Fermi Resonance in Substituted *Z*-3-Methylene Phthalides

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Summary. The absorption bands of the C=O Stretching vibrations of a series of thirty-nine substituted *Z*-3-methylene phthalides (**1a–s**, **2a–h**, **3a–f**, **4a–c**, and **5a–c**) were measured in $CHCl_3$ and CCl_4. The two-level *Fermi* resonance effect on the infrared spectra of the above compounds was investigated after deconvolution and band separation. The wave numbers of the unperturbed fundamental C=O stretching vibrations exhibit excellent linear correlations with *Hammet*'s constants of substituents and ^{13}C NMR chemical shifts of the C=O group.

Keywords. *Z*-3-Methylene phthalides; Infrared spectra; *Fermi* resonance; Correlation analysis of unperturbed ν(C=O) values.
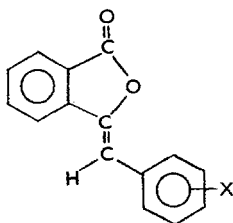
Fermi-**Resonanz in substituierten *Z*-3-Methylenphthaliden**

Zusammenfassung. Die Absorptionsbanden der C=O-Streckschwingung von 39 substituierten *Z*-3-Methylenphthaliden (**1a–s**, **2a–h**, **3a–f**, **4a–c** und **5a–c**) wurden in $CHCl_3$ und CCl_4 vermessen. Durch Dekonvolution und Bandentrennung konnte der Einfluß *Fermi*-Resonanz auf die Infrarotspektren der obengenannten Verbindungen untersucht werden. Die Wellenzahlen der ungestörten C=O-Streckschwingungen ergeben ausgezeichnete lineare Korrelationen mit den *Hammet*schen Substituentenkonstanten und den ^{13}C-NMR-Verschiebungen der Carbonylgruppe.

Introduction

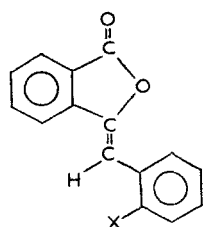Several α, β-unsaturated and aromatic six- and five-membered lactones exhibit a significant splitting of their absorption bands in the region of the carbonyl stretching vibrations [1–5]. Such a splitting is assumed to result from a *Fermi* resonance of the fundamental C=O stretching vibration with the first overtone of an out-of-plane C-H deformation vibration of the unsaturated or aromatic part of molecule [1, 3, 4]. The infrared spectra of several substituted *Z*-3-methylene phthalides have been investigated previously [6–9]; however, neither a convincing experimental evidence nor a detailed theoretical study of the *Fermi* resonance effect has been reported for these substances so far.

The aim of the present work was to record the infrared spectra of a series of substituted Z-3-methylene phthalides (**1a–s, 2a–h, 3a–h, 4a–c, 5a–c**) in $CHCl_3$ and CCl_4 in the region of 1850–1700 cm^{-1} under precise quantitative conditions and to investigate in detail the splitting of the absorption bands by *Fermi* resonance.

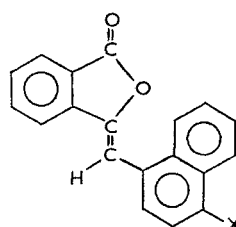|	X			X
1a	4-NH$_2$		**1k**	4-Br
1b	4-OCH$_3$		**1l**	3-F
1c	4-CH$_3$		**1m**	3-Cl
1d	3-CH$_3$		**1n**	3-CF$_3$
1e	H		**1o**	2,4-Cl$_2$
1f	4-F		**1p**	4-NO$_2$
1g	3-OCH$_3$		**1q**	4-NHCOCH$_3$
1h	2,4-F$_2$		**1r**	3-NO$_2$
1i	4-I		**1s**	3,5-F$_2$
1j	4-Cl			

	X			X
2a	OH		**3a**	NH$_2$
2b	OCH$_3$		**3b**	H
2c	CH$_3$		**3c**	I
2d	F		**3d**	Cl
2e	I		**3e**	Br
2f	Cl		**3f**	NO$_2$
2g	Br			
2h	NO$_2$			

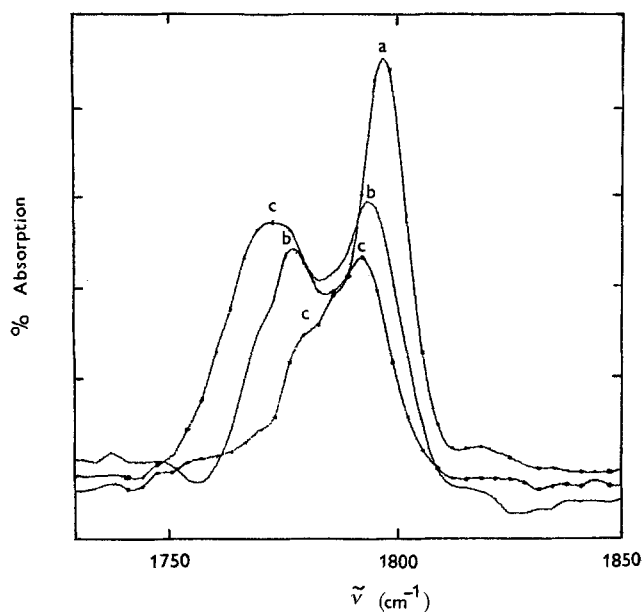|	X			X
4a	H		**5a**	H
4b	NH$_2$		**5b**	CH$_3$
4c	NO$_2$		**5c**	CH$_2$CH$_3$

Fig. 1. Infrared spectra of *Z*-3-phenylmethylene phthalide (1e) in mixtures of *n*-hexane and $CHCl_3$; a: 3:0, *b*: 2:1, *c*: 1:2

Results and Discussion

The infrared spectra of *Z*-3-phenylmethylene phthalide (1e) in mixtures of *n*-hexane and trichloromethane are shown in Fig. 1. In pure *n*-hexane, a strong absorption band at 1796.8 cm^{-1} belonging to the fundamental C=O stretching vibration occurs; only a weak shoulder at its lower wave number side indicates a little splitting. With increasing amount of the more polar trichloromethane in the mixture, the splitting of the absorption band becomes more pronounced. Finally, in pure trichloromethane a clear doublet absorption band with peaks at 1792.0 and 1774.8 cm^{-1} is observed. The above described behavior of compound 1e in *n*-C_6H_{14}/$CHCl_3$ mixtures conspicuously resembles that of cyclopentanone, a fact which can be regarded as a strong experimental evidence of the presence of *Fermi* resonance interaction [10].

The infrared spectra of other substituted *Z*-3-methylene phthalides behave similarly. In tetrachloromethane, all compounds exhibit more or less unstructured v(C=O) absorption bands. In trichloromethane, significant splitting caused by *Fermi* resonance interactions occur (with the exception of compounds 5a–c; (Table 1). Obviously, in this solvent the wave numbers of the fundamental C=O stretching vibration (v_{01}(C=O)) are close to the wave numbers of the first overtone of an out-of-plane C-H deformation vibration (ω_{02}(CH) $\approx 2\omega_{01}$(CH)), resulting in an intermolecular vibrational effect (*Fermi* resonance). The absence the v(C=O) band splitting and the *Fermi* resonance effect in phthalide itself [1] and in *Z*-3-alkylidene phthalides (5a–c) suggests that the first overtone of the ω_{01}(CH) vibration of the substituted phenyl ring is probably involved in the vibrational interaction.

It has been shown that *Fermi* resonance can influence the effects of substituents on the wave numbers of carbonyl stretching vibrations in several series of aromatic compounds [11, 12]. This implies that, if a correlation between spectroscopic and

Table 1. IR spectroscopic data (cm^{-1}) of compounds **1–5** prior to band separation

| | Unresolved data $(\mathrm{CHCl_3})$ | | $\omega_{01}(CH)(\mathrm{CHCl_3})$ | $\nu_{01}(\mathrm{C=O})(\mathrm{CCl_4})$ |
	Peak A	Peak B		
1a	1783.5	1764.8	862.0	1790.8
1b	1788.6	1768.0	870.0	1792.8
1c	1787.6	1762.6	860.8	1794.4
1d	1786.2	1768.0	869.2	1795.2
1e	1792.0	1774.8	870.4	1796.8
1f	1788.8	1769.6	868.0	1796.4
1g	1788.8	1771.6	868.4	1796.0
1h	1790.4	1771.0	870.4	1798.0
1i	1787.2	1774.0	869.5	1798.8
1j	1790.0	1778.8	876.8	1796.8
1k	1790.4	1778.5	860.8	1795.2
1l	1788.8	1776.0	865.0	1798.8
1m	1790.0	1775.3	887.6	1800.4
1n	1791.0	1774.2	867.2	1801.6
1o	1790.8	1775.0	870.4	1799.2
1p	1793.6	1779.2	864.8	1802.4
1q	1788.8	1770.8	870.2	1792.8
1r	1803.4	1792.8	872.3	1803.2
1s	1798.4	1782.4	876.8	1802.4
2a	1782.4	1764.4	869.2	1784.8
2b	1788.2	1768.8	870.4	1794.4
2c	1787.2	1770.4	873.1	1794.8
2d	1790.0	1772.3	872.4	1796.8
2e	1785.6	1775.0	870.4	1800.4
2f	1782.4	1769.2	870.4	1798.8
2g	1786.8	1776.2	872.4	1800.4
2h	1792.0	1784.0	871.6	1802.8
3a	1776.4	1763.2	873.6	1786.8
3b	1787.2	1776.0	872.9	1795.2
3c	1784.4	1766.4	870.4	1793.6
3d	1786.0	1766.4	873.6	1795.2
3e	1784.8	1766.4	862.0	1795.2
3f	1789.6	1770.0	865.0	1795.2
4a	1786.0	1768.0	867.2	1794.8
4b	1782.4	1764.8	871.0	1791.6
4c	1792.0	1772.0	873.0	1799.6
5a	1774.5	–	–	1788.8
5b	1775.9	–	–	1790.0
5c	1783.6	–	–	1796.4

Table 2. *Fermi* doublet components (cm^{-1}) for compounds **1–4** in $CHCl_3$

	Perturbed data[a]		Unperturbed data[b]		
	Peak A	Peak B	$\nu_{01}(C = O)$	$\omega_{02}(CH)$	W_{AB}
1a	1787.2 (1.56)	1764.6 (5.77)	1769.4	1782.4	9.2
1b	1785.0 (1.99)	1767.9 (4.94)	1773.9	1782.9	9.2
1c	1788.1 (2.46)	1768.2 (4.23)	1775.5	1780.8	9.6
1d	1789.6 (2.46)	1770.2 (4.01)	1777.6	1782.2	9.4
1e	1793.1 (1.61)	1771.8 (5.23)	1776.8	1788.1	9.0
1f	1789.8 (3.05)	1770.5 (3.83)	1779.1	1781.2	9.6
1g	1791.3 (2.30)	1772.2 (3.87)	1779.3	1784.2	9.2
1h	1791.3 (3.34)	1772.3 (3.00)	1782.3	1781.3	9.5
1i	1792.4 (2.47)	1773.9 (3.98)	1781.0	1785.3	9.0
1j	1785.0 (2.52)	1777.6 (4.36)	1780.3	1782.3	3.6
1k	1791.9 (2.66)	1774.1 (3.87)	1781.3	1784.6	8.7
1l	1791.1 (3.14)	1773.1 (3.41)	1782.1	1782.9	9.4
1m	1789.6 (2.83)	1777.2 (3.83)	1782.5	1784.3	6.1
1n	1794.8 (2.66)	1776.7 (3.90)	1784.0	1787.5	8.9
1o	1792.4 (3.50)	1775.1 (3.02)	1784.4	1783.1	8.6
1p	1796.1 (3.33)	1778.9 (2.44)	1788.8	1786.2	8.5
1r	1798.0 (3.63)	1781.8 (2.14)	1788.5	1785.6	8.3
1s	1797.7 (1.42)	1784.4 (4.98)	1787.3	1794.7	5.5
2a	1800.8 (3.91)	1781.4 (1.96)	1794.3	1787.9	9.1
2b	1790.1 (1.96)	1769.1 (5.01)	1775.0	1784.2	9.4
2c	1784.0 (2.94)	1771.0 (3.14)	1777.3	1777.7	6.5
2d	1790.7 (3.48)	1771.9 (3.72)	1781.0	1781.6	9.4
2e	1790.3 (3.60)	1772.8 (2.89)	1782.5	1780.6	8.7
2f	1787.5 (4.41)	1769.2 (1.80)	1782.2	1774.5	8.3
2g	1789.7 (3.82)	1773.1 (3.24)	1782.1	1780.7	8.3
2h	1792.0 (3.08)	1780.8 (2.85)	1786.5	1786.3	5.6
3a	1777.1 (3.75)	1764.1 (4.15)	1770.3	1770.9	6.5
3b	1785.4 (2.51)	1774.6 (4.61)	1778.4	1781.6	5.2
3c	1785.1 (4.99)	1765.8 (1.78)	1780.0	1770.9	8.5
3d	1786.5 (4.68)	1765.9 (1.97)	1780.4	1772.0	9.4
3e	1785.4 (5.15)	1765.7 (1.85)	1780.2	1770.9	8.4
3f	1790.7 (2.57)	1769.7 (0.48)	1787.4	1773.4	7.6
4a	1787.0 (3.62)	1767.1 (3.45)	1777.3	1776.8	9.5

[a] after band separation (integrated intensities $(1 \cdot mol^{-1} \cdot cm^{-2})$ in parentheses); [b] corrected for *Fermi* resonance

structural properties is to be assessed, wave numbers free from *Fermi* resonance effects have to be obtained; only those will depend solely on the C=O bond force constants [13]. For this reason, we applied relations based on the method of *Langseth* and *Lord* as improved by *Nyquist et al.* for cases involving two-level interactions [14] and calculated the approximate wave numbers of bands corrected for *Fermi* resonance effects (Table 2). The extent of these effects depends on the

Table 3. Linear correlations for compounds **1–3** $(y = ax + b)$;

	y (solvent)	x (solvent)	n^a	r^b	s^c	F^d	a	b
1[e]	$\nu_{01}(C = O)$ (CHCl$_3$)	σ	18	0.993	0.62	1104	14.00 ± 0.42	1777.7
1	$\nu(C=O)$ (CCl$_4$)	σ	21	0.925	1.33	113	9.36 ± 0.88	1795.6
1	$\nu(C=O)A^g$ (CHCl$_3$)	σ	20	0.738	2.71	22	8.35 ± 1.80	1789.3
1	$\nu_{01}(C=O)$ (CHCl$_3$)	$\delta(C=O)$ (CDCl$_3$)	12	0.983	0.91	296	-13.00 ± 0.75	3947.6
1	$\nu_{01}(C=O)$ (CCl$_4$)	$\delta(C=O)$ (CDCl$_3$)	12	0.948	1.06	88	-8.20 ± 0.87	3164.7
1	$\nu(C=O)A^g$ (CHCl$_3$)	$\delta(C=O)$ (CDCl$_3$)	12	0.697	2.47	9	-6.27 ± 2.04	2835.5
2[f]	$\nu_{01}(C=O)$ (CHCl$_3$)	σ	10	0.931	1.39	52	11.09 ± 1.54	1779.2
2[f]	$\nu(C=O)$ (CCl$_4$)	σ	10	0.916	1.12	41	7.99 ± 1.24	1796.9
2[f]	$\nu(C=O)A^g$ (CHCl$_3$)	σ	10	0.428	2.55	2	3.78 ± 2.83	1789.5
3	$\nu_{01}(C=O)$ (CHCl$_3$)	σ	5	0.996	0.44	373	11.16 ± 0.58	1777.8
3	$\nu(C=O)$ (CCl$_4$)	σ	5	0.945	1.38	25	9.09 ± 1.82	1793.2
3	$\nu(C=O)A^g$ (CHCl$_3$)	σ	5	0.423	5.41	0	0.52 ± 7.14	1773.3

[a] number of compounds used in the correlation; [b] correlation coefficient; [c] standard deviation; [d] F-score; [e] compounds **1h** and **1o** omitted; [f] compounds **1h** and **1o** included; [g] perturbed data, for peak A after band separation

degree of interaction between the wave numbers of bands involved [14, 15]. It has been found that the more intense band in the *Fermi* doublet is associated with the fundamental $\nu_{01}(C=O)$ stretching vibration, whereas the less intense band can probably be assigned to the first overtone $(\omega_{02}(CH))$ of the out-of-plane C–H deformation vibration $(\omega_{01}(CH))$. The vibrational interaction between $\nu_{01}(C=O)$ and $\omega_{02}(CH)$ in compounds **1–4** can be expressed by the *Fermi* resonance coefficient w_{AB} which varies with the structure of investigated compound in the region of 9.6–3.6 cm^{-1}. The components of the *Fermi* doublets of compounds **1q**, **4b**, and **4c** could not been determined because of the low solubility of these substances in trichloromethane.

The ν_{01} (C=O) wave numbers measured in CCl$_4$ (Table 1) and the unperturbed ν_{01} (C=O) wave numbers, *i.e.* those corrected for *Fermi* resonance, in CHCl$_3$ (Table 2) were correlated with Hammett's substituent constants [16] as well as with ^{13}C NMR chemical shifts of the carbonyl group [17]. The statistical results of these
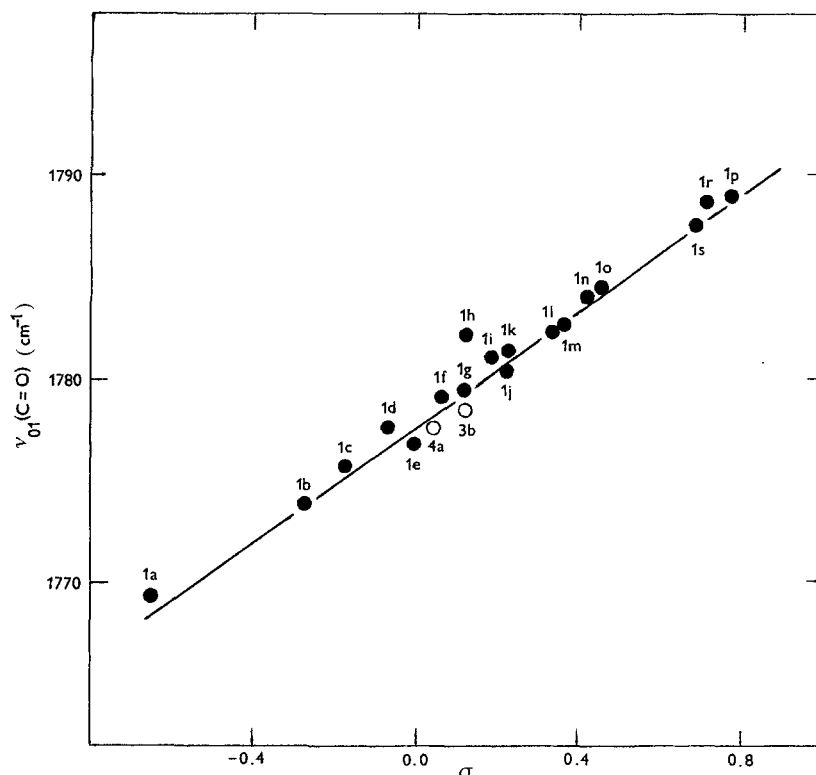
Fig. 2. Dependence of the wave numbers of the unperturbed fundamental C=O stretching vibration ($CHCl_3$) on the *Hammett* σ values for *meta-* and *para-*substituted Z-3-naphthylmethylene phthalides (●) and Z-3-naphthylmethylene phthalides (○)

correlations are listed in Table 3. It is evident that all correlations for unperturbed ν_{01}(C=O) wave numbers in $CHCl_3$ are statistically most significant, especially with respect to values reported previously [6, 9] where the arithmetic means of the wave numbers of the two peaks of the unresolved doublet have been used for analysis.

In the series of *meta-* and *para-*substituted Z-3-phenylmethylene phthalides, an excellent linearity of ν_{01} C=O vs. σ was obtained for twenty-one experimental values (Fig. 2). The correlation includes also a few 2, 4- and 3, 5-disubstituted compounds, the σ values of which were calculated assuming additivity of σ_p and σ_m values. The wave numbers of Z-3-1-naphthylmethylene and Z-3-(2-naphthyl-methylene) phthalides (**3b** and **4a**) also fit the correlation quite well if corresponding σ_α values are used for 1- and 2-naphthyl substituents. In the case of *ortho-*substituted Z-3-phenylmethylene phthalides, σ_p values were used for *ortho-*substituents, and the graph in Fig. 3 is a result of correlating ten experimental values, including two 2, 4-disubstituted derivatives (**1h**, and **1o**). Z-3-(2-Hydro-xyphenyl methylene) phthalide (**2a**) has been excluded from the correlations
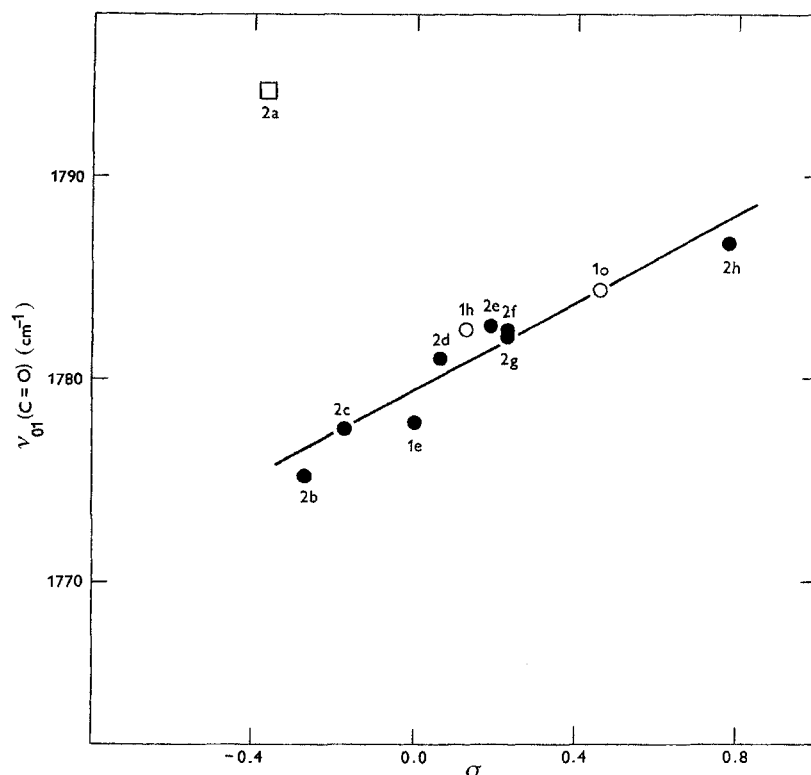
Fig. 3. Dependence of the wave numbers of the unperturbed fundamental C=O stretching vibration ($CHCl_3$) on the *Hammet* σ values for *ortho* ($\bullet$) and *ortho, para* ($\circ$) substituted Z-3-phenylmethylene phthalides; $\square$: omitted from correlation

because of an intermolecular hydrogen bond formed between the hydroxy group and the lactone ring oxygen or the side chain double bond. Fig. 4 shows that the unperturbed $v_{01}(C=O)$ wave numbers correlate also very well with $\delta(C=O)$ available for twelve selected substituted compounds of series **1** [17]. The correlations for the series of 4-substituted 1-naphthylmethylene derivatives (**3a–f**) using σ_p constants are just illustrative and less significant due to the small number of compounds available. It is evident from the results in Table 3 that the wave numbers of the carbonyl stretching vibration are more sensitive to substituent effects in the polar solvent, *i.e.* trichloromethane, than in the less polar tetrachloromethane. The efficiency of the transmission of substituent effects for the series of *para-* and *meta-* substituted compounds (**1**) is by 20% higher than those estimated for *ortho-*substituted (**2**) and 1-naphthyl derivatives (**3**).

Finally, it can be concluded that the splitting of the strong absorption bands of substituted Z-3-methylene phthalides in the region of 1850–1700 cm^{-1} arises from *Fermi* resonance and the wave numbers of unperturbed $v_{01}(C=O)$ vibration correlate excellently with substituent constants and corresponding ^{13}C NMR data.
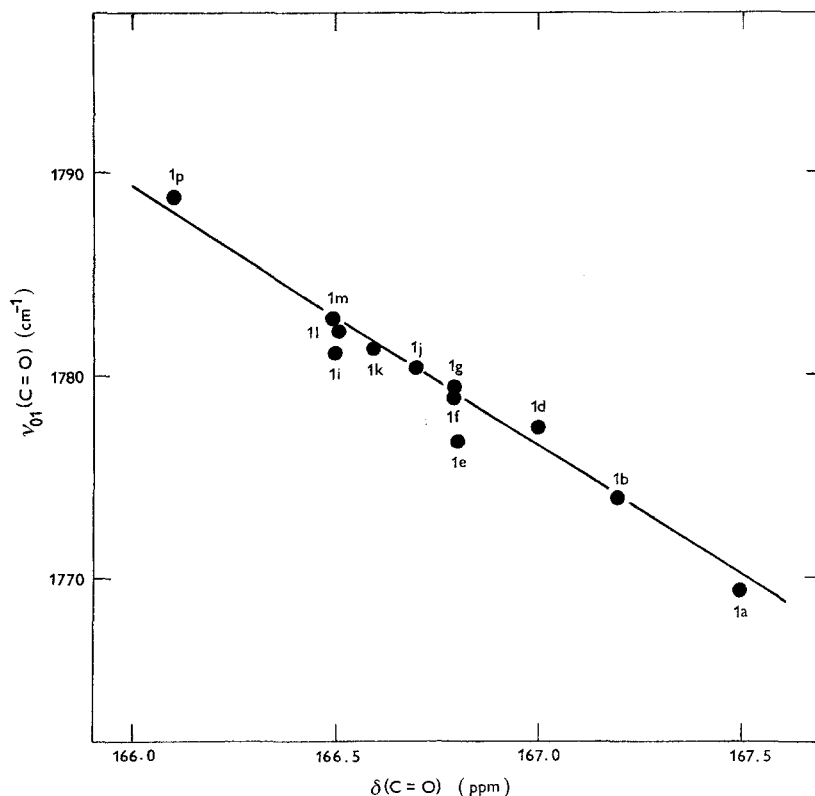
Fig. 4. Dependence of the wave numbers of the unperturbed fundamental C = O stretching vibration (CHCl$_3$) on the ^{13}C NMR chemical shift (CDCl$_3$) of the C = O group for substituted Z-3-phenylmethylene phthalides

Experimental

The preparation and some properties of compounds 1–5 have been described previously [18–25]. The substances were purified by recrystallization and, in the case of 5c, by distillation prior to IR measurements.

The IR spectra were recorded on a Zeiss Specord M-80 spectrometer at room temperature using NaCl cells of 0.1, 0.5, and 1.0 cm thickness. The concentrations of the solutions were 8.10^{-3} mol · dm^{-3}, 2.10^{-3} mol· dm^{-3}, and 8.10^{-4} mol·dm^{-3}. Peak positions were determined with an accuracy of ± 0.2cm^{-1} against polystyrene standard spectra. The absorption intensities of the *Fermi* doublet components were determined after mathematical deconvolution and separation of overlapping bands. Curve analysis was performed by a digital curve-fitting routine. For establishing evidence of *Fermi* resonance effects, the IR spectra of 2.10^{-3} mol·dm^{-3} solutions of 3-phenylmethylene-phthalide (1e) in mixtures of *n*-hexane and trichloromethane were measured using a NaCl cell and compared with those obtained for cyclopentanone under the same conditions. All solvents employed in this investigation were of spectroscopic purity (Uvasol, Merck).

Acknowledgments

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