A Discussion of the Absorption Spectra of Substituted 4-Pyridones and Their 4-Thio Analogues

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The absorption spectra of 3-hydroxy-1-aryl-4-pyridones, 2-carbethoxy-5-hydroxy-1-aryl-4-pyridones and their 4-thio analogues are reported. The thio compounds exhibit a red shift in the characteristic long wavelength maximum, which can be explained with the help of the inductive effect when oxygen is replaced by sulphur. Similarly, with the help of the first-order inductive effect, a red shift in the bands is discussed. This shift is produced by the substitution of a carbethoxy group at position 2 of the pyridone ring (the charge distributions in the ring are calculated from Hückel molecular orbitals). Finally, a red shift produced by substitution onto the nitrogen in the ring is examined with the help of the mesomeric effect.

In the literature, there is not much data available about the absorption spectra of 3-hydroxy-1-aryl-4-pyridones (III), 2-carbethoxy-5-hydroxy-1-aryl-4-pyridones (V) and their 4-thio analogues (IV) and (VI). However, the UV spectra of 4-pyridone (I) and 4-thiopyridone (II) have been reported previously[1], and they both exhibit a characteristic $\pi - \pi^*$ band at 2560 Å (log $\varepsilon_{max} = 4.16$) and at 3410 Å (log $\varepsilon_{max} = 4.17$) respectively. We have measured the absorption spectra of pyridones IV—VI. Only the intense long wavelength maximum is reported in the Table; in the first part compounds III and IV, and in the second part compounds V and VI.

All sulphur compounds (IV) and (VI) show red (bathochromic) shifts of approximately 700 Å. There is also a red shift on going from compounds (III), (IV) to (V), (VI) of approximately 100 Å. Finally, different substituents attached to the nitrogen atom in the ring also produce a shift. The substituents (R's) in compounds (III) and (IV), as well as in compounds (V) and (VI), when ordered as follows:

(A)   1'-naphthyl < phenyl < 4'-chlorophenyl < 4'-bromophenyl

(B)   1'-naphthyl < 4'-tolyl < phenyl < 4'-chlorophenyl < 4'-bromophenyl < < 3'-nitrophenyl

form a sequence, in which for each successive compound a red shift of not more than 50 Å is observed. We wish to discuss and rationalize these by examining the effect of substituent on the absorption spectrum of compound (I).

In the spectrum of compound (II), a red shift of 850 Å in the long wavelength maximum is observed. This agrees with the similar shifts observed in other

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spectra of sulphur compounds when compared with the spectra of their corresponding oxygen compounds. The replacement of sulphur by oxygen would cause an inductive effect on the molecule. The electrons on oxygen are much more firmly bound than those on sulphur, since oxygen is more electronegative than sulphur (on the Mulliken scale[2] they have values of 9.99 and 7.60, respectively). Evidence for this comes from the values of their ionisation potentials; the ionisation potentials of oxygen and sulphur are 13.61 eV and 10.36 eV, respectively[3]. Therefore, the excitation of electrons in the thio compound will require less energy than for the oxygen compounds; this holds not only for unsaturated, but also for saturated sulphur compounds which absorb at longer wavelengths than their respective oxygen compounds.

A Hückel molecular orbital (HMO) calculation[4] predicts a similar trend for the first A_1 transition in (I) and (II). For the basic parameters of HMO theory (α_X and β_{CX} for heteroatoms), we adopted the values suggested by Streitwieser[5]:

$$\alpha_{\ddot{O}} = \alpha_C + 2\beta_{CC}; \; \alpha_{\ddot{N}} = \alpha_C + 1.5\beta_{CC}; \; \alpha_{\ddot{S}} = \alpha_C$$

$$\beta_{C\ddot{O}} = \beta_{CC}; \; \beta_{CN} = \beta_{CC}; \; \text{and} \; \beta_{C\ddot{S}} = 0.8\beta_{CC}$$

With the above parameters, we have calculated that the first A_1 transition in 4-pyridone is 1.8 β, whereas in 4-thiopyridone it is only 1.0 β. Therefore, the calculated difference of 0.8 β corresponds to the experimental shift of 850 Å. We have obtained then a similar result: an average shift of 678 Å for compounds (III) and (IV), and an average shift of 729 Å for compounds (V) and (VI), with 2-carbethoxy-5-hydroxy-1-(1′-naphthyl)-4-pyridone having a somewhat higher shift (835 Å). The simple HMO theory cannot, of course, predict the observable transition energies correctly, but the application of such a theory gives a fair insight into the origin of the experimental data. We assume therefore, that for all investigated species, the red shift in the spectra of the sulphur compounds is the result of the inductive effect.

We wish now to consider the effect of the carbethoxy group on the spectra of compounds (V) and (VI), and make a comparison with the spectra of (III) and (IV). The carbethoxy group is the substituent which can be classified as an electron acceptor with respect to the unsaturated ring[6]. The carbethoxy group will produce a first-order inductive effect on the bands of molecules (I) and (II)[7]. The inductive effect of the carbethoxy substituting group would produce the observable red shift in the spectra of the substituted molecules. To predict this, we have used the same reasoning as that of Moffitt[8] and Murrell[7] for the case of the nonalternants*. The charge distributions of the exited A_1 state and the ground state for compounds (I) and (II) are different, and because of this we expect a first-order inductive effect on the bands. The change in the net charge distribution for the first transition ($\psi_1 - \psi_{-1}$) is calculated using the expression:

$$\psi_{-1}^2 - \psi_1^2 = \sum_\mu (C_{-1\mu}^2 - C_{1\mu}^2) \; \varphi_\mu^2$$

This calculation gives a net charge of —0.22 on C-atom 2, and +0.21 on C-atom 5. It follows, that introducing an acceptor group such as —COOR at position 2,

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* The first-order inductive effect will show itself only for non-alternants, because alternants have identical net charge distributions in the ground and excited states.

or a donor group such as —OH at position 5 will produce a red shift. If we had the reverse situation: —COOR at position 5 and —OH at position 2, then we might expect a blue (hypsochromic) shift. The numerical value of the shift is given by the expression:

$$\Delta E_\mu = (C^2_{-1\mu} - C^2_{1\mu})\, \alpha'_\mu$$

However, the above expression requires some knowledge of the value for α'_μ, For example, α'_μ in azulene is —4750 cm.$^{-1}$ for the substituent —COOEt. In benzene, α'_μ is —11850 cm.$^{-1}$ for the substituent —COOH. In our compounds, α' expected to be somewhere in between these two values. This conclusion is based on the HMO theory, and as usual, care should be taken in interpreting the results.

Finally, we wish to examine the mesomeric effect of substituents on nitrogen in the pyridone ring. Methyl*, naphthyl, tolyl, and phenyl produce different

TABLE

The intense long wavelength maximum of substituted 4-pyridones and their 4-thio analogues.

	4-Pyridones*		4-Thio analogues**		
	$\lambda_{max.}$ (in Å)	log ε_{max}	$\lambda_{max.}$ (in Å)	log ε_{max}	Shift (in Å)
3-Hydroxyl-1-(1'-naphthyl)-4-pyridone	2925	4.27	3590	4.25	665
3-Hydroxy-1-phenyl-4-pyridone	2990	4.26	3675	4.42	685
3-Hydroxy-1-(4'-chlorophenyl)-4-pyridone	3020	4.21	3705	4.11	685
3-Hydroxy-1-(4'-bromophenyl)-4-pyridone	3040	4.09	3715	4.08	675
2-Carbethoxy-5-hydroxy-1-(1'-naphthyl)--4-pyridone	2930	4.06	3765	4.18	835
2-Carbethoxy-5-hydroxy-1-(4'-tolyl)--4-pyridone	3080	3.87	3790	4.01	710
2-Carbethoxy-5-hydroxy-1-phenyl-4-pyridone	3090	4.04	3800	4.19	710
2-Carbethoxy-5-hydroxy-1-(4'-chlorophenyl)-4-pyridone	3125	3.93	3840	4.07	715
2-Carbethoxy-5-hydroxy-1-(4'-bromophenyl)-4-pyridone	3145	3.88	3846	3.96	695
2-Carbethoxy-5-hydroxy-1-(3'-nitrophenyl)-4-pyridone	3150	4.00	3890	4.26	710

The spectra were recorded on a Perkin-Elmer Spectrophotometer model 137 UV. In all experiments, ethanol has been used as solvent.
    * All compounds except 3-hydroxy-1-phenyl-4-pyridone (see: V. Hahn and K. Kukolja, *Croat. Chem Acta* **33** (1961) 137) have been recently made. The syntheses of the derivatives of 4-pyridone are published (see: K. Blažević and V. Hahn, *Croat. Chem. Acta* **38** (1966) 113).
    ** The syntheses of the derivatives of 4-thiopyridone are described in Ph. D. Thesis of K. Blažević, University of Zagreb, and will be published soon.

    * This spectrum has been reported by Berson *et al.*[9]; they have observed the first π—π^* band at 2810 Å. The methyl group has the property of being a mesomeric substituent, because it can achieve such an orientation which will extend the delocalization of the pyridone ring, but, being less capable of doing this than, for example, the phenyl ring, the observed red shift is smaller. It is worth mentioning however, that a small inductive effect might be present due to a charge distribution of — 0.10 in nitrogen. It is difficult to say how important this is for the shift in the first π—π^* transition in our compounds.

red shifts. We observed an increase in the red shift in the above order. The mesomeric effect favours a shift to longer wavelength in the absorption band.

We consider now the mesomeric effect on substituting phenyl with Cl, Br or NO_2. The observed red shifts are in the expected order. The shift can be atributed to the effect of Cl, Br and NO_2 substituents on the properties of the pyridone ring to which the phenyl group is attached, and it is very small for halogens, and slightly bigger for the NO_2 group. Such a shift can be associated with the mesomeric effect produced by the π-orbitals of Cl or Br and the π-molecular orbitals of the nitro group on substitution into the phenyl ring*. Cl and Br have both donor and acceptor properties, and this might be the reason why they exhibit the same behaviour as the strong acceptor nitro group.

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IZVOD

Diskusija o apsorpcionim spektrima substituiranih 4-piridona i njihovih 4-tio analoga

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Snimljeni su apsorpcioni spektri 3-hidroksi-1-aril-4-piridona, 2-karbetoksi-5--hidroksi-1-aril-4-piridona i njihovih 4-tio analoga i s pomoću induktivnog efekta oksigena s obzirom na sulfur objašnjen je batokromni pomak karakteristične π—π* vrpce u spektrima tio-spojeva. Uz pomoć induktivnog efekta prvoga reda karbetoksi grupe, diskutira se i batokromni pomak izazvan supstitucijom karbetoksi grupe u položaju 2 piridonskog prstena (raspored gustoće naboja u prstenu izračunat je pomoću Hückelove teorije molekularnih orbitala). Konačno se pomoću mezomernog efekta supstituenata na dušiku u prstenu diskutira batokromni pomak karakteristične vrpce.

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* For the alternant hydrocarbons the mesomeric effect is more important than the second-order inductive effect.