

ULTRA-VIOLET ABSORPTION SPECTRA OF SOME 2-HYDROXY-6-METHYLBENZOPHENONES AND THEIR BEHAVIOUR WITH REGARD TO POLYVINYLCHLORIDE

B. ARVENTIEV, L. SINGUREL, H. OFFENBERG, T. NICOLAESCU and T. BACIU

Department of Organic Chemistry, "Al. I. Cuza", University of Jassy, Rumania

Abstract—Ultra-violet absorption spectra have been recorded for a series of 2-hydroxybenzophenones in CCl_4 and ethanol. The photostabilizing action of some 2-hydroxybenzophenones for PVC have been compared with "Tinuvin P".

THE u.v. absorption spectra of 2-hydroxy-6-methylbenzophenones (I, III, IV, V, VI and VIII) and some corresponding 2-methoxy-6-methylbenzophenones have been recorded over the range 280–420 $\text{m}\mu$ in CCl_4 and in ethanol.

As is shown in Fig. 1, the absorption spectrum of 2-hydroxy-4,6-dimethylbenzophenone (I) in CCl_4 shows a well pronounced maximum, but in ethanol there is no maximum and the spectrum differs but little from the absorption spectra of 2-methoxy-4,

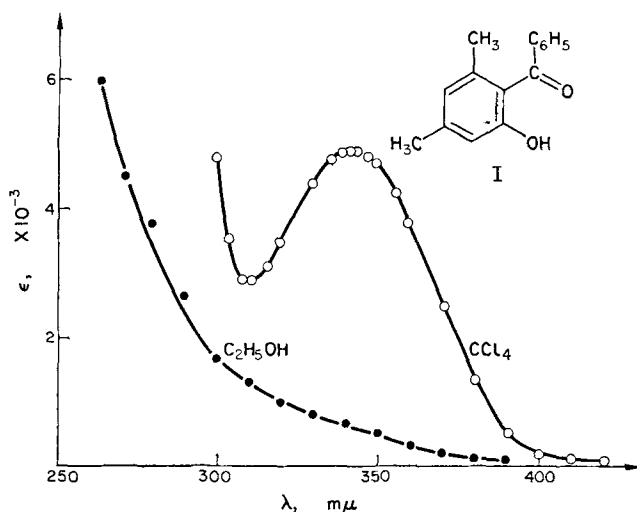


FIG. 1. Absorption spectrum of 2-hydroxy-4,6-dimethylbenzophenone I in CCl_4 and ethanol.

6-dimethylbenzophenone (II) (Fig. 2). The same behaviour is shown also by 2-hydroxy-6-methylbenzophenones III, IV and V.

With 4-nitro-2-hydroxy-6-methylbenzophenones VI (Fig. 3) and VIII in CCl_4 the absorption spectra have well pronounced maxima, while in the ethanol the maxima are feeble; nevertheless they differ from 4-nitro-2-methoxy-6-methylbenzophenone VII (Fig. 4).

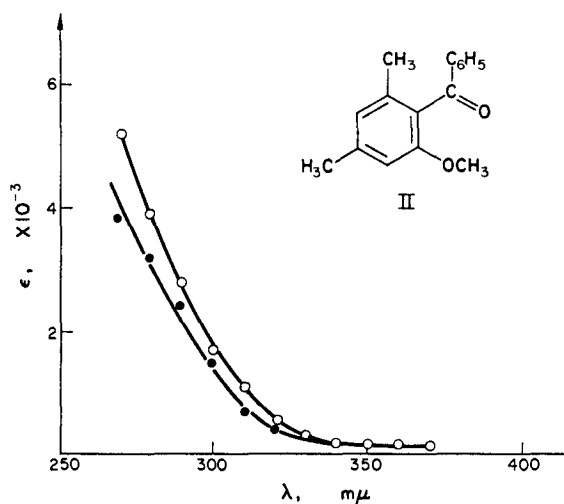


FIG. 2. Absorption spectrum of 2-methoxy-4,6-dimethylbenzophenone II in CCl_4 and ethanol.

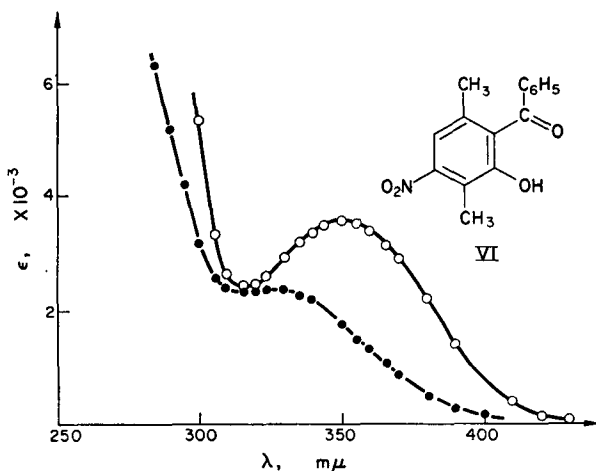


FIG. 3. Absorption spectrum of 4-nitro-2-hydroxy-6-methylbenzophenone VI in CCl_4 and ethanol.

For comparison we have recorded also the absorption spectra of a series of unsubstituted 2-hydroxybenzophenones with CH_3 at position 6. As can be seen in Fig. 5, with 2-hydroxy-4-methylbenzophenone (X) in both CCl_4 and ethanol the curves have well pronounced maxima, differing only slightly from one another, but considerably from 2-methoxy-4-methylbenzophenone XI (Fig. 6). The same effect is evident also with 2-hydroxybenzophenones XII, XIV, XVI, XVIII, XIX, XX and XXI and with the O-methylated derivatives 2-methoxy-5-methylbenzophenone and 2-methoxy-4,5-dimethylbenzophenone and with 4-bromo-2-methoxy-benzophenone.

Recently Hrdlovič, Belluš and Lazár⁽¹⁾ have recorded u.v. absorption spectra for a series of 2-hydroxybenzophenones having different substituents in position 4 or 5,

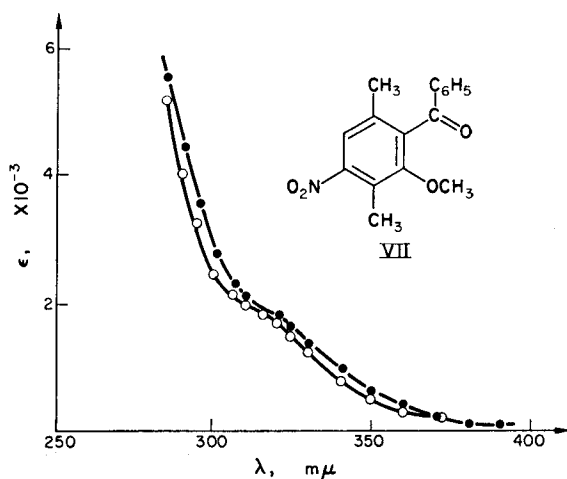


FIG. 4. Absorption spectrum of 4-nitro-2-methoxy-6-methylbenzophenone VII in CCl₄ and ethanol.

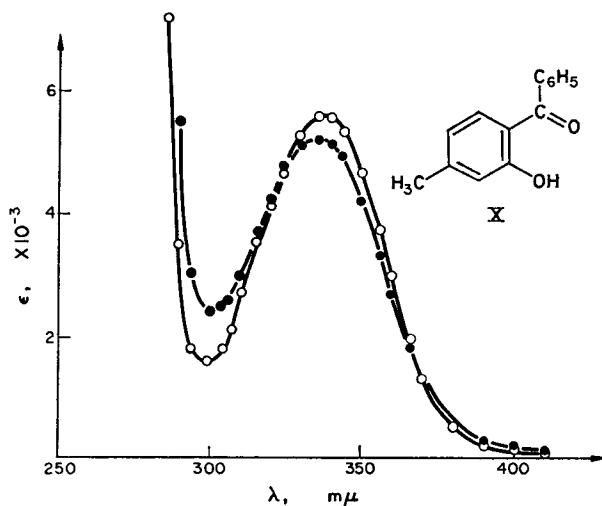


FIG. 5. Absorption spectrum of 2-hydroxy-4-methylbenzophenone X in CCl₄ and ethanol.

and also for 2-hydroxy-4-methylbenzophenone (X) and 2-hydroxy-5-methylbenzophenone (XII) in aqueous ethanol (50 per cent by volume) for determining their dissociation constants. The values of λ max. in absolute ethanol obtained by us for these 2-hydroxybenzophenones differ but little from the values obtained in aqueous ethanol by these authors.

Table 1 shows values of λ max. and $\epsilon \cdot 10^{-3}$ max. in CCl₄ and in C₂H₅OH of the 2-hydroxybenzophenones. It shows also $\Delta\nu_{C=O}$ (the differences between $\nu_{C=O}$ of 2-methoxybenzophenone and $\nu_{C=O}$ of the corresponding 2-hydroxybenzophenone); they are reproduced from the previous work.⁽²⁾

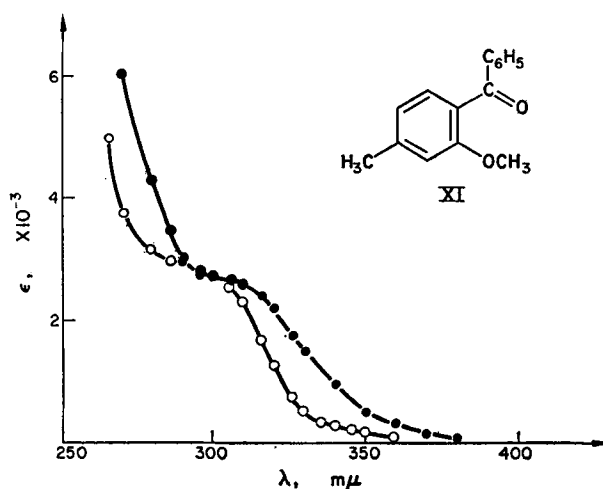
FIG. 6. Absorption spectrum of 2-methoxy-4-methylbenzophenone XI in CCl_4 and ethanol.

TABLE 1

No.	Compound, m.p., colour	In CCl_4			In $\text{C}_2\text{H}_5\text{OH}$		
		λ max ($\text{m}\mu$)	ϵ 10^{-3} max	$\Delta\nu_{\text{C}=\text{O}}$ (cm^{-1})	λ max ($\text{m}\mu$)	ϵ 10^{-3} max	$\Delta\nu_{\text{C}=\text{O}}$ (cm^{-1})
1	2-hydroxy-4,6-dimethylbenzophenone (I) 140° , colourless.	343	4.90	47	Absence of max		-1
2	2-hydroxy-3,6-dimethylbenzophenone (III) 104° , colourless.	350	2.60	50	Absence of max		2
3	2-hydroxy-3-isopropyl-6-methylbenzophenone (IV), 97° , colourless.	350	3.40	48	Absence of max		5
4	4-bromo-2-hydroxy-3,6-dimethylbenzophenone (V), 117° , white-yellow.	345	3.70	43	Absence of max		7
5	4-nitro-2-hydroxy-3,6-dimethylbenzophenone (VI), 171° , yellow.	350	3.50	45	Feeble max		0
6	4-nitro-2-hydroxy-3-isopropyl-6-methylbenzophenone (VIII), $130-131^\circ$, yellow.	347	4.50	45	Feeble max		1
7	2-hydroxy-4-methylbenzophenone (X), 65° , white-yellow.	338	5.60	40	336	5.20	37
8	2-hydroxy-5-methylbenzophenone (XII), 84° , yellow.	353	4.70	35	349	4.10	27
9	2-hydroxy-4,5-dimethylbenzophenone (XIV), 111° , yellow.	350	5.70	32	348	5.30	23
10	4-bromo-2-hydroxybenzophenone (XVI), 83° , white-yellow.	335	6.00	45	330	4.80	36
11	4-bromo-2-hydroxy-5-methylbenzophenone (XVIII), 122° , white-yellow.	346	5.80	45	342	5.30	35
12	4-bromo-2-hydroxy-3-methylbenzophenone (XIX), 96° , white-yellow.	341	5.70	57	342	5.60	47
13	4-nitro-2-hydroxy-3-methylbenzophenone (XX), 98° , yellow.	355	5.00	47	353	4.20	48
14	3-nitro-2-hydroxy-5-methylbenzophenone (XXI), 68° , yellow.	362	5.20	1	359	4.40	1

Considering $\Delta\nu_{C=O}$ as the measure of strength of intramolecular hydrogen bond, it is seen that only 2-hydroxybenzophenones show relatively great values of $\Delta\nu_{C=O}$; this means that strong intramolecular hydrogen bonds give absorption in the mentioned range with well pronounced maxima. With 2-hydroxy-6-methylbenzophenones which have in ethanol small values of $\Delta\nu_{C=O}$, u.v. spectra in ethanol have no maxima.

3-nitro-2-hydroxy-5-methylbenzophenone (XXI) is an exception, but it is known⁽³⁾ that in this case the intramolecular hydrogen bond involves the NO_2 — group and not the $C=O$ group.

The feeble maxima observed with 4-nitro-2-hydroxy-6-methylbenzophenones VI and VIII in ethanol could be explained by the presence in small quantity of molecules with strong intramolecular hydrogen bonds.

In the previous publications, we supposed that the weakening of the hydrogen bond with 2-hydroxy-6-methylbenzophenones in the crystalline state and in strongly polar solvents is due to disturbance of the coplanarity of the $C=O$ group with the phenyl ring which contains OH ; this is caused by the steric interference of CH_3 — group in position 6.

The photostabilizing action of some of the 2-hydroxybenzophenones studied in the present paper has been investigated using P.V.C. sheets of Rumanian production of different recipes and compared with "Tinuvin P" and in some cases with diphenylisododecylphosphite and with organic compounds of tin.

The results showed that the 2-hydroxybenzophenones added in concentrations similar to "Tinuvin P" decrease the efficiency of photostabilizer in some cases. At smaller concentration, the effectiveness is not diminished. If we take into account the fact that, after a certain time of irradiating with u.v. the colour of the sheet remains constant, we may conclude that the appeared colour is due to change of the structure of the photostabilizer—i.e. of 2-hydroxybenzophenone. With other mixtures, the efficiency is not diminished for concentrations similar to "Tinuvin P".

EXPERIMENTAL

All the 2-hydroxybenzophenones, with the exception of XXI, have been prepared by oxidative decyclization with CrO_3 of the corresponding 2,3-diphenylbenzofurans, followed by alkaline hydrolysis of the resulting 2-benzoyloxybenzophenones.

2-hydroxybenzophenone XXI has been obtained by direct nitration of 2-hydroxy-5-methylbenzophenone. 2-methoxybenzophenones have been obtained by methylation with dimethyl sulphate of 2-hydroxybenzophenones in aqueous solutions of $NaOH$.

The products have been purified by repeated crystallization in ethanol.

u.v. spectrophotometry

The u.v. absorption spectra have been recorded on the spectrophotometer VSU-1 Carl Zeiss-Jena. The concentrations of solutions have been in all cases 2.10^{-4} mol/l. The thickness of the quartz cell was 5 mm.

The photostabilizing action

The mixtures of P.V.C. with photostabilizers have been made taking into account the recipes for carpets and hard sheets utilized in normal plant production. The test pieces have been rolled at 165° – 170° for 5 min. The duration of exposure to u.v. rays in the phade-O-meter with electric arc have been 0–20–100–200 hr, 0–100–200–400 hr and 0–100–200–300–400 hr.

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