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Journal of Molecular Liquids 136 (2007) 138 – 146

journal of MOLECULAR LIQUIDS

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Vibrational spectroscopy and molecular orbital calculations of *N*,*N*-dimethylacrylamide and *N*,*N*-dimethylpropionamide – Conformational equilibrium in the liquid state –

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Received 30 October 2006; accepted 20 February 2007
Available online 4 April 2007

Abstract

Molecular vibrations of *N*,*N*-dimethylacrylamide (DMAA) and *N*,*N*-dimethylpropionamide (DMPA) in the liquid state were studied by means of Raman and IR spectra over the wide frequency range. It has been established in our previous work that DMPA involves two rotational isomers within its propionyl $CH_3–CH_2–C(=O)–$ group. In the present work, it is revealed that, like DMPA, DMAA also involves two rotational isomers, the planar *cis* and nonplanar staggered ones, within its acryl $CH_2=CH–C(=O)–$ group. The terminal methylene carbon of the acryl group locates *cis* to the O atom within the amide O=C–N plane (the planar *cis* conformer) or above the amide plane (the nonplanar staggered conformer). This is well supported by theoretical MO calculations. Torsion potential energy surfaces (PES) for the C–C–C–O dihedral angle θ of the acryl group show that a global minimum appears at *ca.* $\theta=0°$ (the planar *cis* conformer) and a local minimum at *ca.* $\theta=130°$ (the nonplanar staggered conformer). The geometry optimization followed by normal frequency analyses showed that theoretical Raman and IR bands for the conformers satisfactorily reproduce the observed ones. The enthalpy for the conformational change from the planar *cis* conformer to the nonplanar staggered one was experimentally evaluated by analyzing the integrated intensity changes of the bands in the range 700–800 cm^{-1}. The value thus obtained for the acryl group of DMAA is *ca.* 9 kJ mol^{-1}, which is significantly higher than the corresponding value for the propionyl group of DMPA (5 kJ mol^{-1}).

Keywords: DMAA; DMPA; Vibrational spectroscopy; DFT calculations; Conformation

1. Introduction

N,*N*-Dimethylformamide (DMF) and its methyl substituted analogue *N*,*N*-dimethylacetamide (DMA) are aprotic donor solvents with similar physicochemical properties as the solvent. The metal-ion complexation with halide ions is enhanced in DMA over DMF, which is ascribed to the steric effect among solvent molecules bound to the metal ion [1]. The solvation steric effect has so far been studied by means of thermodynamic [2], kinetic [3], and structural techniques [4]. As *N*,*N*-dimethylpropionamide (DMPA) involves a bulkier propionyl $CH_3–CH_2–C(=O)–$ group than DMA [2b], the solvent may be interesting in view of the solvation steric effect, as well. Indeed, liquid DMPA involves two conformers, the planar *cis* and nonplanar staggered ones, in equilibrium, and the former with the C–C–C–O dihedral angle $\theta=0°$ of the propionyl group is more stable by *ca.* 5 kJ mol^{-1} than the latter with $\theta=90°$ [5]. Furthermore, the reverse is the case, *i.e.*, the nonplanar staggered conformer is more stable than the planar *cis* one, in the solvation sphere of some small metal ions [6]. The conformation thus changes upon solvation, which indicates that the steric hindrance plays a significant role in the conformation of solvent molecules in the coordination sphere. The conformation of propionamide (PA) has also been found by microwave spectroscopy and *ab initio* calculations [7,8]. According to Sathyanarayana [9], the planar *cis* conformer is also more stable than the nonplanar staggered one with PA,

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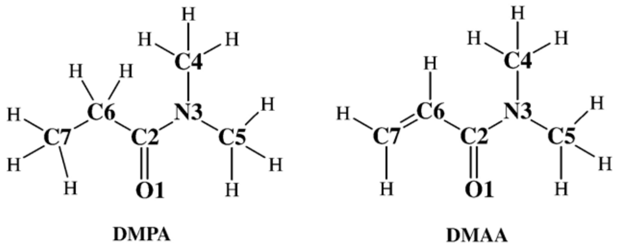
doi:10.1016/j.molliq.2007.02.007



Scheme 1.

whereas a single conformer with the C–C–C–O dihedral angle $\theta = 20$–40° has been reported for *N*-methylpropionamide (NMPA) [10–12].

With *N*,*N*-dimethylacrylamide (DMAA) (Scheme 1), an analogue of DMPA, the rotation along the C–C bond within the acryl $CH_2{=}CH{-}C({=}O){-}$ group may be also possible, like the propionyl group. The steric hindrance among solvent molecules in the coordination sphere might also lead to a conformational change. However, as far as we know, no attention has been paid so far for the conformational change of DMAA. According to Marstokk et al. [13], it is revealed by microwave spectroscopy for a DMAA analogue acrylamide (AA) that the *syn* conformation with the C–C–C–O dihedral angle $\theta = 0°$ (planar) is more stable than the *skew* one with $\theta = 155°$ (nonplanar). Theoretical calculations have also been reported for AA and *N*-methylacrylamide [14].

In the present work, we report Raman and IR spectra and theoretical DFT calculations for DMAA. The enthalpy of conformational change has been obtained by analyzing Raman spectra at various temperatures. It will be demonstrated that DMAA also involves two rotational isomers with respect to the acryl group, like the propionyl group of DMPA. Raman and IR spectra of DMAA will be discussed in comparison with those of DMPA.

2. Experimental section

2.1. Materials

N,*N*-Dimethylacrylamide (Tokyo Kasei Kogyo) was stored with molecular sieves 4 Å for several weeks, and then distilled under a reduced pressure. The water content was less than 100 ppm by a Karl–Fisher test. All samples were prepared in a glove box under an atmosphere of argon, in which water and oxygen contents were kept within 1 ppm.

2.2. Raman and IR spectroscopic measurements and data analyses

Raman and IR spectra were obtained using a FT–Raman/IR spectrometer (Perkin Elmer GX-R). The sample liquids for Raman spectral measurements were filled and stirred in a quartz cell thermostated at a given temperature within ±0.3 K during measurements. The optical resolution was 2.0 cm^{-1}. IR spectra were obtained using a transmission cell of variable path-length with ZnSe windows (SPECAC 7500), and the effective path-length of 20.8 μm was evaluated by the interferogram method. During the measurements, the sample and detector compartments were purged with dry nitrogen. The optical resolution was 1.0 cm^{-1}. Spectral data were accumulated 256 and 32 times for Raman and IR measurements, respectively, to achieve a sufficient signal-to-noise ratio.

Raman spectra of DMAA obtained over a given frequency range were deconvoluted to extract single Raman bands. A single Raman band is assumed to be represented as a *pseudo*-Voigt function, *i.e.*, a linear combination of Lorentzian $f_L(v)$ and Gaussian $f_G(v)$ components $f_v(v) = \gamma f_L(v) + (1-\gamma) f_G(v)$, where the parameter γ $(0<\gamma<1)$ is the fraction of the Lorentzian component. The intensity I of a single Raman band was evaluated according to $I = \gamma I_L + (1-\gamma) I_G$, where I_L and I_G denote integrated intensities of the Lorentzian and Gaussian components, respectively. A nonlinear least-squares curve-fitting program, RAMCAL, based on the Marquardt–Levenberg algorithm [15,16], was developed in our laboratory and used throughout the analyses. Total Raman intensity at a given frequency is thus obtained as the sum of intensities of single bands, which are calculated using the optimized band parameters. Total intensity $I_{calc}(v)$ thus calculated was compared with the observed one $I_{obsd}(v)$, and the goodness of the fit was estimated in terms of the Hamilton R factor, $R = (\sum (I_{obsd}(v) - I_{calcd}(v))^2 / \sum I_{obsd}(v)^2)^{1/2}$. Observed intensities were indeed reproduced with $R<0.01$. The uncertainties of the van't Hoff plots in Fig. 6 were estimated by taking into account the standard error of the refined band parameters on the basis of the error propagation analysis.

2.3. Theoretical calculations

Theoretical calculations have been carried out at levels of the Hartree–Fock (HF) theory, the second-order Moller–Plesset perturbation (MP2) theory [17], and the density functional theory taking into account an electron correlation effect with Becke's 3 parameters [18] and Lee–Yang–Parr correlation functional (B3LYP) [19], in combination with the 6-31G(d), 6-311+G(d,p) and aug-cc-pvDZ [20] basis sets. The relaxed torsion potential energy surface (PES) was calculated with respect to the C–C–C–O dihedral angle of DMAA, and full geometry optimizations for local minima followed by normal frequency analyses for the optimized geometries were carried out. All theoretical calculations were carried out using the *Gaussian03* program package [21], on the Compaq AlpherServer GS320 and IBM eServer p5 model 595 and 570 at the Computing and Communications Center, Kyushu University.

3. Results and discussion

3.1. Observed Raman and IR spectra

Raman and IR spectra obtained for DMAA are shown in Figs. 1a and 2a, respectively. Raman bands at 764, 1146, 1420 and 1614 cm^{-1} are consistent with the reported ones [22–24], but the bands at 717, 790 and 983 cm^{-1} cannot be explained in terms of the sole planar *cis* conformer. Raman and IR spectra