Physicochemical study of 3′- and 4′-substituted 2-hydroxy--5-methylbenzophenone

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Ultraviolet absorption spectra, ionization constants (pK'), and chemical shifts of protons of the hydroxyl group δ(OH) of eight 3′- and 4′-substituted 2-hydroxy-5-methylbenzophenones were measured. A satisfactory σ/ϱ correlation for pK' and δ(OH) was found. However, the slope value of these relationships indicated that the transfer of electronic effect of the substituent was approximately 5 times smaller than that in the case of substitution on the ring bearing the hydroxyl group.

Измерены УФ абсорпционные спектры, константы ионизации (pK') и химический сдвиг гидроксильной группы δ(OH) восьми производных 3′- и 4′-замещенного 2-гидрокси-5-метилбензофенона. Определена удовлетворительная σ/ϱ корреляция для pK' и для δ(OH). Величина касательной этих зависимостей определяет, что перенос электронного эффекта заместителя является в пять раз слабше, чем в случае замещения на ядре на котором находится гидроксильная группа.

In the previous works some physicochemical quantities of the ground and excited states of 2-hydroxybenzophenone derivatives were examined and correlated with empirical parameters [1—5] or quantum chemical indices [6, 7]. Protolytic equilibria in the excited state were studied in detail [1, 6, 8]. The lowest triplet state [9] with 2-hydroxybenzophenone was estimated on the basis of quenching in the range of 263—241 kJ mol^{-1} All these works helped to gain more knowledge on this group of compounds which are used as stabilizers against photooxidative degradation of plastics iniciated by light [10].

To supplement these studies, also derivatives of 2-hydroxybenzophenone substituted on the second benzene ring in the positions 3′ and 4′ were prepared. Though it can be expected that the effect of the substituents on this second ring will be less pronounced, these measurements supplement the whole picture about the physicochemical behaviour of 2-hydroxybenzophenone derivatives. In the present

work the u.v. and i.r. spectra, dissociation constants (pK'), and chemical shifts of protons of the hydroxyl group of 2-hydroxy-5-methylbenzophenone derivatives substituted in the positions 3′ and 4′ were measured and the empirical σ/ϱ correlations were examined.

Experimental

The 3′- and 4′-substituted derivatives of 2-hydroxy-5-methylbenzophenone were prepared by the Fries rearrangement of the appropriate esters catalyzed with $AlCl_3$ or by the action of light. The esters of substituted benzoic acid with *p*-cresol were prepared by Schotten—Bauman benzoylation of aqueous solutions of sodium *p*-cresolate with chloride of the appropriate acid.

Melting points are uncorrected.

Ultraviolet absorption spectra were measured with a single-beam nonrecording VSU-1 (Zeiss, Jena) apparatus in methanol, chloroform, in the mixture of 0.1 M-HCl and methanol (40% by volume), and in the mixture of 0.1 M-NaOH and methanol (40% by volume).

Infrared spectra were measured on a double-beam recording Specord IR-75 (Zeiss, Jena) spectrophotometer in the mixture of CCl_4 : $CDCl_3$ (1 1) in KBr cells of 0.115 mm thickness at $c = 10^{-1}$ M l^{-1} in the region of 1500—1800 cm^{-1} characteristic of the absorption band belonging to carbonyl group present in the studied derivatives.

^{1}H-N.m.r. spectra were measured on a BS 467 apparatus (Tesla, Brno) with a temperature probe BP 4675 at 60 MHz in deuterated chloroform and deuterated dimethyl sulfoxide (5% w/v) at laboratory temperature, and in $CDCl_3$ at elevated temperature 68°C. Hexamethyldisiloxane was used as internal standard.

Ionization constants were determined by spectrophotometric titration in aqueous methanol (40% by volume) after the procedure described in [1]. The pH values of the buffer solutions were measured by means of a Radiometer PHM 4 (Radiometer, Copenhagen) with a glass electrode G 200 B and a calomel electrode K-100. The glass electrode was standardized with 0.05 M solution of sodium tetraborate (pH 9.18) at 25°C and with a buffer solution of pH 6.5. The dissociation constants were not corrected to the effect of the ionic strength.

2-Hydroxy-3′,5-dimethylbenzophenone

4-Methylphenyl 3-methylbenzoate (10 g; 0.04 mol) was thoroughly stirred with anhydrous $AlCl_3$ (10.7 g; 0.08 mol) and heated at 130°C for 5 h. After decomposition of the reaction mixture with 10% HCl and ice, the reddish-brown product was extracted with ether. After drying the extract over anhydrous Na_2SO_4, ether was distilled off. The product was 3 times crystallized from ethanol. A yellow crystalline substance (5.4 g; 54%) of m.p. 54—55°C was obtained.

For $C_{15}H_{14}O_2$ (226.28) calculated: 79.57% C, 6.25% H; found: 79.52% C, 6.19% H.

2-Hydroxy-5-methyl-3′-methoxybenzophenone

The solution of 4-methylphenyl 3-methoxybenzoate (3 g; 0.0124 mol) in methanol (450 ml) was irradiated by an immersion high-pressure lamp TG 81 (Quarzlampengesellschaft, Hanau) in a quartz reactor at 20°C for 10 h. After evaporation of the solvent, the mixture of compounds was dissolved in ether, extracted with 15% aqueous solution of NaOH several times. The combined alkali extracts were neutralized with HCl and extracted with ether. After drying and evaporation of ether, the product was dissolved in $CHCl_3$ and separated on a column (1300 × 15 mm) filled with polycaprolactam powder using chloroform as eluting agent. From the first fractions a yellow crystalline compound (1.02 g; 34%) of m.p. 130°C was obtained after evaporation of chloroform and crystallization from ethanol.

For $C_{15}H_{14}O_3$ (242.28) calculated: 74.40% C, 5.28% H; found: 74.28% C, 5.75% H.

Results and discussion

The values of the measured physicochemical quantities are summarized in Table 1.

The λ_{max} values indicated that the effect of the substituents on the position of the longest-wavenumber band was not significant. A moderate hypsochromic shift was observed with the compounds bearing electron-withdrawing substituents. It was similar as with the 4-substituted derivatives, while with the derivatives bearing electron-donating groups in the position 5 a significant bathochromic shift was observed [2].

The ionization constants of the hydroxyl group were only moderately affected and obeyed the one-parameter correlation (Fig. 1)

$$pK' = 10.43 - 0.62\,\sigma \qquad (r = 0.89,\ s = 0.22,\ n = 8)$$

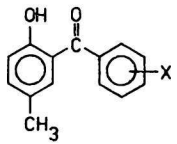
For the substituents in the position 3′ with regard to 2-hydroxybenzoyl group and for those in the position 4′ with regard to the same group, σ_m and σ_p constants, respectively, were chosen. The correlation was significantly better when the 4′-OCH_3 derivative ($r = 0.975$) was not considered. The slope of this relationship was 5 times lower than that (−3.32) of the analogous relationship with 4- and 5-substituted derivatives [1]. It means that the transfer of electronic effects between the rings *via* the carbonyl group was evidently smaller. With regard to the small effect of the substituents present on the second ring on pK_a of the hydroxyl group it can be expected that the contribution of the intramolecular hydrogen bond will be small and constant with all derivatives in the correlation between pK_a and σ.

The effect of the substituents on chemical shift of the proton of the hydroxyl group is described similarly by a satisfactory one-parameter correlation (Fig. 2)

$$\delta(OH) = 11.68 - 0.307\,\sigma \qquad (r = 0.88,\ s = 0.11,\ n = 8)$$

Table 1

Characteristics of the 3′- and 4′-substituted 2-hydroxy-5-methylbenzophenones



X	M.p. °C	Ref.	M.p. °C	λ_{max} nm	pK′	ν(CO) cm^{-1} (CCl_4)	δ(OH) t = lab. ($CDCl_3$)	δ(OH) t = 68°C ($CDCl_3$)	δ(OH) t = lab. ($DMSOd_6$)	σ_m	σ_p	$\Delta\delta$(OH) 22—68°C
H	84	[11]	84	351	10.48	1634	11.68	11.55[b]	10.46	0.00		0.13
3′-NO_2	104—105	[12]	102—103	353	9.92	1636.5[a]	11.45	11.31	10.31	0.71		0.14
3′-Cl	72	[13]	69—70	353	10.18	1635.5	11.60	11.45	10.38	0.37		0.15
3′-CH_3	—	—	54—55	348	10.55	1635	11.75	11.65	10.48	−0.07		0.10
3′-OCH_3	—	—	130—132	344	10.50	1635[a]	11.70	11.57	10.44	0.12		0.13
4′-Cl	71	[14]	69	352	10.27	1636	11.52	11.50	10.35		0.23	0.02
4′-CH_3	89.5—90	[15]	88—88.5	348	10.56	1636	11.75	11.61	10.63		−0.17	0.14
4′-OCH_3	108—109	[16]	108—109	342	10.40	1634	11.70	11.55	10.12		−0.26	0.15

a) Measured in the mixture of $CDCl_3 : CCl_4$ (1 : 1).
b) Measured in 1,1,2,2-tetrachloroethane at 145°C.

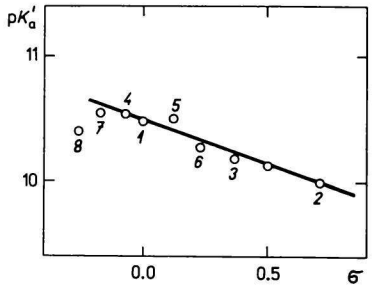


Fig. 1. The relationship pK' *vs.* σ.

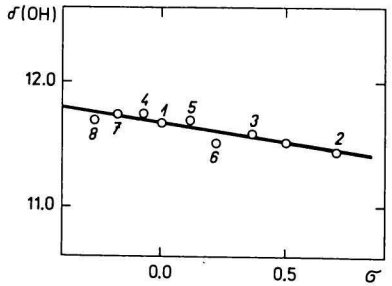


Fig. 2. The relationship δ(OH) *vs.* σ.

For 4- and 5-substituted derivatives of 2-hydroxybenzophenone a two-parameter correlation between δ(OH) and σ^- and σ values, respectively, was found with the slopes of $\varrho_1 = -1.273$ and $\varrho_2 = +1.228$ [4]. This correlation emphasizes the fact that strong electron-withdrawing and electron-donating substituents strengthen the intramolecular hydrogen bond. This effect was not observed with the 3′- and 4′-substituted derivatives probably due to the weak transfer of the electronic effect *via* the carbonyl group.

The effect of the substituents on chemical shift of the proton of the hydroxyl group was followed also in deuterated dimethyl sulfoxide. It can be assumed that in this solvent the intramolecular hydrogen bond will be partially or totally broken up. We obtained also a satisfactory one-parameter correlation with the slope value somewhat higher than that of the analogous correlation in deuterated chloroform

$$\delta(\mathrm{OH}) = 10.48 - 0.326\,\sigma \qquad (r = 0.871,\ s = 0.11,\ n = 7)$$

The small difference in the slopes of the above-mentioned correlations in polar and nonpolar media led to the conclusion that the indirect transmission of the electronic effects *via* the intramolecular hydrogen bond was small for this system.

Elevated temperature brought about only a small shift of protons of the hydroxyl group as it was observed with 2-hydroxybenzophenone [17]. In the given temperature range the intramolecular hydrogen bond was only little broken up. The effect of the polarity of the solvent on δ(OH) was more significant. However, this shift was roughly the same with all derivatives and therefore the effect of the substituents on the intramolecular hydrogen bond could not be deduced.

On the other hand, the δ(OH) could be taken for the measure of the intramolecular effect of the solvent indicated by the shift of the longest-wavenumber band. As seen from Table 1, the shifts of λ_{max} with the studied derivatives were small, thus, the correlation between these two quantities was not significant (Fig. 3). With the 4- and 5-substituted derivatives of 2-hydroxybenzophenone this correlation was observed [4].

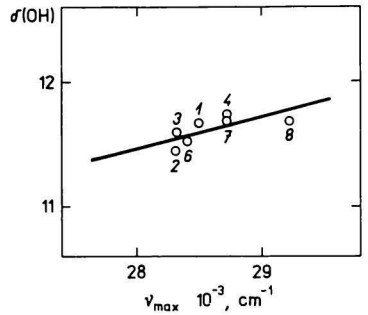


Fig. 3. The relationship δ(OH) *vs.* λ_{max}.

The stretching vibrations of the carbonyl group (Table 1) varied with the studied derivatives within the range of 2 cm^{-1} and no significant correlation was observed between ν(CO) and σ. It was probably due to the existence of the intramolecular hydrogen bond which seemed to compensate the unambiguous electronic effect of the substituents. When studying the effect of the substituents on the vibrations of carbonyl group with the derivatives substituted in the positions 4 and 5, similar observations were made [18].

In conclusion it can be stated that the electronic effect of the substituents between the rings *via* the carbonyl group was approximately 5 times smaller than that of the substituents on benzene ring bearing the *o*-phenol group and that the intramolecular hydrogen bond probably did not play any role.

References

1. Hrdlovič, P., Belluš, D., and Lazár, M., *Collect. Czech. Chem. Commun.* ***33,*** 59 (1968).
2. Hrdlovič, P. and Belluš, D., *Chem. Zvesti* ***22,*** 508 (1968).
3. Schubertová, N. and Hrdlovič, P., *Chem. Zvesti* ***23,*** 495 (1969).
4. Hrdlovič, P., Schubertová, N., and Palovčík, R., *Collect. Czech. Chem. Commun.* ***36,*** 1942 (1971).
5. Hrdlovič, P., Schubertová, N., Arventiev, B., and Wexler, H., *Collect. Czech. Chem. Commun.* ***36,*** 1948 (1971).
6. Kyseľ, O., *Collect. Czech. Chem. Commun.* ***39,*** 3256 (1974).
7. Kyseľ, O. and Jány, I., *Chem. Zvesti* ***28,*** 70 (1974).
8. Klöpfer, W., *Advan. in Photochem.* ***10,*** 311 (1977).
9. Klöpfer, W., *J. Polym. Sci. Symposium,* No. ***57,*** 205 (1976).
10. Ranby, B. and Rabek, J. F., *Photodegradation, Photooxidation and Photostabilization of Polymers,* p. 372. Wiley, New York, 1975.
11. Cox, E. H., *J. Amer. Chem. Soc.* ***49,*** 1030 (1927); *Beilstein II,* ***8,*** 199.
12. Saharia, G. S. and Sharman, B. R., *J. Indian Chem. Soc.* ***33,*** 788 (1956).
13. Aggarwal, S. C. and Saharia, G. S., *J. Indian Chem. Soc.* ***37,*** 295 (1960).
14. Malik, V. P. and Saharia, G. S., *J. Sci. Ind. Res.* ***15B,*** 633 (1956).
15. Shriner, R. L. and Moffet, R. B., *J. Amer. Chem. Soc.* ***63,*** 1964 (1941).
16. Gupta, A. R. and Saharia, G. S., *J. Indian Chem. Soc.* ***35,*** 133 (1958).
17. Merrill, J. R., *J. Phys. Chem.* ***65,*** 2023 (1961).
18. Hrdlovič, P., *Thesis.* Polymer Institute, Slovak Academy of Sciences, Bratislava, 1967.

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