Substituent Effects in Infrared Spectroscopy. Part 5.[1] Carbonyl Stretching Frequency in *meta*- and *para*-Substituted Aromatic Carbonyl Compounds

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Substituent effects for carbonyl stretching frequencies of *m*- and *p*-substituted acetophenones, benzophenones, benzoic acids, and alkyl benzoates are investigated by means of a correlation analysis. The validity of the Hammett, Hammett–Brown, and Exner equations is checked by means of numerous substituents and several limitations of these equations are shown. Coupling between carbonyl groups in dicarbonyl centrosymmetric molecules, dependence of substituent constants on solvent, and dependence of transmission coefficients of substituent effects along the ArCOY series on the Y group are shown.

EXNER,[2-4] BROWNLEE,[5] LAURENCE,[1] and their co-authors have analysed linear relationships between i.r. 'group frequencies' and the Hammett and Taft σ-type substituent constants. They concluded previous studies should be repeated and extended using a broader set of compounds while maintaining the highest attainable precision. This paper reports additional measurements on a wider range of ring-substituted acetophenones, benzophenones, benzoic acids, and alkyl benzoates, and establishes some features of substituent effects on carbonyl stretching frequencies. Thus the dependence of sensitivity to substituent effects on group Y in XArCOY compounds, the coupling between carbonyl vibrators in centrosymmetric dicarbonyl compounds YCOArCOY, and the relationship between effects of *meta* and *para* $-M$ substituents are outlined in equations

TABLE 1

Carbonyl group frequencies (cm^{-1}) of ring-substituted acetophenones, benzophenones, methyl benzoates, and ethyl benzoates [a]

Substituent	ArCOMe *a*	ArCOMe *b*	ArCOPh	$ArCO_2Me$	$ArCO_2Et$
4-NMe_2	1 672.6	1 655.3	1 649.8	1 714.0	1 708.7
4-NH_2	1 677.1	1 657.0	1 654.1	1 716.4	1 712.3
4-NHCOMe	1 686.4	1 673.3			
4-OEt	1 682.7	1 669.7			
4-OMe	1 683.1	1 669.7	1 659.1	1 721.9	1 716.1
4-OH	1 684.7	1 665.4	1 660.4	1 722.4	1 717.9
4-SMe	1 685.5	1 672.5			
4-Ph	1 688.6	1 676.2	1 663.5		
4-Bu^t	1 687.9	1 676.3			
4-Pr^i	1 687.6	1 676.1			
4-Et	1 687.6	1 676.1			
4-Me	1 687.3	1 675.7	1 662.2	1 726.5	1 721.4 [d]
4-F	1 691.5	1 680.1	1 665.8		1 725.7 [d]
4-Cl	1 691.6	1 681.0	1 665.7		
4-Br	1 693.3	1 681.5	1 666.3	1 729.1 [c]	1 724.7 [d]
4-I	1 692.9	1 681.2		1 731.0	
4-CO_2Me				1 730.2 (I.r.) 1 735.3 (Raman)	
4-CO_2H			1 667.1	1 731.5	
4-COMe	1 692.6 (I.r.) 1 699.4 (Raman)				
4-CF_3	1 699.1	1 687.5	1 670.1		
4-CN	1 698.1	1 688.9			1 729.2 [d]
4-NO_2	1 700.6	1 690.3	1 671.9	1 735.0	1 729.9
4-Aza	1 702.4	1 695.0	1 672.7	1 738.3	1 733.1
H	1 691.2	1 679.9	1 664.8	1 728.4	1 722.1
3-NH_2	1 688.3	1 674.7	1 662.3	1 725.1	
3-OH	1 691.0	1 679.3	1 663.5	1 728.4	
3-OMe	1 689.6	1 679.8			
3-Ph	1 691.2	1 680.5			
3-Me	1 689.7	1 678.0		1 726.5	
3-F	1 696.1	1 686.1			
3-Cl	1 695.7	1 685.2		1 733.1	
3-Br	1 695.3	1 684.9		1 732.3	
3-I	1 694.7	1 683.9		1 732.0	
3-CO_2H	1 696.1	1 685.0	1 668.4	1 732.9	
3-CF_3	1 698.0	1 688.5			
3-CN	1 700.4				
3-NO_2	1 701.2	1 691.4		1 736.3	
3-Aza	1 695.8	1 688.4	1 667.1	1 733.3	1 728.1

[a] CCl_4 as solvent. [b] Propan-2-ol as solvent. [c] The dissymmetry of this band is attributed to Fermi resonance by solvent effects. The frequency is corrected according to ref. 13. [d] Slightly dissymmetric band.

(1)—(4). Equations (1) and (2) are the well known Hammett and Hammett–Brown equations.[6] Equations (3) and (4) are direct correlations between experimental quantities. The former, advanced by Exner [6] for comparison of *meta* and *para* $-M$ substituent effects, has never been used for carbonyl vibrators. The latter permits a more precise transmission coefficient of substituent effects (π) to be obtained than the usual coefficient ρ.

$$\nu = \nu^{\circ} + \rho\sigma_{m,p} \qquad (1)$$

$$\nu = \nu^{\circ} + \rho^{+}\sigma_{p}^{+} \qquad (2)$$

$$(\nu - \nu^{\circ})_{p} = \lambda(\nu - \nu^{\circ})_{m} \qquad (3)$$

$$\nu_{\mathrm{XArCOY}} = \pi_{\mathrm{Y}}\nu_{\mathrm{XArCOMe}} + c \qquad (4)$$

TABLE 2

Carbonyl group frequencies (cm^{-1}) of ring-substituted benzoic acids (monomers and dimers, CCl_4 as solvent)

Substituent	$ArCO_2H$	$(ArCO_2H)_2$
4-NMe_2	1 726.2	1 679.8
4-NH_2	1 730.2	1 685.2
4-$NHCO_2Et$	1 736.4	1 690.9
4-NHCOMe	1 738.8 [a]	1 693.8
4-N=NPh	1 741.1	1 695.8
4-NCS	1 743.3	1 696.9
4-OEt	1 735.3	1 688.7
4-OMe	1 735.9	1 689.9
4-OH	1 736.0	1 691.6
4-OCOMe	1 741.1	1 695.3
4-OCOPh	*b*	1 696.7
4-OSO_2Ph	1 744.5	1 698.7
4-SMe	1 738.7	1 692.3
4-Ph	1 740.0	1 693.3
4-Bu^t	1 738.4	1 693.1
4-Pr^i	1 739.6	1 694.0
4-Me	1 738.9	1 695.7
4-CH_2Ph	1 739.2	1 694.1
4-CH_2Br	1 742.1	1 697.9
4-CH_2Cl	1 742.7	1 698.3
4-F	1 743.4 [a]	1 698.3
4-Cl	1 744.1	1 697.1
4-Br	1 744.7 [a]	*c*
4-I	1 743.9	*c*
4-COPh	1 745.1	1 699.9
4-CO_2Me	1 745.2	1 700.1
4-CO_2H	1 741.2	
4-COMe	1 745.5	*b*
4-COH	1 747.2	1 700.5
4-CF_3	1 749.1	1 703.8
4-CN	1 750.8 [a]	1 704.9
4-NO_2	1 751.1	1 706.1
4-SO_2F	1 752.6	1 707.5
3-NMe_2	1 738.8	1 692.3
3-NH_2	1 739.8	1 695.6
3-$NHCOCH_2Cl$	1 743.1	*b*
3-N=NPh	1 744.0	1 698.9
3-N_3	1 745.0	1 699.9
3-NCS	1 746.8	1 701.6
3-OH	1 742.2	1 699.3
3-OMe	1 740.7	1 696.5
3-OEt	1 741.1	1 695.8
3-OCOMe	1 744.1	1 699.0
3-OCOPh	*b*	1 699.9
3-OSO_2Ph	1 746.6	1 700.9
3-Ph	1 742.2	1 695.1
3-Me	1 740.5	1 696.0
3-CH_2Ph	1 740.9	1 694.9
3-CH_2Cl	1 743.3	1 698.0
3-CH_2Br	1 743.4	1 698.4
3-F	1 746.2	1 701.2
3-Cl	1 746.8	1 702.5 [a]
3-Br	1 745.8	1 700.2
3-I	1 745.6	1 699.5
3-CO_2Me	1 746.3	1 700.3
3-COPh	1 744.9	1 699.9
3-COMe	1 745.5	*b*
3-COH	1 746.7	1 702.1
3-CF_3	1 749.1	1 703.4
3-CN	1 750.1 [a]	1 705.7
3-NO_2	1 751.2	1 707.9
3-SO_2F	1 752.9	1 707
H	1 742.5	1 695.9

[a] Slightly dissymmetric band. [b] Overlapping of two carbonyl bands. [c] Doublet of unknown origin.

RESULTS

Carbonyl stretching frequencies (CCl_4 as solvent) are given in Tables 1 and 2. Both the numbers and kinds of substituent data within each series offer substantial assurance of a critical analysis by equations (1)—(4) at variance with previous investigations.[7-12] In the Discussion we shall also use our previously published data on benzaldehydes [13] and data from Spaargaren and his co-workers [14] on *NN*-dimethylbenzamides. For methyl benzoates our results are at variance with those of Deady and his co-workers [15] but in good agreement with those of Klopman and Noack.[16]

TABLE 3

Fit of ν(CO) to the Hammett equation (1)

Series	Equation (1,*m*,*p*)	*n* [a]	*r* [b]	ψ [c]	s_ρ [d]
$ArCONMe_2$	$\nu = 1\,644.7 + 8.9\,\sigma_{m,p}$	15	0.976	0.23	0.6
ArCOPh	$\nu = 1\,663.1 + 13.1\,\sigma_{m,p}$	16	0.973	0.24	0.8
$ArCO_2Et$	$\nu = 1\,721.4 + 13.0\,\sigma_{p}$	10	0.964	0.28	1.3
$ArCO_2Me$	$\nu = 1\,726.9 + 13.9\,\sigma_{m,p}$	17	0.978	0.21	0.8
$ArCO_2H$	$\nu = 1\,740.4 + 14.6\,\sigma_{m,p}$	60	0.967	0.26	0.5
$(ArCO_2H)_2$	$\nu = 1\,695.1 + 14.9\,\sigma_{m,p}$	57	0.948	0.32	0.7
ArCOMe	$\nu = 1\,689.1 + 17.1\,\sigma_{m,p}$	33	0.972	0.24	0.7
ArCOH	$\nu = 1\,704.9 + 16.0\,\sigma_{m,p}$	20	0.948	0.33	1.3

[a] Number of *meta*- and *para*-substituents. [b] Correlation coefficient. [c] Exner criterion.[6] [d] Standard deviation of the slope ρ.

TABLE 4

Fit of ν(CO) to the Hammett–Brown equation (2)

Series	Equation (2,*p*)	*n* [a]	*r* [b]	ψ [c]	$s_{\rho\pm}$ [d]
$ArCONMe_2$	$\nu = 1\,646.0 + 6.6\,\sigma_p^{+}$	8	0.960	0.30	0.8
ArCOPh	$\nu = 1\,665.1 + 8.1\,\sigma_p^{+}$	13	0.984	0.19	0.4
	$\nu = 1\,665.0 + 8.5\,\sigma_p^{+}$ [e]	12	0.994	0.12	0.3
$ArCO_2Et$	$\nu = 1\,723.7 + 8.4\,\sigma_p^{+}$	10	0.983	0.20	0.5
	$\nu = 1\,723.6 + 8.7\,\sigma_p^{+}$ [e]	9	0.987	0.17	0.5
$ArCO_2Me$	$\nu = 1\,728.7 + 8.5\,\sigma_p^{+}$	9	0.992	0.13	0.4
	$\nu = 1\,728.6 + 8.7\,\sigma_p^{+}$	8	0.995	0.10	0.3
$ArCO_2H$	$\nu = 1\,742.8 + 9.3\,\sigma_p^{+}$	21	0.980	0.21	0.4
	$\nu = 1\,742.7 + 9.6\,\sigma_p^{+}$ [e]	19	0.983	0.19	0.4
$(ArCO_2H)_2$	$\nu = 1\,697.5 + 9.5\,\sigma_p^{+}$	18	0.971	0.25	0.6
	$\nu = 1\,697.2 + 9.9\,\sigma_p^{+}$ [e]	16	0.981	0.20	0.5
ArCOMe	$\nu = 1\,691.5 + 10.7\,\sigma_p^{+}$	19	0.989	0.15	0.4
	$\nu = 1\,691.3 + 11.1\,\sigma_p^{+}$	17	0.996	0.09	0.3
ArCOH	$\nu = 1\,708.0 + 11.0\,\sigma_p^{+}$	12	0.978	0.22	0.7
	$\nu = 1\,707.8 + 11.6\,\sigma_p^{+}$	11	0.986	0.17	0.6

[a] Number of *para*-substituents. [b] Correlation coefficient. Exner criterion.[6] [d] Standard deviation of the slope ρ^+. [e] Substituents *p*-OH and *p*-NHCOMe excluded.

Fits of ν(CO) by a least-square treatment to equations (1), (2), and (4) are given in Tables 3—5. The Exner equation (3) needs a special statistical treatment as mentioned by the author.[17]

DISCUSSION

Hammett Equation (1).—Results in Table 3 show that the correlations between ν(CO) and σ are satisfactory according to the correlation coefficient ($r \geqslant 0.95$). The variation in frequency through the investigated series may be largely attributed to electronic effects. These effects are not transmitted equally in each series as shown by the ρ values varying significantly from 8.9 to 17.1 cm^{-1}. Previously reported [7,8,18] equal ρ values are in error.

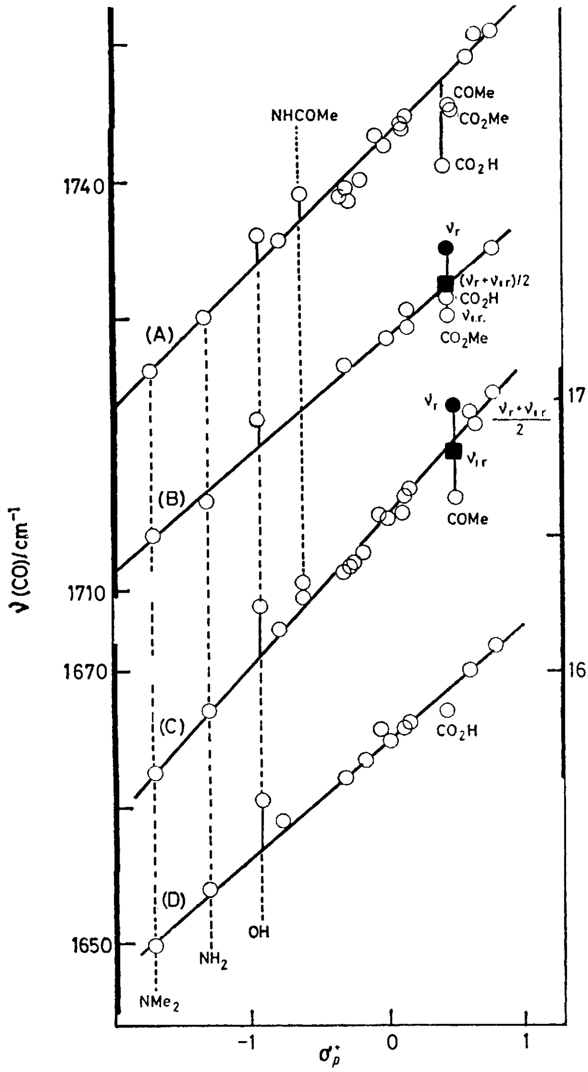

FIGURE 1 Correlation of ν(CO) with σ_p^+ for benzoic acids (A), methyl benzoates (B), acetophenones (C), and benzophenones (D). Substituents *p*-OH and *p*-NHCOMe deviate upwards and *p*-COX downwards. The mean (■) of i.r. (○) and Raman (●) frequencies places *p*-COMe (B) and *p*-CO$_2$Me (C) on the regression line

However the Exner criterion [6] ψ remains greater than 0.2 and sometimes 0.3. Such a lack of precision makes the analysis of deviations difficult. Nevertheless, analysis of the residuals shows (i) no '*meta* effect' as observed by Exner for ν(CN) or ν(NO$_2$) vibrators of benzonitriles [4] or nitrobenzenes [3] and (ii) deviation of $+M$ substituents in the *para*-position in such a direction that a more negative σ_p constant should be required (except with *NN*-dimethylbenzamides, see later).

Hammett-Brown Equation (2).—Our recent conclusion [19] that *m*- and *p*-substituted acetophenones must be treated separately for carbonyl frequency correlations with σ^+ is supported by benzoic acids (monomer and dimer) and methyl benzoates. Indeed we find a significant difference between the coefficients ρ_p^+ and ρ_m^+ at a confidence level greater than 99% (from a student *t* test). Since σ_m^+ differs slightly from σ_m, equation (2, *meta*) is of no interest and only equation (2, *para*) will be investigated. Table 4 shows a significant improvement, the ψ criterion becoming less than 0.2 in each series. Two kinds of deviation clearly appear in Figure 1: a positive one for *p*-OH and *p*-NHCOMe in each series and a negative one for *p*-COMe in the acetophenone series, *p*-CO$_2$Me in the methyl benzoate series, and *p*-CO$_2$H in the benzoic acid series.

Deviations of *p*-OH and *p*-NHCOMe are probably due to solvent effects since σ^+ constants were mostly determined in 90% acetone–water and applied to measurements made in CCl$_4$. Eliminating these two substituents significantly improves each correlation (see Table 4). By plotting carbonyl frequencies measured in propan-2-ol * *versus* those measured in CCl$_4$ (Figure 2), we were able to find which substituents behave quite differently in an apolar solvent and a hydroxylic one. The electronic effects of substituents *p*-OH, *p*-NH$_2$, *m*-aza, and *p*-aza undoubtedly differ in the two solvents. Deviations of *p*-NHCOMe, *m*-NH$_2$, and *p*-NMe$_2$ are less evident. Surprisingly *p*-NH$_2$ and *p*-NMe$_2$ showed no deviation at all in Figure 1. Probably this only means that it is unrealistic to transfer results obtained in

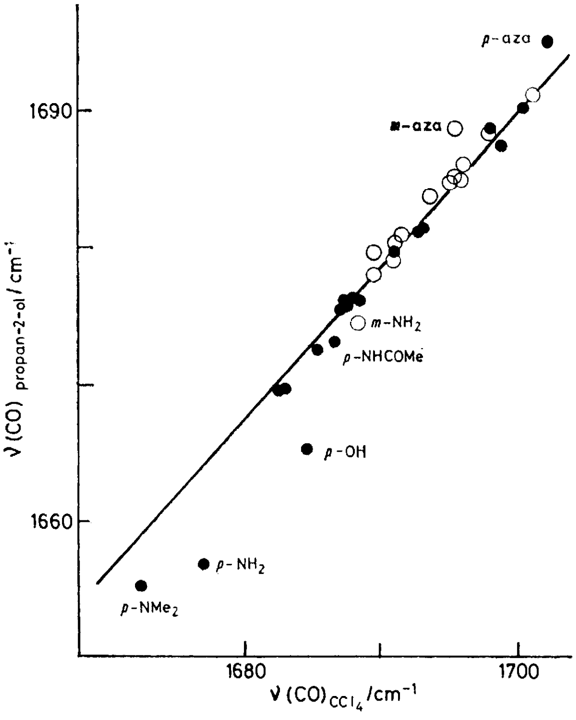

FIGURE 2 Plot of carbonyl frequencies measured in propan-2-ol against carbonyl frequencies measured in CCl$_4$ for *meta* (○) and *para*- (●) substituted acetophenones

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* Acetone–water is not transparent and could not be used.

propan-2-ol to acetone–water and/or that σ^+ values determined by Brown for some strong resonance donor substituents are not quite reliable.[20] Whatever the explanation, when studying the intertwined relationships between structure and solvation, the use of σ constants should be restricted, and replaced by direct correlations between experimental quantities.

Deviations observed in the centrosymetric molecules YCOArCOY are attributed to a coupling effect between the two carbonyl groups. Indeed i.r. and Raman frequencies do not coincide: by i.r. spectroscopy we observe the antisymmetric vibration ν_{as} and by Raman spectroscopy the symmetric one ν_s. The arithmetic mean $(\nu_s + \nu_{as})/2$ ought to express approximately the force constant of the carbonyl bond and using this value the substituents *p*-CO_2H in the benzoic acid series, *p*-CO_2Me in the methyl benzoate series, and *p*-COMe in the acetophenone series fall on the line. We do observe this in Figure 1. Finally a very low difference $\nu_{as} - \nu_s$ (*ca.* 6 cm^{-1}) is expected compared with other dicarbonyl compounds such as acid anhydrides (*ca.* 65 cm^{-1}) or acyl peroxides (*ca.* 25 cm^{-1}) since the extent to which the frequency coupling effect between two carbonyl groups occurs depends particularly upon their proximity. This very small coupling could not have been suspected without the help of the Hammett–Brown equation and this gives support to such an empirical analysis of ' group frequencies '.

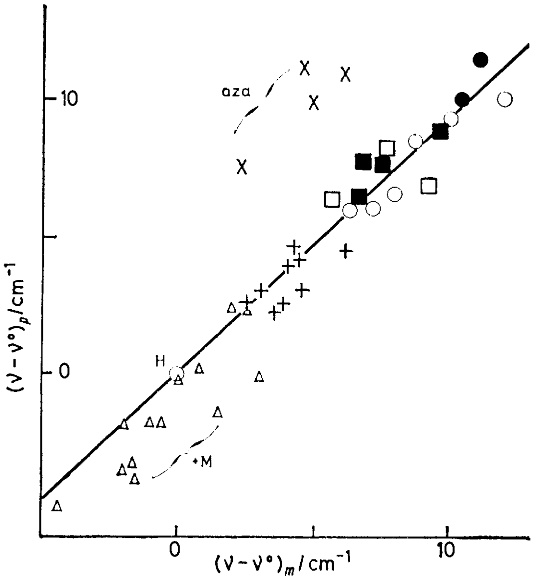

FIGURE 3 Mutual dependence of carbonyl frequency shifts $(\nu - \nu°)$ of *meta*- and *para*-substituted carbonyl compounds with $-M$ substituents (● SO_2F, ○ NO_2, □ CN, ■ CF_3, + COX, × aza) and with weakly $+M$ substituents (△ Me, CH_2Cl, CH_2Ph, and N=NAr)

Exner Equation (3).—Equation (3) does not contain any constant specific for a certain series and therefore can be tested in a single graph for all series ArCOY each one of which involves only a small number of $-M$ substituents. In Figure 3 $(\nu - \nu°)$ for *meta*- and *para*-derivatives are plotted against each other. Equation (3) shows a good linear dependence for the $-M$ substituents NO_2, CN, CF_3, SO_2F, and COX. Excluded are

$$(\nu - \nu°)_p = (0.95 \pm 0.03)(\nu - \nu°)_m$$
$$r\ 0.991 \qquad s\ 0.9\ cm^{-1} \qquad n\ 25$$

(i) the endocyclic $-M$ aza substituent and (ii) Me, CH_2X, and N=NAr which have a weak $+M$ effect due to the strong electron-attracting power of the carbonyl groups. In connection with the transmission of substituent effects across the benzene nucleus, attention has been paid to the values of λ and particularly to its dependence on the solvent.[21] In the apolar solvent CCl_4, our value, λ 0.95 ± 0.03, varies from that, 1.15 ± 0.02, found by Exner [2] from $\nu(OH)$ measurements of benzoic acids. Anomalous values of λ in pure aprotic solvents have previously been noted [21] and complementary verification of the Exner equation in apolar solvents (especially by spectroscopic measurements) is needed.

Dependence of Transmission Coefficient on Group Y.—Large standard deviations of ρ in equation (1) and the splitting of the Hammett–Brown plot [equation (2)] into two separate lines for *meta*- and *para*-substituents led us to choose the acetophenone series as standard and to compare other series to it by means of equation (4). Results of the corresponding regressions are summarized in Table 5. π is nothing less than the ratio $\rho_{ArCOY} : \rho_{ArCOMe}$ but this ratio is determined with high precision (see standard deviations of π in Table 5) both from *meta*- and *para*-substituents and without involving empirical σ constants. The sensitivity to substituent effects strongly decreases from benzaldehydes to *NN*-dimethylbenzamides in the sense of the $+M$ electron-donating power of group Y: H = Me > OH > OMe ≃ OEt > NMe_2. This may be explained by competition between the $+M$ effects of groups Y and phenyl, each providing an alternative source of electrons for absorption by the doubly-bonded oxygen atom. This deconjugation of the phenyl with the carbonyl group was also observed from Raman intensity measurements.[22] The deconjugation is so strong in *NN*-dimethylbenzamides that σ_p^+ constants are no longer necessary for $+M$ substituents. The low π value found for non-planar benzophenones is best explained by stereochemical effects.

TABLE 5

Fit of $\nu(CO)$ to equation (4)

Series	π [a]	n [b]	r [c]	s_π [d]
ArCOH	1.02	19	0.973	0.06
ArCOMe	1.00			
$ArCO_2H$	0.89	31	0.994	0.02
$ArCO_2Me$	0.83	19	0.992	0.02
$ArCO_2Et$	0.82	12	0.991	0.03
ArCOPh	0.75	17	0.994	0.02
$ArCONMe_2$	0.58	15	0.959	0.05

[a] Transmission coefficient relative to the standard acetophenone series (π = 1). [b] Number of *meta*- and *para*-substituents. [c] Correlation coefficient. [d] Standard deviation of the coefficient π.

EXPERIMENTAL

Chemicals.—We are grateful to Professor O. Exner, Prague, for a gift of 30 substituted benzoic acids, and we also thank Professor J. P. Doucet, Paris, for a gift of *p*-trifluoromethylbenzophenone.

Procedure.—This has been already described.[19] Raman spectra were recorded for CCl_4 solution (1M) with a Coderg T 800 spectrophotometer equipped with an Ar^+ laser source.

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