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Vibrational and electronic spectral studies of hydrogen – bonding in aminoanthraquinones – trichloroacetic acid systems

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The hydrogen bonding interaction sites and proton transfer equilibrium constants K_{PT} between trichloroacetic acid (TCA) and a series of aminoanthraquinones(AAQ) have been investigated using Fourier-transform–infrared (FT-IR) and UV-VIS spectra in 1,2-dichloroethane and acetonitrile

Keywords: hydrogen bonding, aminoanthraquinones, trichloroacetic acid

Aminoanthraquinones have been widely applied in material science; for example, they have been used in the development of artificial photosynthetic systems,[3] charge conducting materials,[4] electrode coating,[5] coating of metal surfaces[6] and optoelectronic display devices.[7] Moreover, they have many potential biological applications.[8-10] Despite thier biological relevance and their bi-functional basicities (they contain NH_2 and C=O groups), their hydrogen-bonded complexes and proton transfer equilibria with various proton donors have not been studied. Consequently, we have studied the hydrogen bonding chemistry of these organic dyestuffs to throw light on their behaviour in strong acidic media, which may, in turn, help in understanding their mode of reactions in many of their potential applications.

Accordingly, the current contribution is aimed to synthesise and characterise some crystalline forms of hydrogen-bonded complexes of AAQ and TCA complexes by using FTIR spectroscopy. Another aim of this work was the spectrophotometric determination of the equilibrium constants of the 1:1 proton transfer complex formation between TCA and AAQ in 1,2-dichloroethane and acetonitrile.

The FTIR spectra of the crystalline AAQ and the hydrogen-bonded complex between TCA and 1,5-diaminoanthraquinone were recorded on a Perkin Elmer Paragon 1000 Spectrophotometer with a resolution power of 2 cm^{-1}, in KBr pellets.

The electronic spectra were recorded on a Shimadzu 160A UV–VIS recording spectrophotometer, using 1-cm matched silica cells in the wavelength range of 200–800 nm. The equilibrium constants of 1:1 proton transfer complex formation in all investigated systems and the thermodynamic parameters, were calculated as previously described.[16-18]

The FTIR spectra of the investigated AAQ in the stretching frequency region of both the amino and the carbonyl groups suggested the absence of the intramolecular hydrogen bond between the amino and the carbonyl groups of the AAQ nucleus except for 1,2-diaminoanthraquinone. This result is based on the formation of a complex band in the amino group stretching region and the shift of the carbonyl stretching frequency to a lower one at 1620 cm^{-1} in 1,2-diaminoanthraquinone FTIR spectra. The FTIR spectra of the hydrogen bonded complex between TCA and 1,5-diaminoanthraquinone confirmed that the hydrogen bonding interaction occurs between the acidic proton and the NH_2 group of the AAQ moiety.

The electronic spectra of the studied aminoanthraquinones showed a band lying between 460 and 480 nm, which was attributed to an n-π* transition. It has been observed that the decrease in the absorbance of the n-π* band, with the gradual increase in the TCA concentration, might be due to the protonation of the amino group until the band completely disappeared. Figure 1 represents the electronic spectra of the hydrogen bonding interaction between 1-aminoanthraquinone and TCA in 1,2-dichloroethane at 25°C. Three isosbestic points are recorded, the first one could be attributed to the molecular complex formation, the second one, which appeared at a lower TCA concentrations, was presumably due to a 1:1 proton transfer equilibrium and the third one, which appeared at the higher TCA concentration, could be ascribed to a 2:1 proton transfer equilibrium, including the carbonyl group.

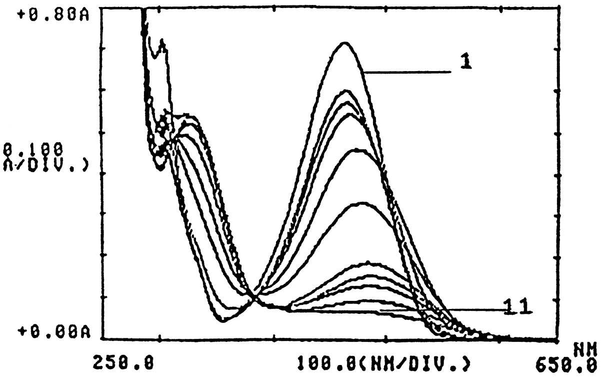

Fig.1 Absorptione spectra of 10^{-4} M 1-aminoanthraquinone in the presence of different concentrations of TCA at 25°C: (1) 0.0, (2) 5×10^{-2}, (3) 8×10^{-2}, (4) 1.5×10^{-1}, (5) 3×10^{-1}, (6) 5×10^{-1}, (7) 8×10^{-1}, (8) 1.0, (9) 1.2, (10) 1.5 and (11) 2.0 mol/l

The electronic spectra, representing the hydrogen bonding interaction between TCA and 1,2-diaminoanthraquinone reveal only one isosbestic point at 400 nm because of the 1:1 proton transfer equilibrium. However, the isosbestic points corresponding to the formation of the molecular complex and 2:1 proton transfer equilibrium were not found. It seems that the participation of the 1-amino group hydrogen atom, in intramolecular hydrogen bonding formation with the neighboring carbonyl group and the other amino group, would increase the electron density on the nitrogen atom of 1-amino group , therefore, the proton transfer has taken place in a single concerted step mechanism.. The proton transfer equilibrium constants between TCA and aminoanthraquinones were computed by the minimum and maximum absorbances method. Aminoanthraquinones, 1:1 proton transfer equilibrium constants, the position of the isosbestic points, together with the concentration range are collected in Table 1.

Comparing the calculated K_{PT} values for 1-amino-, 1,4-diamino- and 1,5-diaminoanthraquinone–TCA complexes at 25°C showed that the ratios of K_{PT} values of 1-amino- and

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Table1 Electronic spectral data for the proton transfer reaction between aminoanthraquinones and TCA in 1,2-dichloroethane at 25°C

Anthraquinone derivative	K_{PT}	λ_{PT}/nm	Isosbestic points /nm	Concentration range/mol/l
1-Amino	6.26	463	250, 370, 500	$5x10^{-2}$ – 2
2-Amino	0.92	450	370, 500	0.15 – 1.5
1,2-Diamino	914.26	475	400	$2x10^{-3}$ – $3x10^{-2}$
1,4-Diamino	17.41	544	250, 370, 500	$5x10^{-2}$ – 1.2
1,5-Diamino	56.96	475	250, 370, 500	$2x10^{-2}$ – 0.4

1,4-diaminoanthraquinones-TCA and those of 1,4-diamino- and 1,5-diaminoanthraquinone-TCA systems, were nearly equal; *i.e.*, 1:3. However, the ratio of K_{PT} values for the 1-amino- and 1,5-diaminoanthraquinones-TCA complex was nearly equal to 1:9. In other words, although 1,5-diaminoanthraquinone and its 1,4-analogy had the same number of amino- groups, the former was three times more reactive towards TCA. This trend means that the reactivity of the diaminoanthraquinone towards TCA depends on the relative positions of the two amino- groups, where, if they are in direct conjugation (1,4-position), the stepwise proton transfer process will be retarded and if they are located on two isolated aromatic rings (1,5-position), the process will be enhanced. The aminoanthraquinone structure, which is characterised by two aromatic rings, one quinonoid ring and one or two amino groups, created systems with special steric inhibition resources for such interaction with TCA. On the other hand, one cannot disregard the possibility of intermolecular hydrogen bonding between the aminoanthraquinone molecules and the orientation of the amino group to an out of plane position. These factors would explain the decrease in the K_{PT} values of the investigated systems except for the 1,2-diaminoanthraquinone-TCA system, which showed high K_{PT} values, confirming the presence of a relatively higher electron density on its 1-amino group nitrogen atom via an intramolecular hydrogen bonding formation.

The proton transfer equilibria between trichloroacetic acid and aminoanthraquinones were followed spectrophotometrically in acetonitrile. This solvent was chosen to conduct this investigation, owing to its higher dielectric constant (ϵ = 36) and its Lewis basicity character. The calculated K_{PT} values for 1-aminoanthraquinone and TCA interaction in acetonitrile, extended to 24.0 l/mol compared with 6.0 l/mol that was calculated in the non-polar solvent, 1,2-dichloroethane. These results could be rationalised in terms of the dielectric constant of acetonitrile (ϵ = 36) compared with 10.4 for 1,2-dichloroethane, which may increase the intermolecular hydrogen-bond bridge polarisation between the 1-amino-isomer and TCA. This polarisation increases the K_{PT} value in acetonitrile four times more than that in 1,2-dichlorethane which is nearly the same ratio between the dielectric constants for both solvents. One also could not disregard the hydrogen bonding solvation interaction between acetonitrile and TCA, which is presumably responsible for the lower K_{PT} values compared with other results in the literatures.[17,22] The K_{PT} for the hydrogen bonding interaction between 1,2-diaminoanthraquinone and TCA recorded a strongly lower value, 2.0 l/mol, compared with 900 l/mol that was computed in 1,2-dichloroethane. The higher polarity of the medium in the presence of acetonitrile enhances the intramolecular hydrogen bond bridge polarisation in case of 1,2-diamino isomer. This process, in turn may increase the solvation of the amino- group and the system would become sterically hindered. Hence, the intermolecular hydrogen bonding between 1,2-diamino- isomer and TCA is retarded or the hydrogen bonding solvation of the free TCA is increased, leading to a lower K_{PT} value, 2.0 l/mol.

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