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Effect of Substituents on Ultraviolet Absorption Spectra of Derivatives of *o*-Hydroxybenzophenone

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UV absorption spectra of 14 derivatives of *o*-hydroxybenzophenone in ionized and unionized form in aqueous ethanol and in unionized form in hexane have been measured. Influence of substituents and solvents on the absorption band with the longest wavelength was discussed. The shift of this band under the influence of substituents in the unionized form was correlated with Hammett's σ constants.

Derivatives of *o*-hydroxybenzophenone are known as efficient photostabilizers. High absorption efficiency in the near ultraviolet region is a fundamental prerequisite for this application. Absorption spectra of derivatives of *o*-hydroxybenzophenone were measured by several authors [1—3]. Recently W. L. Dilling [4] investigated the influence of solvents on the shift of absorption bands in benzophenone and its hydroxy derivatives.

The purpose of this work is to follow the influence of substituents at positions 4 and 5 in *o*-hydroxybenzophenone and solvents at the absorption band with the longest wavelength.

Experimental

Ultraviolet absorption spectra were measured on a VSU-1 manual spectrophotometer of Carl Zeiss, Jena. The accuracy of reading of the absorption maxima was ± 2 mm. The equipment was calibrated on the lines of a mercury high-pressure arc HQE 40.

Derivatives of *o*-hydroxybenzophenone used for measurement were prepared according to [5]. Ethanol and hexane used as solvents were spectrally pure. Hydrochloric acid and sodium hydroxide were analytically pure.

Results and discussion

Determination of the nature of the respective transitions of derivatives of 2-hydroxybenzophenone is empirically possible on the basis of benzophenone and its hydroxy derivatives.

Benzophenone displays in the ultraviolet region two absorption bands. The absorption band with $\lambda_{max} = 254$ nm in ethanol is attributed to the $\pi \rightarrow \pi^*$ transition and the second with $\lambda_{max} = 334$ nm in ethanol is attributed to the $n \rightarrow \pi^*$ transition this being indicated by its low intensity, hypsochronic shift with growing solvent polarity and by its fine structure in non-polar solvents. In *p*-hydroxybenzophenone the band $\lambda_{max} = 246$ nm in ethanol belongs to the $\pi \rightarrow \pi^*$ transition and the second absorption band $\lambda_{max} = 293$ nm according to G. Porter [6—8] was related to an intramolecular charge transfer and was marked *p*-CT. In *o*-hydroxybenzophenone the band $\lambda_{max} = 260$ nm in ethanol is again $\pi \rightarrow \pi^*$ and the second $\lambda_{max} = 337$ nm in ethanol was marked by W. L. Dilling [4] *o*-CT. This designation of different absorption bands of derivatives of *o*-hydroxybenzophenone was used in Table 1, quoting values of λ_{max} of the respective derivatives in various solvents.

Ultraviolet absorption spectra of derivatives of *o*-hydroxybenzophenone retain essentially the character of the spectrum of *o*-hydroxybenzophenone. The absorption band about 260 nm is moderately influenced by substituents of derivatives of *o*-hydroxybenzophenone. More markedly affected by substituents is the absorption band with the longest wavelength, which is shifted in the region 310—380 nm.

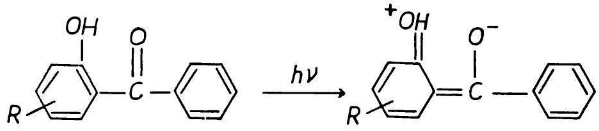
Table 1

Ultraviolet spectra of derivatives of *o*-hydroxybenzophenone

R	0.1 M-HCl 50 vol. % of ethanol		0.1 M-NaOH 50 vol. % of ethanol		Hexane	
	$\pi \to \pi^*$ λ_{max} nm	*o*-CT λ_{max} nm	$\pi \to \pi^*$ λ_{max} nm	$\pi \to \pi^*$ λ_{max} nm	$\pi \to \pi^*$ λ_{max} nm	*o*-CT λ_{max} nm
1. H	263	337	242	382	258	338
2. 5-NO_2	256	311	245	401	252 267 287	315
3. 5-$COCH_3$	259	320[a]	246	326	244 258	335
4. 5-COC_6H_5	258 280[a]	325	248	350	252	337
5. 5-Cl	260	345	245	395	258	349
6. 5-CH_3	263	349	243	398	255	352
7. 5-OCH_3	255	370	245	410	251	372
8. 5-OH	256	380	—[c]	—[c]	—[d]	—[d]
9. 4-NO_2	271	348	241 259	430	271	359
10. 4-Cl	271	329	244	380	271	331
11. 4-CH_3	276	338	242	382	253 270	338
12. 4-OCH_3	242 291[b]	325	242 275[a]	372	241 283[b]	326
13. 4-OH	245 290[b]	320		345	—[d]	—[d]
14. 4-$OCOCH_3$	269	328	243	350	—[d]	—[d]

a) Shoulder; *b*) Band belongs to *p*-CT; *c*) Compound oxidizes in alkaline solution by atmospheric oxygene; *d*) Compound is insoluble in this solvent.

In derivatives with a hydroxyl or alkoxyl group in position 4 the absorption band appears at about 290 nm, analogically as in *p*-hydroxybenzophenone. In consequence of the molecule of *o*-hydroxybenzophenone not being plane [9—12] the different absorption bands can be attributed to the respective parts of the molecule as follows: The absorption band with λ_{max} around 260 nm is caused by the phenylcarbonyl group. The absorption band with the longest wavelength is produced by interaction of the electron-donor hydroxyl group in ortho position with the electron acceptor carbonyl group in excited state according to equation:



The absorption band with λ_{max} around 290 nm is caused by analogical interaction of the electron-donor group in *para*-position.

Table 2

Influence of substituents on the absorption band with the longest wavelength in derivatives of *o*-hydroxybenzophenone

R	$\tilde{\nu}_{max} \cdot 10^{-3}$ [cm^{-1}]	σ_R^- (*a*)	$\sigma_{OH} - \sigma_{CO}$ (*c*)
1. H	29.67	0	0
2. 5-NO_2	32.15	0.64	0.56
3. 5-$COCH_3$	31.25	0.60	0.21
4. 5-Cl	28.99	—0.24	—0.14
5. 5-CH_3	28.63	—0.13	—0.08
6. 5-OCH_3	27.03	—0.50 (*b*)	—0.25
7. 5-OH	26.31	—0.61 (*b*)	—0.36
8. 4-NO_2	28.74	0.08	—0.09
9. 4-Cl	30.40	—0.10	0.14
10. 4-CH_3	29.59	—0.02	0.09
11. 4-OH	31.25	—0.25	0.36
12. 4-OCH_3	30.77	—0.11	0.39

a) Ref.[15]; *b*) Ref. [16]; *c*) Ref. [5].

The effect of substituents on physical chemical magnitudes in series of structurally related compounds are quantitatively characterized by Hammett's σ constants. Correlations of shifts of absorption bands in electron spectra with σ constant have limited validity only, even though there were established in certain cases satisfactory linear correlations.

For derivatives of *o*-hydroxybenzophenone an equation put forward by C. N. R. Rao [13, 14] was used:

$$\tilde{\nu}_{max} = \tilde{\nu}_0 + \varrho\sigma_R^-,$$

where $\tilde{\nu}_{max}$ is the position of the maximum of the absorption band in cm^{-1}, σ_R^- is the resonance part of Hammett's constant defined on the basis of phenol dissociation constants. If we choose for derivatives substituted at position 5, σ_R^- for the *para*-position and for derivatives substituted at position 4, σ_R^- for the *meta*-position we obtain satisfactory correlations (Fig. 1 and 2). It is a shortcoming of these correlations that the gradient has a different sign for derivatives substituted at position 5 (ϱ = 4320) and at position 4 (ϱ = —7760).

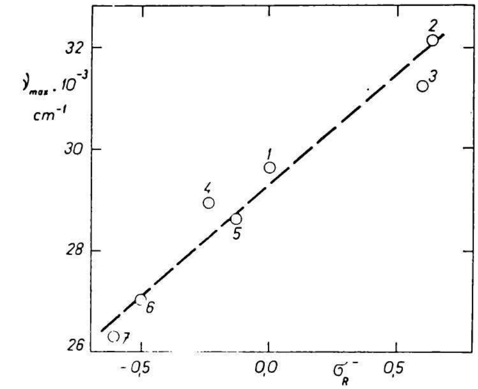


Fig. 1. Dependence of the $\tilde{\nu}_{max}$ on σ_R^- for derivatives of o-hydroxybenzophenone substituted at position 5.
Correlation constants calculated by the least squares method are slope $\varrho = 4320$ intercept, $\tilde{\nu}_0 = 29\,290$, correlation coefficient $r = 0.99$, standard deviation $s = 240$. (Numbers correspond to the sequence in Table 2.)

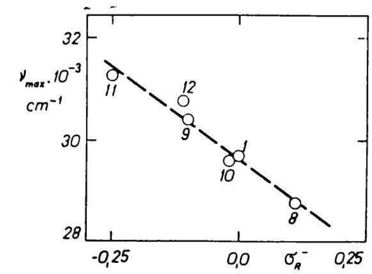


Fig. 2. Dependence of the $\tilde{\nu}_{max}$ on σ_R^- for derivatives of o-hydroxybenzophenone substituted in position 4.
Correlation constants: $\varrho = -7760$, $\tilde{\nu}_0 = 29\,550$, $r = 0.98$, $s = 280$. (Numbers correspond to the sequence in Table 2.)

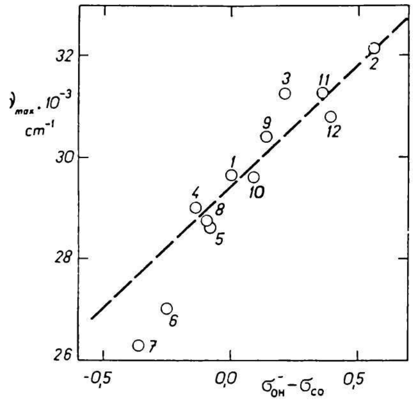


Fig. 3. Dependence of the $\tilde{\nu}_{max}$ on $\sigma_{OH}^- - \sigma_{CO}$ for derivatives of o-hydroxybenzophenone. Correlation constants: $\varrho = 4840$, $\tilde{\nu}_0 = 29\,420$, $s = 740$, $r = 0.85$. (Numbers correspond to the sequence in Table 2.)

A more general correlation is obtained in case of use of the difference of the given substituent with regard to the hydroxyl σ_{OH}^- and the carbonyl group σ_{CO} in the form

$$\tilde{\nu}_{max} = \tilde{\nu}_0 + (\sigma_{OH}^- - \sigma_{CO}).$$

This dependence is more general because it is valid for derivatives substituted in position 4 and 5 (Fig. 3).

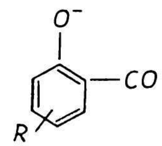
Both relations indicate that regarding the influence of substituents on the shift of absorption bands above all their resonance effect becomes apparent.

The absorption band with the longest wavelength is shifted bathochromically if there are in *para*-position against one another on the trisubstituted benzene nucleus of derivatives of *o*-hydroxybenzophenone substituents of the same type. For instance in derivates substituted at position 4 it can be observed the bathochromic shift if in *para*-position opposite to the electron-acceptor carbonyl group there is an electron-acceptor group. In derivatives substituted at position 5, at the *para*-position opposite to the electron-donor hydroxyl group there should be an electron-donor group.

A similar effect was observed in derivatives of *o*-nitrophenol substituted at position 4 and 5 for the absorption band with the longest wavelength [17].

Solvents with different polarity as f. i. ethanol and hexane have a relatively small influence on the shift of the absorption band with the longest wavelength, only, this being in accord with measurements of W. L. Dilling [4].

In the ionized form of derivatives of *o*-hydroxybenzophenone two bands were observed in the absorption spectra. The absorption band with λ_{max} of about 245 nm is nearly constant for all derivatives. The absorption band with the longest wavelength is bathochromically shifted against the non dissociated form. It belongs to the group



and is influenced by substituents. However, we were not succesful in qualitative and quantitative characterization of the influence of substituents on its shifts. A small bathochromic shift was observed in derivatives with the substituents $-COCH_3$ and $-COC_6H_5$ in the dissociated form in comparison with the non dissociated one, but the extinction coefficient has changed hyperchromically.

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VPLYV SUBSTITUENTOV NA ULTRAFIALOVÉ ABSORPČNÉ SPEKTRÁ DERIVÁTOV *o*-HYDROXYBENZOFENÓNU

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Zmerali sa ultrafialové absorpčné spektrá derivátov *o*-hydroxybenzofenónu v ionizovanej a neionizovanej forme vo vodnom etanole a v neionizovanej forme v hexáne. Diskutuje sa o vplyve substituentov a rozpúšťadiel na absorpčný pás s najväčšou vlnovou dĺžkou. Posun tohto pása vplyvom substituentov pri neionizovanej forme sa koreloval s Hammettovými σ konštantami.

ВЛИЯНИЕ ЗАМЕСТИТЕЛЕЙ НА УЛЬТРАФИОЛЕТОВЫЕ СПЕКТРЫ ПОГЛОЩЕНИЯ ПРОИЗВОДНЫХ 2-ОКСИБЕНЗОФЕНОНА

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Измерялись ультрафиолетовые спектры поглощения 14 производных 2-оксибензофенона ионизированной формы в водном этаноле и неионизированной формы в водном этаноле и в гексане. Обсуждается влияние заместителей и растворителей на длинноволновую полосу поглощения. Наблюдается коппелящие между сдвигом этой полосы под влиянием заместителей у неионизированной формы и σ константами Гамметта.

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REFERENCES

1. Van Allan J., Tinker J. F., *J. Org. Chem.* ***19***, 1243 (1954).
2. Balabán L., *Chem. prům.* ***15***, 411 (1965).
3. Holčík J., Karvaš M., Pospíšil A., *Chem. prům.* ***15***, 288 (1965).
4. Dilling W. L., *J. Org. Chem.* ***31***, 1045 (1966).
5. Hrdlovič P., Belluš D., Lazár M., *Collection Czech. Chem. Commun.* ***33***, 59 (1968).
6. Porter G., Suppan P., *Proc. Chem. Soc.* ***1964***, 191.
7. Porter G., Suppan P., *Pure Appl. Chem.* ***9***, 499 (1965).
8. Porter G., Suppan P., *Trans. Faraday Soc.* ***62***, 3375 (1966).
9. Moriconi E. J., O'Connor W. F., Forbes W. F., *J. Am. Chem. Soc.* ***82***, 5454 (1960).
10. Rekker R. F., Nautha W. T., *Spectrochim. Acta* ***8***, 348 (1956).
11. Rekker R. F., Nautha W. T., *Rec. trav. chim.* ***77***, 714 (1958).
12. Rekker R. F., Nautha W. T., *Rec. trav. chim.* ***80***, 747, 764 (1961).
13. Rao C. N. R., *Chem. Ind.* ***1956***, 666.
14. Rao C. N. R., *Chem. Ind.* ***1957***, 1239.
15. Taft R. W., Jr., *Steric Effect in Organic Chemistry*, Chap. 13 (Editor M. S. Newman). J. Wiley, New York 1957.
16. Taft R. W., *J. Am. Chem. Soc.* ***79***, 1045 (1957).
17. Hanckok C. K., Clague A. D., *J. Am. Chem. Soc.* ***86***, 4942 (1964).

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