Fig. 4. Diffusion constant as function of temperature. The solid dots and the open circles belong to two different series. The deviation of the one open circle may be due to the thermostat working imperfectly.

In Fig. 4 the diffusion constants are plotted against the temperature distance from the critical point. The points belong to two different series with different prisms and samples used for filling up the prisms. Minor impurities in the samples are certainly different in the two series. Moreover, certain reactions seem to take place inside the prism. This is shown by the fact that the critical temperature has not been constant the whole time, but has decreased from day to day so that it had to be checked at all individual diffusion measurements at the selected temperatures.

In Fig. 4 the diffusion constant does not extrapolate exactly to zero at the critical temperature. However, no conclusions can be drawn from this, especially as the exact determination of the critical temperature has been a difficult undertaking, and the temperature regarded as critical may have been one or two millidegrees below the actual temperature.

The diffusion constant seems to approach zero by lowering the temperature down to the critical by 0.37 cm² per day and °C.

Throughout the whole period of the investigations the encouragement and interest shown by Professor O. Hassel of the University of Oslo has been of inestimable value.

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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 mμ, log ε = 4.31; infl. 330 mμ, log ε = 3.58), 2-hydroxy-4,6-dimethoxyacetophenone (Fig. 2; max. 288 mμ. log ε = 4.24; infl. 320 mμ, log ε = 3.60) and 2-hydroxy-ω,4,6-trimethoxyacetophenone (Fig. 3; max. 288 mμ, log ε = 4.31; infl. 323 mμ, log ε = 3.62) in 95 % ethanolic solution show a close resemblance to each other and to the spectra of flavanones [1,2] and 2-benzylcoumaran-3-ones [1] that have the group
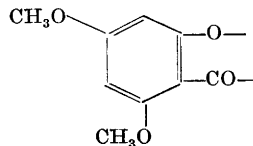
in common and are unsubstituted in the isolated phenyl group. It is, therefore, to be concluded that this type of spectrum represents the absorptional properties of the aroyl group in question when coplanar or nearly coplanar.

Methylation of the two acetophenones mentioned leads to a quite different type
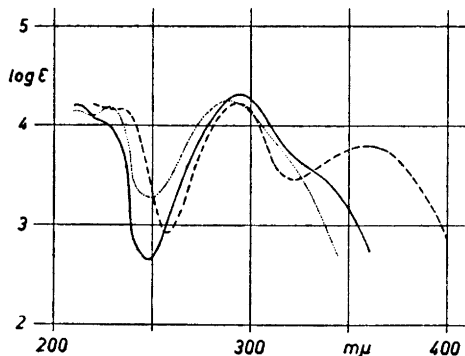
Fig. 1. ——————— 2-hydroxy-4,6-dimethoxy-benzaldehyde in 95 % ethanol. — — — — 2-hydroxy-4,6-dimethoxybenzaldehyde in 0.05 N NaOH in 48 % aqueous ethanol. ······ 2,4,6-trimethoxybenzaldehyde in 95 % ethanol.
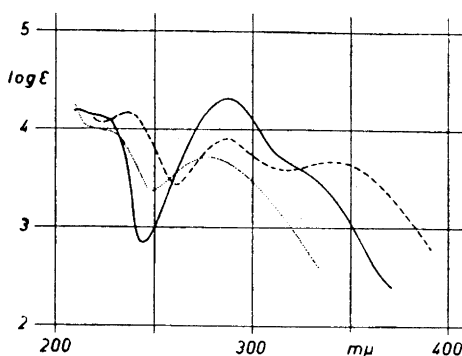

Fig. 3. ——————— 2-hydroxy-ω,4,6-trimethoxy-acetophenone in 95 % ethanol. — — — — 2-hydroxy-ω,4,6-trimethoxyacetophenone in 0.05 N NaOH in 48 % aqueous ethanol. ······ ω,2,4,6-tetramethoxyacetophenone in 95 % ethanol.

of spectra, characterised by much lower overall molar extinction, especially at longer wave-lengths. Cram and Cranz[3] already have observed this effect of two o-methoxyl groups in the case of the dimethyl ethers of 2,6-dihydroxyaceto-phenone and 2,6-dihydroxy-3-methylaceto-phenone. 2,4,6-Trimethoxyacetophenone (Fig. 2) has a maximum at 274 mμ, log $\varepsilon = 3.76$ and ω,2,4,6-tetramethoxyaceto-phenone (Fig. 3) a maximum at 278 mμ, log $\varepsilon = 3.72$. 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 aceto-phenones, exhibits but a slightly lower molar extinction in the main band (max. 289 mμ, log $\varepsilon = 4.25$) compared with the parent 2-hydroxy compound. Again, the inflexion in the latter becomes less pronounced by methylation.
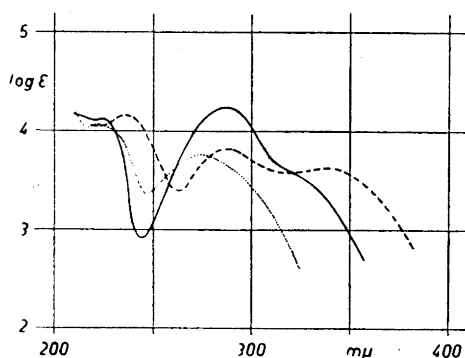
The reduction of the K-band intensity due to steric hindrance of coplanarity in aroyl compounds with one or two ortho-methyl groups has been studied by Braude and Sondheimer[4]. They deduced a quantitative relation between the band intensity and the mean angle between the planes of the benzene nucleus and the acyl group in the ground electronic state of the molecule. The mean angles are smaller in the substituted benzaldehydes than in the aceto-phenones, as, beside the mere 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 aceto-phenones with two o-methoxy groups can be conveniently explained by the hindrance to coplanarity of the aroyl group mainly produced by the steric interaction of either of the o-

Fig. 2. ——————— 2-hydroxy-4,6-dimethoxy-acetophenone in 95 % ethanol. — — — — 2-hydroxy-4,6-dimethoxyacetophenone in 0.05 N NaOH in 48 % aqueous ethanol. ······ 2,4,6-trimethoxyacetophenone in 95 % ethanol.

groups and the group forming the second link of the side carbon chain. In this respect, the effect of o-methoxyl resembles that of o-methyl groups. A hindrance to coplanarity by a steric interaction between the carbonyl oxygen and one o-methoxyl group is not evident from the intensity data, since the spectra of 2-methoxyacetophenone, 2-methoxybenzaldehyde, their parent hydroxy compounds, flavanone and 2-benzylcoumaran-3-one, are all very like each other [5],[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 hypsochromic shifts when compared with 2-hydroxyacetophenone: 5.5 mμ for the most intense band and 22 mμ 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-methoxyl groups possibly contributes to its somewhat individualistic spectral behaviour [1].

From the spectra in 0.05 N sodium hydroxide/48 % aqueous ethanol solution of 2-hydroxy-4,6-dimethoxybenzaldehyde (Fig. 1; max. 294 mμ, log $\varepsilon = 4.21$; max. 359 mμ, log $\varepsilon = 3.79$), 2-hydroxy-4,6-dimethoxyacetophenone (Fig. 2; max. 288 mμ, log $\varepsilon = 3.82$; max. 338 mμ, log $\varepsilon = 3.62$) and 2-hydroxy-ω,4,6-trimethoxyacetophenone (Fig. 3; max. 288 mμ, log $\varepsilon = 3.90$; max. 342 mμ, log $\varepsilon = 3.67$) 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 [6]), was prepared by demethylation of 2 g of *2,4,6-trimethoxybenzaldehyde*, m.p. 120° (see acknowledgement) with aluminium bromide (1.05 moles) in benzene solution. It was purified by repeated recrystallisations from aqueous methanol 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-ω,4,6-trimethoxyacetophenone*, m. p. 104° (103—104° reported) were prepared by the procedure described for the latter compound [6]. 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 [9]) was obtained by methylation of phloroacetophenone (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, recrystallisations from methanol-ethanol, and final sublimation under vacuum.

ω,2,4,6-Tetramethoxyacetophenone, m. p. 56.5°—57°[1], was purified by washing with alkali, repeated recrystallisation from ether and 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/l. 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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