Protolytic dissociation of cyanophenols in ground and excited states in alcohol and water solutions

Beata Szczepanik*, Stanisław Styrcz

Institute of Chemistry, Jan Kochanowski University, Swietokrzyska 15G, 25-426 Kielce, Poland

ABSTRACT

The effect of cyano substituents on acidity in ground and excited states of mono- and dicyanophenols was investigated. The equilibrium dissociation constants of 3,4-dicyanophenol in ground and lowest excited states in water solution and the change of these constants in the excited state during the transfer to the ground state for *o*-, *m*-, *p*-cyanophenol and 3,4-dicyanophenol in alcohol and water solutions were determined. It was shown that the cyano substitution increases the acidity of *ortho*-, *meta*- and dicyano-derivative in ground state in comparison to the phenol, which makes the anions of these derivatives appear in solutions from methanol to 1-butanol. In the excited state the acidity of investigated compounds changes significantly in comparison to the ground state. 3,4-Dicyanophenol is the strongest acid in the lowest excited singlet state, while *p*-cyanophenol is the weakest one in both alcohol and water solutions.

The distribution of the electronic charge and dipole moments of all investigated cyanophenols in ground and excited states were determined on the basis of *ab initio* calculations using the GAMESS program.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Phenol and other hydroxyarenes such as 1- and 2-naphtol are known to show a strong increase in their acidity in the excited state [1–4]. The introduction of hydroxyarenes of an electron acceptor group, such as cyano, nitro or sulphonate groups, into the aromatic ring changes their acidity in both ground and excited states. The electronic excitation of cyano derivatives of 1- and 2-naphtol with the substituent at 5- or 6-positions in the distant ring results in a remarkable change in their acidity in the excited state in water. These compounds also function as photoacids in polar nonaqueous solvents. This property of derivatives of naphtol with one or two cyano groups is used to name these compounds "super" photoacids [1–9].

The pK_a of 2-naphtol drops from 9.5 to 2.8 in its first excited singlet state (S$_1$). In the case of monocyano-substituted 2-naphthol-5-cyano-2-naphthol, pK_a decreases from 8.75 in the ground state to −0.8 in the excited state. The doubly substituted CN derivatives (5,8-dicyano-2-naphtol) are almost as strong as a mineral acid with pK_a = −4.5 in the excited state. The proton transfer to different organic polar solvents such as alcohols or dimethyl sulphoxide is observed in cyanonaphthols in the excited state, which results in the appearance of low energy RO$^-$ emission in the fluorescence spectrum in these solvents [4].

The effect of a substituent on the prototropic equilibria of phenols in S$_1$ state was investigated by Wehry and Rogers [10] long ago. They calculated the dissociation constants in the S$_1$ state of the series of *meta*- and *para*-substituted phenols. Schulman and others investigated the photoacidity of monocyanophenols in S$_1$ state [1]. According to the Förster cycle and fluorimetric titrimetry, pK_a in the excited state was observed to decrease in water solutions from 7 to 0.6 for *o*-cyanophenol, from 8.3 to 1.9 for *m*-cyanophenol, and from 7.7 to 3.3 for *p*-cyanophenol. An increase in the acidity of *ortho*- and *meta*-derivatives is comparable (about 6 order of magnitude) whereas the change is the weakest in the case of *p*-cyanophenol.

In the present work we studied the protolytic dissociation in ground and excited electronic states in alcohols (from methanol to 1-butanol) of phenol derivatives with two cyano groups: 3,4-dicyanophenol (3,4DCPh) and monocyanophenols: *o*-, *m*- and *p*-cyanophenol (oCPh, mCPh and pCPh). The acidic dissociation constant of 3,4DCPh in the ground state in water and the change of this constant during the transfer from the ground state to the excited one for *o*-, *m*-, *p*-cyanophenol and 3,4-dicyanophenol in alcohol and water solutions were calculated. We present: (i) the results of steady state measurements of the absorption and fluorescence of alcohol and water solutions of investigated compounds and (ii) *ab initio* calculations of the electronic structure, the dipole moments and the molecular geometry of molecules of investigated compounds in electronic ground and excited states.

2. Experimental

2.1. Chemicals

o-Cyanophenol (oCPh), m-cyanophenol (mCPh), p-cyanophenol (pCPh) and 3,4-dicyanophenol (95–98% purity, Sigma–Aldrich) were recrystallized from ethanol/water solutions.

Spectrally pure alcohols were purchased from Merck and Fluka: methanol for spectroscopy (water content max 0.05%), anhydrous ethanol special pure (water content max 0.2%), 1-propanol for UV-spectroscopy (water content max 0.05%) and 1-butanol for UV-spectroscopy (water content max 0.1%). Sulphuric acid was purchased from Apolda (Germany), and sodium hydroxide from P.O.Ch. Gliwice (Poland).

2.2. Methods

The absorption spectra were recorded on a SPECORD M500 UV-VIS spectrophotometer (Carl-Zeiss Jena). The steady-state fluorescence spectra were measured on a KONTRON SFM 25 spectrofluorimeter (Kontron Instruments Germany).

2.3. Quantum chemical calculations

Ab initio calculations in the ground and excited states of cyanophenols molecules were done using the Gaussian 98 program [11].

The distributions of electronic densities and the dipole moments of neutral molecules in ground and first excited states were calculated in the base B3LYP/6-31+G(d).

The optimalization of geometry in the ground state was obtained in the base B3LYP/6-31G(d) and in the excited state in the base RCIS/6-31G(d).

3. Results

3.1. Protolytic dissociation of investigated phenols in alcohol solutions

Figs. 1 and 2 show the steady state absorption and fluorescence spectra of 3,4DCPh, oCPh, mCPh and pCPh measured in neutral alcohol solutions (from methanol to 1-butanol) and in acidic (with the addition of H_2SO_4) and alkaline (with the addition of NaOH) methanol solutions at 293 K.

The absorption spectra obtained in neutral alcohols are attributed to the neutral molecules of all investigated phenols (Fig. 1). The first absorption bands of 3,4DCPh, oCPh and mCPh appear at similar energies ($\sim$33 900 cm^{-1}) in all alcohols. In the case of pCPh, this band is shifted into the blue by about 2000 cm^{-1}. A new additional band of absorption at the long wavelength side appears for 3,4DCPh, oCPh and mCPh, peaking at about 30 000 cm^{-1} (30 500 cm^{-1} for mCPh). The increase of this new band observed during the transfer from methanol to propanol is the biggest for 3,4DCPh and the smallest for mCPh. In the case of pCPh, only a slight increase of the band at about 36 000 cm^{-1} from ethanol to propanol is observed. This new band disappeared in acidified alcohol solution. In alkaline solutions the spectrum corresponding to the anionic form of investigated phenols was recorded. The first absorption band of this spectrum occurs in the same range as the new band observed in neutral alcohols.

The fluorescence spectra obtained in the neutral solution for all o-, m- and p-isomers are ascribed to the neutral form of cyanophenols. In the case of oCPh an additional band of fluorescence appears at the long wavelength side of fluorescence spectrum from methanol to butanol (Fig. 2). For pCPh only a trace of the additional band is observed. The fluorescence spectra of mCA show only a slight broadening, even in acidified methanol solution. In the case
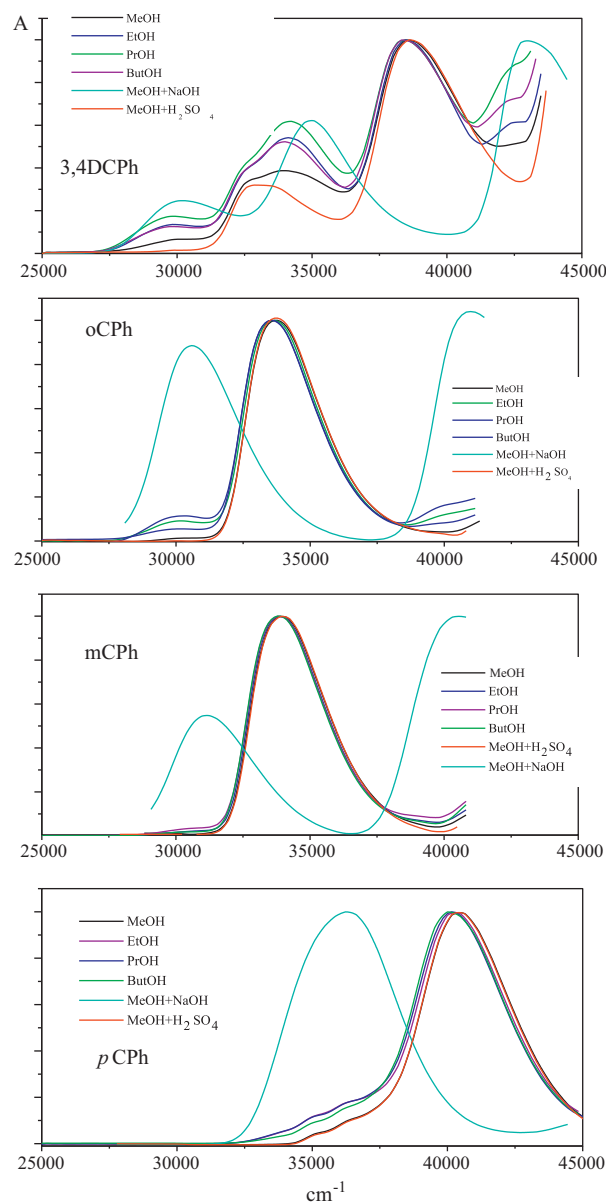
Fig. 1. Absorption spectra of 3,4DCPh, oCPh, mCPh and pCPh in neutral alcohol solution (methanol (MeOH), ethanol (EtOH), propanol (PrOH), butanol (BuOH)) and in acidic and alkaline methanol solutions at 298 K (the absorption spectrum of pCPh was normalized to the second band).

of 3,4DCPh the fluorescence spectrum consists of two bands–band I at 29 100 cm^{-1} ascribed to neutral form of the molecule and band II at the long wavelength side peaking at 24 800 cm^{-1} (Fig. 2). The ratio of band I and band II decreases from 0.94 in methanol to 0.19 in propanol. The band II and traces of the long wavelength band for o- and p-isomers can be ascribed to anionic forms of these compounds.

The fluorescence spectra recorded in alkaline methanol solution show bands peaking at 24 800 cm^{-1}, 26 070 cm^{-1}, 26 180 cm^{-1}, 29 400 cm^{-1} for 3,4DCPh, oCPh, mCPh and pCPh, respectively. These bands result from the presence of the anions of these compounds in solution (Fig. 2).

3.2. Protolytic dissociation of 3,4-dicyanophenol in the ground and excited state in aqueous solution

The absorption spectra of 3,4DCPh in aqueous solutions at different pH-values are depicted in Fig. 3. Alkalization of the solution