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Solvent Effect on the Absorption Spectra of *N*-2,6-Trichlorobenzoquinonimine

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The absorption spectra of solutions of *N*-2,6-trichlorobenzoquinonimine in organic solvents of varying polarities are investigated. The ability of the compound to form molecular complexes in ethanol is discussed. The stability constants of the molecular complexes are determined from the spectra in mixed solvents. The equilibrium constant of the reaction involving the acquisition of a proton by the solute is calculated in water and in water—acetone mixtures.

(Keywords: Molecular complexes; Solvent effects; N-2,6-Trichlorobenzoquinonimine)

Lösungsmitteleffekte auf das Absorptionsspektrum von N-2,6-trichlorbenzochinonimin

Die Absorptionsspektren wurden in Lösungsmitteln verschiedener Polarität untersucht und die Fähigkeit zur Bildung von Molekülkomplexen des Substrats in Ethanol diskutiert, wobei die Stabilitätskonstanten aus Messungen in Lösungsmittelgemischen errechnet wurden. Die Gleichgewichtskonstanten der Protonierung in Wasser und Wasser—Aceton wurden ebenfalls bestimmt.

Introduction

Several investigations[1–3] showed that the absorption spectra of *p*-benzoquinone and related substances belong to aliphatic compounds rather than to aromatic ones and that they exhibit the unsaturated diketone conjugation.

N-2,6-trichlorobenzoquinonimine, as a derivative from *p*-benzoquinone, has a wide application in chemistry[4–7] (e.g. as reagent in colorimetric determination of coumarin in plant material[5] or photometric determination of free or total phenolic acids and propyl thiouracil in human serum[6,7]).

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The spectra of *N*-2,6-trichlorobenzoquinonimine have not been carfully reported previously. So, it is of interest to examine the characteristic absorption properties of this compound as a function of the structure of its molecule.

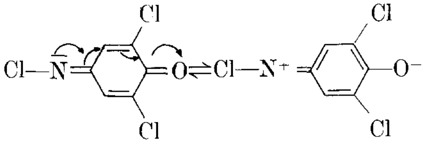
Experimental

The compound under test was of pure grade, Schuchardt, München, (m.p. 65–67 °C). Purification of solvents carried out by the methods commonly used for spectroscopic solvents[8]. The spectra were recorded within the wavelength range 200–600 nm on a Unicam SP 1 750 spectrophotometer.

Results and Discussion

In ethanol solutions (Fig. 1, Table 1), the most intense maximum was observed at 280 nm with an inflection at 273 nm. A shoulder with low intensity in the region 300–310 nm is also observed.

In analogy to the spectra of *p*-benzoquinone[9,10], the bands observed within the 270–280 nm range for the compound under test, are corresponding to the π-π* transitions. The absorption bands with λ_{max} in the range 300–315 nm are corresponding to the π-π* transitions involving charge transfer. The charge transfer takes place from the nitrogen atom to the π-system (n-π*). Such charge transfer can be represented as follows



In polar solvents, the weak n-π* band becomes overlapped by the more intense π-π* band. As a consequence of this, the nature of the absorption spectrum of the compound in ethanol differs from those in chloroform or carbon tetrachloride solvents.

Table 1. *Results obtained in different organic solvents*

Solvent	π-π*		π-π*		π-π* + C.T	
	λ_{nm}	$\epsilon \times 10^{-3}$	λ_{nm}	$\epsilon \times 10^{-3}$	λ_{nm}	$\epsilon \times 10^{-3}$
Ethanol	280	16.8	300	5.7	310	5.14
$CHCl_3$			305	22.2	315	24
CCl_4			305	21.8	315	24

The absorption spectra in $CHCl_3$ and CCl_4 are quite similar as shown in Table 1 and Fig. 1. The spectrum has two absorption maxima at 305 nm and 315 nm. The energies of the electronic transitions and the widths of these two bands are practically identical in these two solvents.

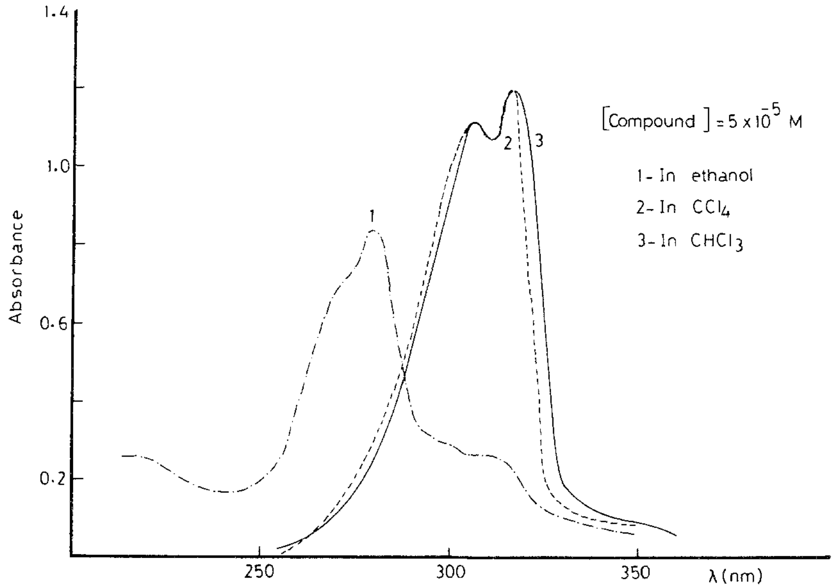


Fig. 1. Spectra in different organic solvents

The absorption spectrum of the compound in 1.2 *N* HCl differs considerably from those of the ethanolic or CCl_4 solutions. A new band is observed at 275 nm and the spectrum does not possess any shoulder in the 300-315 nm region. Also there is a considerable change in the colour of the solution, from pink in alcohol to green blue. All these observations suggest a considerable change in the structure of the molecule owing to salt formation.

Comparing the spectrum of the compund in ethanol with its analogous derivatives which were previously[11] studied. it is found that replacement of chlorine atom in the =N—Cl group by a more effective electron donating group such as —*Ph*, —*Ph*OH, —*Ph*OCH_3 or —*Ph*$N(CH_3)_2$ produces a bathochromic shift in the long wavelength band with an increase in its intensity. In this case the effect of the carbonyl group or the chlorine atoms attached to the ring is similar to that of typical electron accepting groups. The electron accepting properties become more pronounced with increase of the effectivness of the electron donating group.

From the chromophore—auxochrome point of view the chromophore in the above compounds is the quinonimine group. Introduction of such auxochromic groups as $Ph\mathrm{OH}$, $Ph\mathrm{OCH_3}$ or $Ph\mathrm{N(CH_3)_2}$ produces a bathochromic shift. All this is associated with an intensification of electron conjugation.

The effect of increasing amounts of ethanol on the spectra of the compound under test dissolved in $\mathrm{CCl_4}$ were investigated as shown in Fig. 2. The increase of ethanol causes a decrease in the intensity of the charge transfer band. This indicates the existence of complex species resulting probably from the blocking of the lone pair on both $\mathrm{C=O}$ and nitrogen atom through hydrogen bonding with ethanol.

$$X + n\,\mathrm{ROH} \rightleftharpoons X \ldots\ldots\ldots R(\mathrm{OH})_n$$

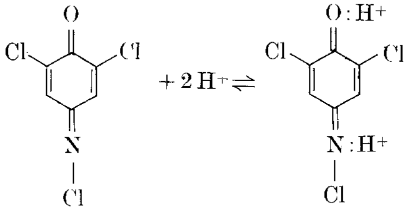
$$K = \frac{[X \ldots R(\mathrm{OH})_n]}{(X)\,(R\mathrm{OH})^n}$$

For such an equilibrium, the following equation may be used:

$$\log \frac{A_0 - A}{A - A_{\min}} = \log K + n \log C_{R\mathrm{OH}} \qquad (1)$$

The plot of $\log \frac{A_0 - A}{A - A_{\min}}$ vs. $\log C_{R\mathrm{OH}}$ is a linear relation from which n was found to be 1.9, indicating that 2:1 molecular complexes are probably formed. Values of K and ΔH were calculated and were found to be 25×10^{-4} and 2.2 kcal/mol respectively. These values reveal that these molecular complexes are not very stable.

Increasing acidity has its strongest effect on the absorption spectra of the compound as shown in Fig. 3. The range of hydrogen ion concentration made it possible to observe the shift of equilibrium from the cationic to the molecular form



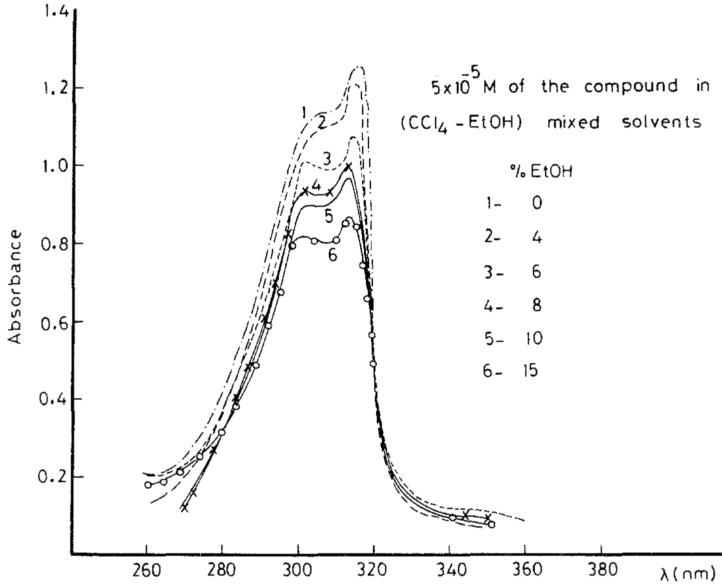


Fig. 2. Effect of increasing amounts of *Et*OH

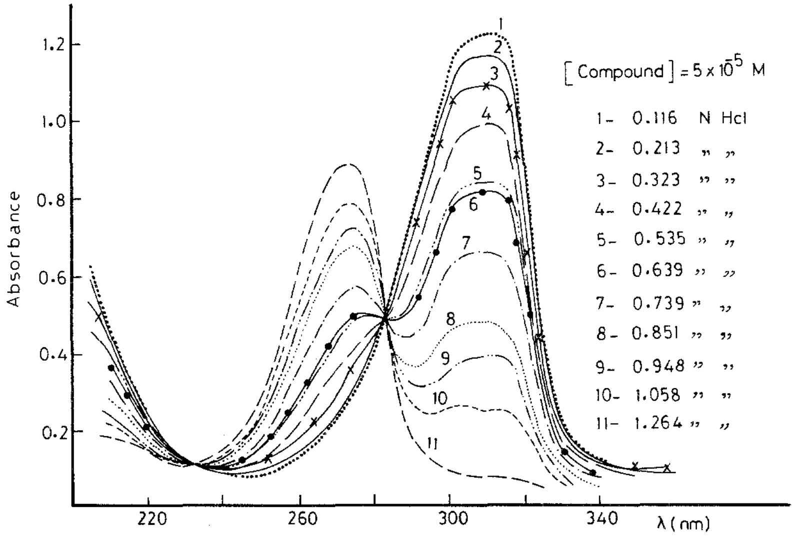


Fig. 3. Effect of $[H^+]$ on the spectrum

The protonation is directed on to the more basic centres at the $C=O$ group and the nitrogen atom.

The isobestic point observed at 284 nm (Fig. 3) indicates the existence of such an acid—base equilibrium. The equilibrium constant was calculated based on the application of equation (2).

$$-\log [H^+] = pK + \log \frac{A - A_{\min}}{A_{\max} - A} + \log \gamma \qquad (2)$$

A plot of the term $\log \frac{A - A_{\min}}{A_{\max} - A}$ as a function of $\log [H^+]$ yielded a linear relationship allowing to calculate a pK value of -0.12.

Such a small pK value of the reaction involving the acquisition of a proton by the compound can be explained by recalling that electron migration in these molecules appears to occur under the influence of two opposite effects[12]. On the one hand, the unshared (p) electrons of nitrogen are displaced towards the ring; on the other hand, there is a tendency for the π electrons to localize at the oxygen and nitrogen atoms, as the most electron negative ones relative to the carbon atom.

The pK value of this compound was also calculated in 50% water—acetone mixture and was found to be -0.19. This value shows the dependence of the pK value on the nature of the solvent[12]. The polar environment probably facilitates the transition of the molecules into a more protoacceptor form, and this has an effect on the shift of the cationic form of the substance.

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