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SUBSTITUENT EFFECTS ON THE CARBONYL STRETCHING VIBRATION IN THE IR SPECTRA
OF SOME SUBSTITUTED BENZOPHENONES.¹

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ABSTRACT

The band frequencies and integrated intensities of the carbonyl stretching absorptions in a series of substituted benzophenones were examined as a function of the inductive and mesomeric effects of the substituents.

INTRODUCTION

Fuson et al.² have reported the C=O band positions for several substituted benzophenones, but no definitive study of the band intensities for this class of compounds has been made. The frequencies and intensities of the C=O bands were recently reported for a large number of alkyl³, and some halogen-substituted³⁻⁴ benzophenones, but no relationship has been established between C=O band intensities and the Hammett σ values. Thomson and Steel⁵ observed a linear relationship when the C≡N stretching band intensities were plotted against the Hammett σ functions for the substituted benzonitriles, but a similar plot for the substituted acetophenone data showed wide scatter⁶.

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In the present communication the frequencies and integrated intensities for the C=O bands in several different substituted benzophenones are presented, and the observed changes in these quantities are discussed in relation to the nature of the substituents. The present objective is to enlarge the conclusions previously drawn²⁻³ as well as to ascertain whether there is any significant regularity between the C=O band intensities and the Hammett reactivity constants.

EXPERIMENTAL SECTION

All the compounds were commercially available in high purity and their melting point data were consistent with the respective literature values. The infrared spectra were recorded using a Perkin-Elmer Model 180 spectrophotometer at the constant I_0 energy mode. For frequency calibration the indene absorption maxima at 1713.4 ± 0.66 and $1609 \pm 0.42 \text{ cm}^{-1}$ were used and the frequency measurements were accurate to $\pm 0.5 \text{ cm}^{-1}$. The integrated absorption intensities (A) are reported in units of $\text{mole}^{-1} \cdot \text{cm}^{-2} \cdot 10^4$, and are calculated by the equation⁷⁻⁸

$$A = 2.303 \times 1.57 \times \epsilon \times \Delta \nu_{1/2} \times 10^{-4}$$

where ϵ is the apparent molar extinction coefficient at the absorption maximum, and $\Delta \nu_{1/2}$ is the band width in cm^{-1} at the half-maximum intensity. The absorption frequencies in the solid phase and in solutions, and their integrated intensities are the average values of three independent measurements for each compound. The mean frequencies and integrated intensities are listed in Table 1. The average relative error is 0.2 cm^{-1} for frequency positions and $0.04 \text{ mole}^{-1} \cdot \text{cm}^{-2}$ for A-values, respectively.

RESULTS AND DISCUSSION

Table 1 illustrates the variations of C=O absorption frequency in different substituted benzophenones. The lowest frequency is observed for 4,4' - bis

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Table I. Carbonyl stretching bands of substituted benzophenones.

Substituents	$\nu_{\text{max}}(\text{cm}^{-1})$		ϵ_{max}	$\Delta\nu_{1/2}$ (cm^{-1})	$A \times 10^4$	σ -values
	Solid	Solution				
4- NO_2	1651.0	1672.8	633	14.2	3.25	0.778
3- NO_2	1654.0	1672.4	847	10.8	3.31	.710
4,4'-di-Cl	1653.0 ^a	1667.5	478	12.5	2.16	.454
4,4'-di-F	1646.2	1665.6	549	11.8	2.34	.124
Unsubstituted	1654.3	1664.8	602	10.7	2.33	0
4- CH_3	1651.8	1662.2	567	14.0	2.87	-.170
3,4-di- CH_3	1653.0	1661.2	485	14.5	2.54	-.239
4,4'-di- CH_3	1645.0	1659.0	551	13.6	2.71	-.340
4,4'-di- OCH_3	1639.5 ^a	1654.0	435	15.5	2.44	-.536
4,4'-di-OH	1632.0 ^a	1646.4	382	16.2	2.24	-.94
4-(CH_3) ₂ N	1641.8	1649.6	463	13.2	2.21	-.830
4,4'-di-(CH_3) ₂ N	1602.8	1640.6	237	13.8	1.18	-.166
2,5-di- CH_3	1666.2 ^b	1668.8	459	14.8	2.46	
2,4-di- CH_3	1659.7 ^b	1664.8	527	13.3	2.53	

^a Represents mean value of two C=O absorptions observed in the solid state, due to crystal splitting.

^b Pure liquid at room temperature ($\sim 25^\circ \text{C}$)

(dimethylamino) benzophenone and the highest for the 4-nitro benzophenone, presumably due to the opposite electronic effects of the two substituents ⁹.

This observation conforms to the behavior observed for the corresponding acetophenones.⁶ In the electron-donating dimethylamino group, the strong + M effect overshadows its weak -I effect, and a structure having an appreciable lower C=O bond order is favored. The C=O band frequency of the chloro- and fluoro- substituted compounds do not change much as compared to the unsubstituted compound. Since the inductive and mesomeric effects of the halogens are of opposite signs⁹, a compensatory action between the two effects is implied which results in a negligible C=O frequency shift.

In Figure 1, the C=O frequencies are plotted as a function of the Hammett substitution constants¹⁰, σ . Although the points are somewhat more scattered in the solid state than in solution, the frequency data in both cases are approximately linearly correlated with the Hammett σ values. The slope of the solid case was 17.7 ± 3.5 with a least square correlation of 0.84, as compared to the corresponding values of 14.3 ± 1.0 and 0.97 for the solution case. Nonetheless, the same combination of factors (i.e., mesomeric and inductive effects) appears to be responsible for the shifts in the C=O stretching band frequency in both the solid phase and in solutions. These results qualitatively agree with similar observations of earlier investigations.^{2-3,6,11-12}

Table I shows the integrated intensities (A) for 13 substituted benzophenones as a function of σ . It clearly demonstrates that the band intensities (as measured by A-values) are variable but the total range of variation with substituent types from 1.2 to 3.3 is high when compared with the range from 1.4 to 2.8 observed by Jones et al.⁶ in similarly substituted acetophenones. In general, substituents with a + M effect and - I effect will both enhance the intensity of the C=O band in benzophenones.

The C=O band in the 4,4'-difluoro- compound is 0.18 unit stronger than in the 4,4'-dichloro-band, indicating that the mesomeric effect alone can not explain the C=O band intensity in these compounds. The inductive contribution

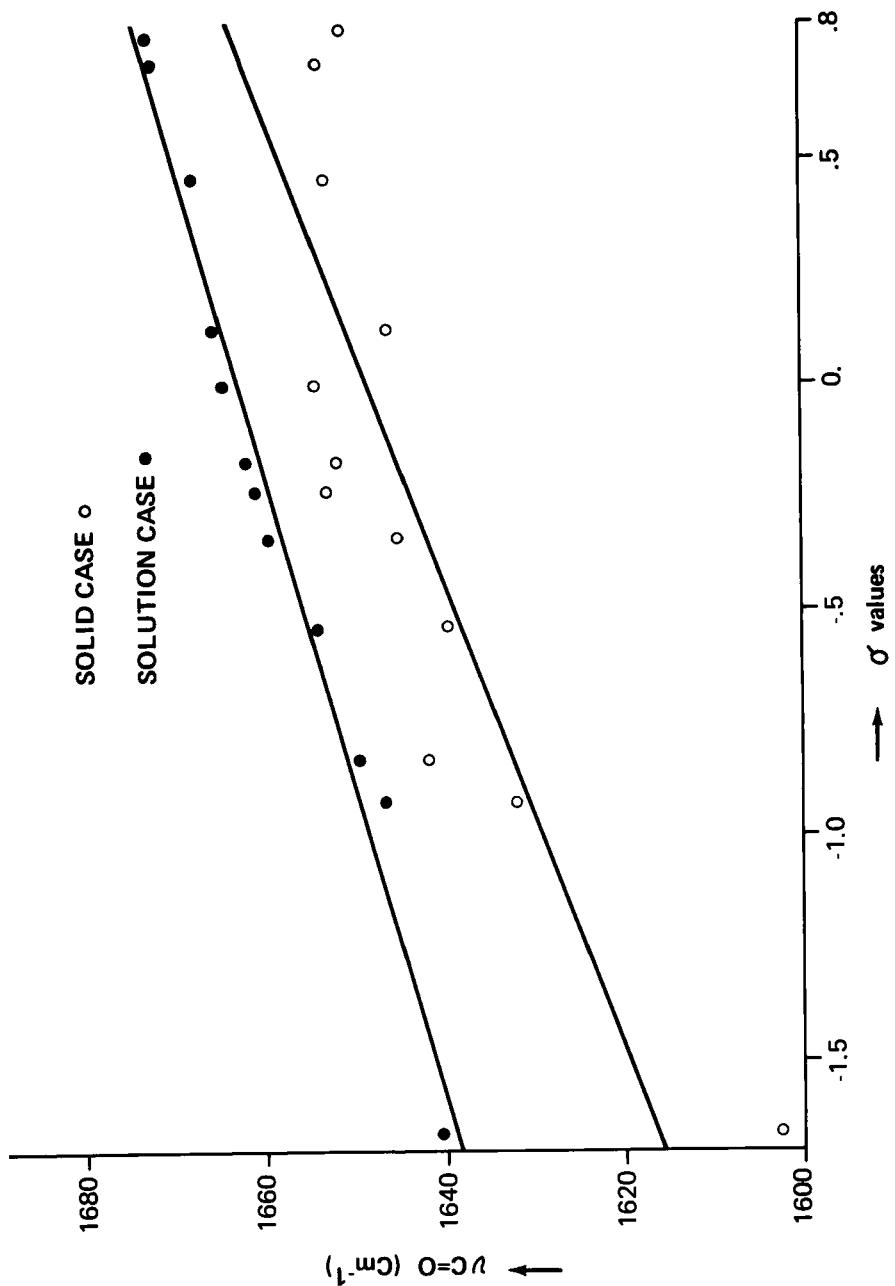


Fig. 1 Relation between σ and the absorption frequency ($\nu_{C=O}$) for substituted benzophenones.

of the substituents to the C=O band intensity is further supported by the observed high intensity value for the meta-nitro derivative. The high intensity for the para-nitro compound (which has a negative mesomeric effect), indicates that there is an appreciable inductive contribution of the para-nitro group to the C=O band intensity.

Comparision of 4-methylbenzophenone with 3,4-dimethyl- and 4,4'-dimethyl-compounds shows that an introduction of a second methyl group at the 3- or 4-position causes a lowering of both frequency and intensity of the C=O absorption, apparently due to the influence of the + I effect of the methyl group. The relatively low intensity of the 3,4-dimethyl- derivative is, however, due to the stronger + I effect of the methyl group at the meta position. The lower intensities in 2,5-dimethyl- and 2,4-dimethyl - compounds might be similarly explained. It is worthwhile to note a less obvious, but very important, point. 2,5-dimethyl- and 2,4-dimethyl- compounds show a frequency which is considerably higher than that of other isomers. It may be assumed that the steric influence of the ortho-methyl group hinders the coplanarity¹³⁻¹⁴ of these conjugated systems, which leads to a decreased conjugation. Consequently, in 2,5-dimethyl- and 2,6-dimethyl-derivatives the frequency is increased and the intensity is lowered. Roos³ also finds a lower frequency for the para-methyl- compounds compared with the ortho- and meta- isomers, which supports the present observation.

Figure 2 shows the dispersions of the integrated intensities of some substituted benzophenones in relation to the Hammett substituent constants. Here it is shown that, with the exception of the 4,4' - dichlorobenzophenone, the C=O band intensities approximate a linear relationship, as observed for frequencies with the Hammett σ values. The slope of this line is 0.64 ± 0.2 with a least square correlation of 0.80. In a qualitative fashion the results clearly establish that for benzophenones the C=O stretching band intensity associated with the meta and para ring substituents is determined by the over-all electronegativity

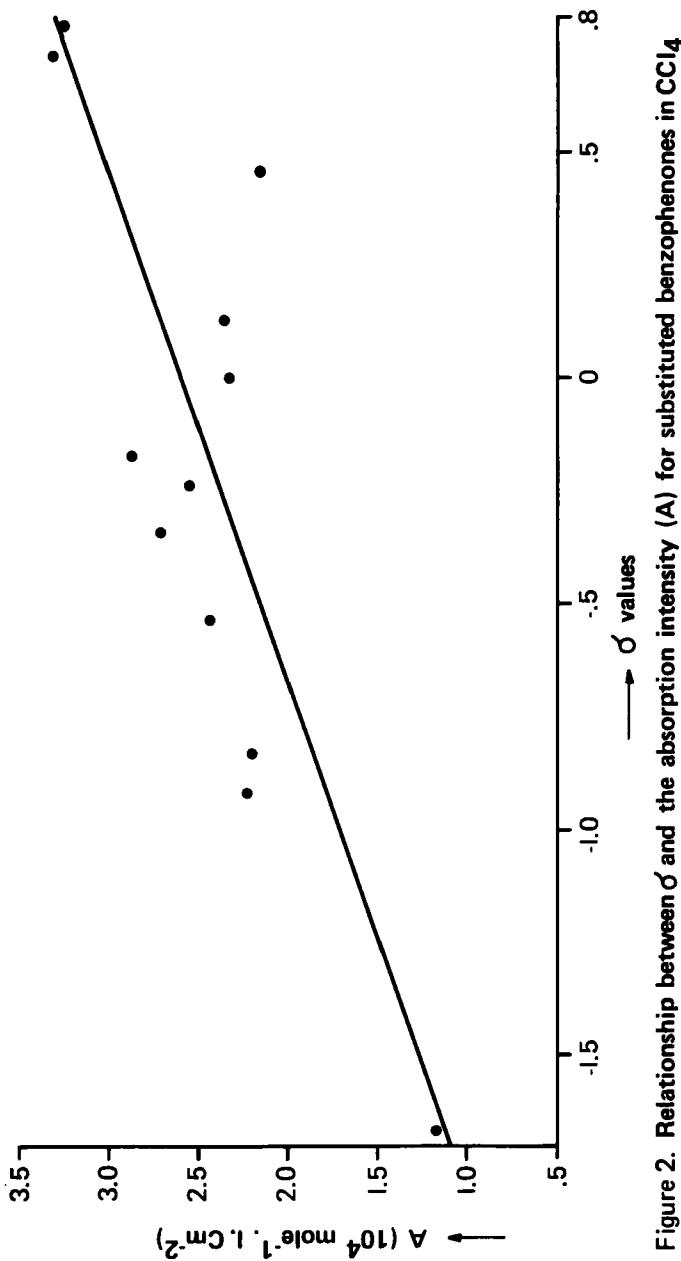


Figure 2. Relationship between σ and the absorption intensity (A) for substituted benzophenones in CCl_4 .

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(M + I effect) of the substituents that control the absorption frequency. This is one example of how integrated intensities may be used to characterize certain functional groups in substituted benzophenones.

CONCLUSION

For the compounds studies, it appears that the stretching frequencies and intensities of the C=O band of benzophenones can be correlated to the substituent effects. The correlations are qualitatively valid. However, they are only approximately quantitatively linear.

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