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The Ultraviolet Absorption Spectra of Some Aroyl Compounds Derived from Phloroglucinol

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The electronic absorption spectra of 2-hydroxy-4,6-dimethoxybenzaldehyde (Fig. 1; max. 294 m\(\mu\), log \(\varepsilon\) = 4.31; infl. 330 m\(\mu\), log \(\varepsilon\) = 3.58), 2-hydroxy-4,6-dimethoxyacetophenone (Fig. 2; max. 288 m\(\mu\), log \(\varepsilon\) = 4.24; infl. 320 m\(\mu\), log \(\varepsilon\) = 3.60) and 2-hydroxy-\(\omega\)-4,6-trimethoxyacetophenone (Fig. 3; max. 288 m\(\mu\), log \(\varepsilon\) = 4.31; infl. 323 m\(\mu\), log \(\varepsilon\) = 3.62) in 95% ethanolic solution show a close resemblance to each other and to the spectra of flavonoids \(^1\) and 2-benzylcoumaran-3-ones \(^2\) that have the group

![Chemical Structure]

in common and are unsubstituted in the isolated phenyl group. It is, therefore, to be concluded that this type of spectrum represents the absorpti onal properties of the aroyl group in question when coplanar or nearly coplanar.

Methylation of the two acetophenones mentioned leads to a quite different type
of spectra, characterised by much lower overall molar extinction, especially at longer wave-lengths. Cram and Cramz already have observed this effect of two o-methyl groups in the case of the dimethyl ethers of 2,6-dihydroxyacetophenone and 2,6-dihydroxy-3-methylacetophenone. 2,4,6-Trimethoxyacetophenone (Fig. 2) has a maximum at 274 μ, log ε = 3.76 and ω,2,4,6-tetramethoxyacetophenone (Fig. 3) a maximum at 278 μ, log ε = 3.72. It cannot be seen from the spectra whether such a maximum results from two bands which presumably would correspond to the most intense band and the inflexion in the parent 2-hydroxy compound. 2,4,6-Trimethoxybenzaldehyde (Fig. 1), in contrast to the corresponding acetophenones, exhibits but a slightly lower molar extinction in the main band (max. 289 μ, log ε = 4.25) compared with the parent 2-hydroxy compound. Again, the inflexion in the latter becomes less pronounced by methylation.

The reduction of the K-band intensity due to steric hindrance of coplanarity in aryl compounds with one or two ortho-methyl groups has been studied by Braude and Sondheimer. They deduced a quantitative relation between the band intensity and the mean angle between the planes of the benzene nucleus and the acyl group in the ground electronic state of the molecule. The mean angles are smaller in the substituted benzaldehydes than in the acetophenones, as, beside the more steric interaction between the carbonyl oxygen and an o-methyl group in the former, an overlap of an o-methyl group and the acetyl-methyl group is possible in the latter. This overlap, in addition, provides a much stronger hindrance to coplanarity than does the overlap of the carbonyl and o-methyl groups.

The low absorption intensities of the acetophenones with two o-methoxyl groups can be conveniently explained by the hindrance to coplanarity of the aryl group mainly produced by the steric interaction of either of the o-

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groups and the group forming the second link of the side carbon chain. In this respect, the effect of o-methoxy resembles that of o-methyl groups. A hindrance to coplanarity by a steric interaction between the carbonyl oxygen and one o-methoxy group is not evident from the intensity data, since the spectra of 2-methoxyacetophenone, 2-methoxybenzaldehyde, their parent hydroxy compounds, flavanone and 2-benzyloloumaran-3-one, are all very like each other 4,1. In fact, slightly higher molar extinctions of the most intense bands are reported for the two mentioned methoxy compounds, of which 2-methoxyacetophenone shows rather marked hypochromic shifts when compared with 2-hydroxyacetophenone: 5.5 μ for the most intense band and 22 μ for the band at the longer wave length 5. On the other hand, the slight reduction in the absorption intensity, which follows the methylation of 2-hydroxy-4,6-dimethoxybenzaldehyde, might be noted.

A steric interaction of the carbonyl group forming the second link of the carbon chain in 1-(2,4,6-trimethoxyphenyl)-3-phenylpropane-1,2-dione with either of the o-methoxy groups possibly contributes to its somewhat individualistic spectral behaviour 4.

From the spectra in 0.05 N sodium hydroxide/48 % aqueous ethanol solution of 2-hydroxy-4,6-dimethoxybenzaldehyde (Fig. 1; max. 294 μ, log ε = 4.21; max. 359 μ, log ε = 3.79), 2-hydroxy-4,6-dimethoxyacetophenone (Fig. 2; max. 288 μ, log ε = 3.82; max. 338 μ, log ε = 3.62) and 2-hydroxy-o-4,6-trimethoxyacetophenone (Fig. 3; max. 288 μ, log ε = 3.90; max. 342 μ, log ε = 3.67) it is seen that the phenolate ions of both acetophenone derivatives absorb much less intensely than the anion of 2-hydroxy-4,6-dimethoxybenzaldehyde. The overlap of the second chain link and either of two o-oxygen atoms thus seems to hinder coplanarity when the possibility of chelate ring formation is eliminated.

Experimental: 2-Hydroxy-4,6-dimethoxybenzaldehyde, m.p. 70.5° (71° reported 5), was prepared by demethylation of 2 g of 2,4,6-trimethoxybenzaldehyde, m.p. 120° (see acknowledgement) with aluminum bromide (1.05 moles) in benzene solution. It was purified by repeated recrystallisations from aqueous methyl alcohol and, finally, by sublimation under vacuum. 2-Hydroxy-4,6-dimethoxyacetophenone, m.p. 82° (various values from 80° to 88° reported, 83°, Ref.7) and 2-hydroxy-o,4,6-trimethoxyacetophenone, m.p. 104° (102—104° reported 8) were prepared by the procedure described for the latter compound 4. They were purified by repeated recrystallisations from methanol and ethanol, respectively, and, finally, by sublimation under vacuum.

2,4,6-Trimethoxyacetophenone, m.p. 101.5° (102—103° reported 8) was obtained by methylation of phloracetophenone (2 g) in 30 ml of acetone with dimethyl sulphate (3.5 moles) and potassium carbonate. It was purified by washing the ether solution with alkali, recrystallisation from methanol-ethanol, and final sublimation under vacuum.

The spectra were determined with a Beckman DU spectrophotometer from solutions of the sublimed compounds in concentrations of 10 to 20 mg/ml. All determinations were carried out immediately after the dissolution. The measurement of 2-hydroxy-4,6-dimethoxybenzaldehyde in 0.05 N NaOH/48 % ethanol was repeated after 2 h and those of both aldehydes in neutral ethanol after 7 days, but the spectra were unchanged.

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