Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 117 (2014) 568–575

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Solvent and structural effects on the UV absorption spectra of *N*-(substituted phenyl)-2-cyanoacetamides

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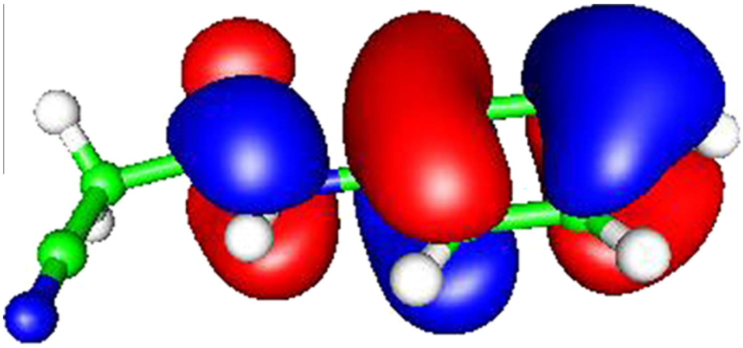
HIGHLIGHTS

- Absorption spectra of selected cyanoacetamides were recorded in 16 solvents.
- Significant shift of the absorption maximum was detected only in DMSO and DMF.
- The effects of solvent were interpreted by Kamlet–Taft LSER concept.
- The effects of substituent were interpreted by Hammett substituent constant.
- The experimental results were interpreted with *ab initio* method MO calculation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 May 2013
Received in revised form 2 August 2013
Accepted 10 August 2013
Available online 22 August 2013

Keywords:
N-(substituted phenyl)-2-cyanoacetamides
UV absorption spectra
Solvent effects
Substituent effects
Ab initio MO calculation

ABSTRACT

UV absorption spectra of *N*-(substituted phenyl)-2-cyanoacetamides have been recorded in the range 200–400 nm in the set of selected solvents. The solute–solvent interactions were analyzed on the basis of linear solvation energy relationships (LSER) concept proposed by Kamlet and Taft. The effects of substituents on the absorption spectra were interpreted by correlation of absorption frequencies with Hammett substituent constant, σ. It was found that substituents significantly change the extent of conjugation. Furthermore, the experimental findings were interpreted with the aid of *ab initio* B3LYP/6-311G(d,p) method. Electronic energies was calculated by the use of 6-311++G(3df,3pd) methods with standard polarized continuum model (PCM) for inclusion of the solvent effect.

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Introduction

Phenylacetamide derivatives are a group of organic compounds with a wide range of activities. They are particularly important for pharmaceutical, agricultural and toxicological applications. Many cyano derivatives of acetamides, which include several phenylacetamides, manifest significant biological and pharmacological activity as antiinflammatory [1], antiviral [2], antileishmanial [3] antitumor [4], insecticidal [5], antimicrobial, bactericidal and fungicidal [6–11]. Some derivatives of cyanoacetamide are also used as dyes [12,13]. Due to their high reactivity, they are also important intermediates in preparation of various organic compounds,

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http://dx.doi.org/10.1016/j.saa.2013.08.040

mostly heterocycles [14,15]. Types of biological activity that one compound may exhibit, in addition to the chemical structure is highly dependent on the nature and strength of interactions that it can be achieved with its environment. Therefore, knowledge of these interactions contributes significantly to the prediction of the type and intensity of biological activity of newly synthesized compounds. One of the methods that is most frequently applied for this purpose is UV spectroscopy [16–27].

Because of wide range of biological activities of phenylacetamide and cyano-acetamide derivatives, newly synthesized *N*-(substituted phenyl)-2-cyanoacetamides can be interesting.

The aim of this work was characterization of synthesized amide by spectrophotometric data, and investigation substituent and solvent effects on their UV absorption spectra.

In this work, absorption spectra of nine *N*-(substituted phenyl)-2-cyanoacetamides have been recorded in the region 200–400 nm in 16 solvents (nine protic and seven aprotic), in order to study the effect of solvents and substituents on the electronic absorption spectra of investigated derivatives.

Linear free energy relationships (LFER) were applied to the UV and ^{13}C NMR chemical shifts in *N*-(substituted phenyl)-2-cyanoacetamides. Quantitative assessment of substituents effect on the absorption spectra of investigated derivatives were interpreted by correlation of absorption frequencies maximum with substituent constant, σ_p [28], expressed by Hammett equation:

$$\nu_{\max} = \nu_0 + \rho\sigma_p \qquad (1)$$

where $\nu_{\max}$ is the absorption frequency at maximum absorbance values, ν_0 is the regression value of the solute property in the reference solvent cyclohexane as a solvent, and ρ is the proportionality constant reflecting the sensitivity of absorption frequencies to the substituents effects. Substituent constant σ_p measures the electronic effect of the substituents.

The effects of solvent polarity and hydrogen-bonding on the absorption spectra are interpreted by linear solvation energy relationship (LSER) using a Kamlet–Taft equation [29]:

$$\nu_{\max} = \nu_0 + \mathrm{s}\pi^* + \mathrm{b}\beta + \mathrm{a}\alpha \qquad (2)$$

where π^* is a measure of the solvent dipolarity/polarizability [30], β is the scale of the solvent hydrogen-bond acceptor (HBA) basicities, and α is the scale of the solvent hydrogen-bond donor (HBD) acidities [31]. The regression coefficients *s*, *b* and *a* in Eq. (2) measure the relative susceptibilities of the solvent-dependent solute property (absorption frequencies) to the indicated solvent parameters.

In this work, we report the synthesis of nine *N*-(substituted phenyl)-2-cyanoacetamides, their UV absorption spectra in 16 solvents of different polarity, and the relationship between solvatochromic properties and structure of these amides. The substituent electronic effect on the absorption is also reported.

Experimental part

The substituents at the phenyl nucleus of synthesized *N*-(4-substituted phenyl)-2-cyanoacetamide are as follows: H (**1**), CH_3 (**2**), C_2H_5 (**3**), I (**4**), Br (**5**), NO_2 (**6**), OH (**7**), COOH (**8**), and $COCH_3$ (**9**). The chemical structure and purity of the investigated compounds was confirmed by melting points, FTIR [BOMEM (Hartmann & Braun) spectrophotometer], ^{1}H and ^{13}C NMR spectra (determined in deuterated DMSO-d6 using a Varian Gemini 200 MHz spectrometer). The chemical shifts are expressed in ppm values referenced to TMS (δ_H = 0 ppm) in the ^{1}H NMR spectra, and the residual solvent signal (δ_C = 39.5 ppm) in ^{13}C NMR spectra. The chemical shifts were assigned by the complementary use of DEPT–, two dimensional ^{1}H–^{13}C correlation HETCOR– and by selective INEPT long-range experiments [32]. All spectra were recorded at ambient temperature.

Electronic absorption spectra (UV) were recorded on a Shimadzu UV-1800 spectrophotometer in 1.00 cm cells at 25 ± 0.1 °C. The UV spectra were taken in spectro-quality solvents (Fluka) in concentration of 4×10^{-5} mol dm^{-3}. All calculations were carried out using the computer program Origin, version 6.1. The validity of the fit was evaluated with respect to the correlation coefficient (*r*), and standard error of the estimate (sd).

Theoretical calculation of optimal geometries and spectral data

The full geometry optimizations of both *cis* and *trans* conformations of studied molecules were carried out by B3LYP method with standard basis set, 6-311G(d,p). Harmonic vibrational frequencies were evaluated at same level to confirm the nature of the stationary points found (to confirm that optimized geometry corresponds to local minimum that has only real frequencies), and to account for the zero point vibrational energy (ZPVE) correction. Global minima were found for every molecule using conformational analysis. Electronic energies were calculated on optimized geometries with B3LYP method. In order to obtain better electronic energies, larger basis set with diffuse functions, 6-311++G(3df,3pd) was used. The solvents (Dimethylsulphoxide – DMSO, water, Ethanol and Acetonitrile – AcN) were simulated with standard polarized continuum model (PCM). Atomic charges (ChelpG method) were calculated on B3LYP/6-311G(d,p) optimized geometries with B3LYP/6-311++G(3df,3pd) method. Theoretical absorption spectra were calculated in gas phase, DMSO, water, ethanol and AcN solution with TD-DFT method on optimized geometry with B3LYP functional and 6-311G(d,p) basis set. Model for calculation of thermodynamic data is given in Supplementary material [33–37]. All calculations were done with Gaussian03 software [38].

Results and discussion

The results of the UV-spectroscopic measurements

The ultraviolet absorption spectra of investigated *N*-(substituted phenyl)-2-cyano acetamides have been recorded in selected protic solvents: Methanol, Ethanol, 1-Propanol, 2-Propanol, 1-Butanol, 2-Methyl-1-propanol (*i*-BuOH), 2-Methyl-2-propanol (*t*-BuOH), Water and 2-Methyl-2-butanol (*t*-AmOH), as well as in aprotic ones: Tetrahydrofuran (THF), 1,4-Dioxane (Dioxane), Acetonitrile (AcN), Dimethylsulfoxide (DMSO), Chloroform, *N,N*-Dimethylformmide (DMF) and Ethylacetate (EtAc) in the range 200–400 nm. The values of maximum absorption frequencies in different solvents are given in Table 1.

The results from Table 1 show that the position of the ultraviolet absorption frequencies significantly depends on the nature of the substituent on the benzene ring, and is of lower dependence with respect to solvent properties.

It can be noted from data in Table 1 that the position of absorption maximum of investigated compounds more depends on the properties of substituents on the benzene ring. All substituents, in both protic and aprotic solvents, showed batochromic shift in regard to the parent compound. The lowest batochromic shift is noticed in the presence of weak electron-donating $-CH_3$ groups, and the largest shift was recorded in the presence of strong electron-attracting $-NO_2$ group.

UV absorption maxima shifts (Table 1) can be attributed to different $\pi \rightarrow \pi^*$ transitions involving the π-electronic system of the investigated compounds (Fig. 1). The π-delocalization originates mainly from the π-electron density shift from the substituted benzene unit, influenced by the substituent, to the C=O group of the

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