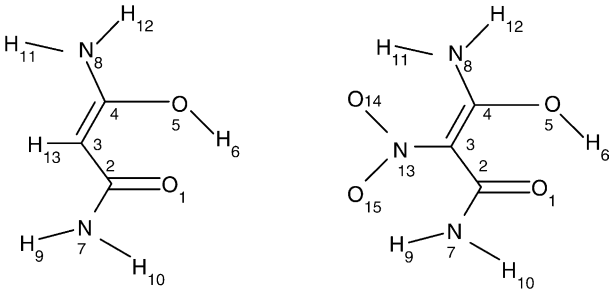

a 2.8 GHz clock and 1 Gb RAM. The 6-311++G(d,p) basis was used at DFT level whereas the B3LYP functional [14–16] was adopted for the correlation energy evaluation. Attempts to calculate the correlation energy at MP2 level failed for the insufficient computer resources.

For solvation effect investigation the well-known PCM-SCRF approach, initially devised by Tomasi and coworkers [17–19] and progressively implemented by Barone et al. (see, e.g. references in the G03 user's manual) was adopted. In this method, the solute molecule is placed into a cavity formed by the envelope of spheres centred on the atomic groups [20,21], in which the dielectric constant is the same as in the vacuum whereas outside it is that of the desired solvent ($\varepsilon = 78.4$ for water). The UAHF (United Atom for Hartree–Fock) radii were used for the molecular cavity building [22,23] and the ΔG_{solv} was evaluated too. The specific solute–solvent effects were checked for two *enol* conformations, adding a water molecule in the neighbouring of the hydrogen bridge. The IR spectra were calculated, both in vacuum and in water solution, taking into account the anharmonicity of the system.

3. Results and discussion

3.1. Malonamide

In agreement with experimental findings [4], the most stable conformation of malonamide is the *syn–anti diketo* form (stabilised by a weak N–H···O hydrogen bridge) shown in Fig. 1 and labelled as **K-3** in the text. According to the present results, its energy is 32.31 kJ/mol lower than that of the *enol* chelate **E-I** conformation (30.04 and 27.73 kJ/mol, if harmonic and anharmonic ZPVE corrections, respectively, are taken into account). This ΔE rises to 43.16 kJ/mol in water solution, so that a keto-enol equilibrium seems to be excluded, even if some evidence of an *enol* form in solution has been reported in the literature [24,25].

The **K-3** optimised geometry in gas phase is very close to that previously obtained at B3LYP/6-31G** level [1] and sufficiently close to the experimental one of the crystal

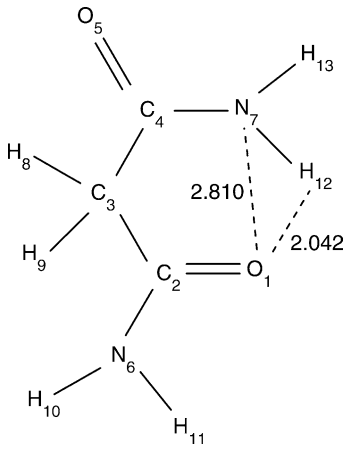

Fig. 1. The most stable conformation of malonamide and the numbering system adopted in the present study.

structure, reported in [2]. Analysis of the geometrical parameters collected in Table 1 evidences a lengthening of about 0.015 Å of the C=O bonds and a shortening of the same order in the C–N bonds, on passing from gas phase to water solution. Similarly, the C_2–C_3–C_4 and N_7–C_4–C_3 bond angles enlarge by about 1° and the O_5–C_4–C_3–C_2 torsion angle increases by about 6°.

A similar trend is observed in the C=O, C–O and C–N bond lengths of the **E-I**, *enol*, conformation, whereas other bond lengths and bond angles evidence very little changes produced by the solvent effect. This conformation shows a strong intramolecular O–H···O hydrogen bond, whose strength, in gas phase, is 79.1 kJ/mol (about 8 kJ/mol lower than obtained at B3LYP/6-31G** level) and decreases to 76.6 kJ/mol if anharmonicity is taken into account. It is, however, strongly weakened in aqueous solution, where $E_{HB} = 41.7$ kJ/mol is found.

Specific solvent effect was tested by adding a water molecule in the neighbouring of the intramolecular hydrogen bond. After full optimisation, water accommodates in such a way to give rise to two weak intermolecular hydrogen bonds (bidentate binding): the former is formed with the keto oxygen whilst the latter involves the adjacent amino group (see Fig. 2). Main geometrical consequences with respect to the isolated molecule in vacuum are once again the lengthening of the C=O bond (from 1.256 to 1.270 Å) and the shortening of the C_2–N bond (from 1.370 to 1.357 Å), accompanied by a lengthening of the O···O (from 2.504 to 2.514 Å) and O···H (from 1.563 to 1.584 Å) distances of the intramolecular hydrogen bridge. The final result of such changes is a modest weakening of the O–H···O bridge energy, quantifiable in about 2 kJ/mol. The Basis Set Superposition Error (BSSE) affects negligibly the hydrogen bond energy (0.29 kJ/mol) since it is of the same order in the chelate and open conformation.

When this cluster is put in water solution, the intermolecular hydrogen bridge between water and NH_2