Infrared Spectra and Theoretical Study of Methyl, Formyl and Acetyl Derivatives of Chromones

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Summary. The C=O stretching frequencies of substituted 2-methylchromones (**3a–3j**), 2-formylchromones (**4a–4j**), 3-formylchromones (**5a–5j**) and 3-acetyl-2-methylchromones (**6a–6i**) were measured in CCl_4 and $CHCl_3$ and correlated with σ^+ substituent constants. Using the results of the infrared spectral investigation and the theoretical calculations by the semiempirical AM1 method, the conformation and the transmission of electronic effects in compounds **4–6** were studied. For the 2-substituted chromone system the transmission factory γ according to the definition of Charton was determined. The preparation of some new 2-methylchromones (**3e–3j**) and 3-(2,2-diformyl-chlorovinyl)-6-methylchromone (**7**) is also described.

Keywords. 2-Methyl-, 2-formyl-, 3-formyl-, and 3-acetyl-2-methylchromones; Infrared spectra; AM1 calculations; Conformation; Transmission of substituent effects.

Infrarot-Spektren und Theoretische Untersuchungen von Methyl-, Formyl- und Acetylderivaten von Chromonen
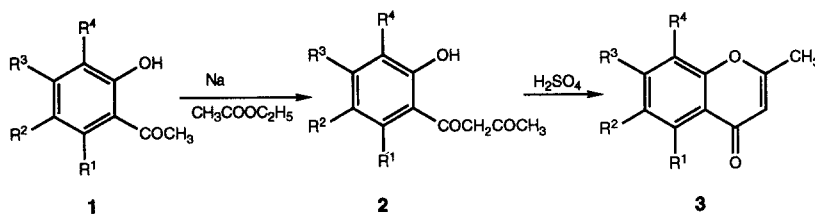
Zusammenfassung. Es wurden die C=O-Streckschwingungsfrequenzen von substituierten 2-Methyl-chromonen (**3a–3j**), 2-Formylchromonen (**4a–4j**), 3-Formyl-chromonen (**5a–5j**) und 3-Acetyl-2-methyl-chromonen (**6a–6j**) in CCl_4 und $CHCl_3$ gemessen und mit den σ^+-Substituentenkonstanten korreliert. Unter Verwendung der IR-Resultate und theoretischer Behandlung mit Hilfe semiempirischer AM1-Rechnungen wurden die Konformationen und die Transmission elektronischer Effekte in den untersuchten Verbindungen **4–6** untersucht. Für die 2-substituierten Chromon-Systeme wurde der Transmissionsfaktor γ entsprechend der Definition von Charton bestimmt. Die Herstellung einiger neuer 2-Methylchromone (**3e–3j**) und 3-(2,2-Diformyl-1-chlorvinyl)-6 methylchromon (**7**) wird ebenfalls beschrieben.

Introduction

The biological importance of chromones [1–3] prompted us to synthesize some new methyl, formyl and acetyl derivatives of chromones. 2-Methylchromones were
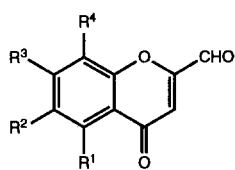
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prepared by treatment of 2-hydroxyacetophenones with ethyl acetate and sodium metal and by cyclization of the resulting β-dicarbonyl compounds [4–8] or by condensation of 2-hydroxyacetophenones with acetic anhydride and sodium acetate to give a mixture of 2-methylchromone and coumarin derivatives [9–11]. A preparation of 2-methylchromones by condensation of β-keto esters with phenols was also described [12, 13]. We prepared 2-methylchromones **3a–3j** by Claisen condensation of substituted 2-hydroxyacetophenones (**1**) with ethyl acetate in presence of sodium metal to give the corresponding (2-hydroxyaroyl) acetone derivatives **2**. Cyclisation of the β-dicarbonyl compounds **2** with conc. H_2SO_4 renders 2-methylchromones in 80–97% yield.
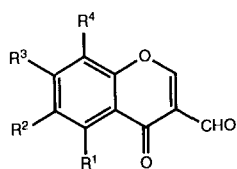

	R¹	R²	R³	R⁴
3a	H	H	H	H
3b	H	CH₃	H	H
3c	H	Cl	H	H
3d	H	Br	H	H
3e	H	Cl	CH₃	H
3f	H	CH₃	H	Cl
3g	H	Cl	Cl	H
3h	H	Cl	H	Cl
3i	-CH=CH-CH=CH-		H	H
3j	H	H	-CH=CH-CH=CH-	

2-Formylchromones **4a–4j** were prepared by condensation of the corresponding 2-methylchromones **3a–3j** with 4-nitroso-N,N-dimethylaniline in presence of ethoxide and by hydrolysis of resulting nitrones by H_2SO_4 as described previously [14].
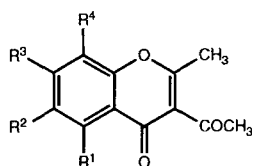

	R¹	R²	R³	R⁴
4a	H	H	H	H
4b	H	CH₃	H	H
4c	H	Cl	H	H
4d	H	Br	H	H
4e	H	Cl	CH₃	H
4f	H	CH₃	H	Cl
4g	H	Cl	Cl	H
4h	H	Cl	H	Cl
4i	-CH=CH-CH=CH-		H	H
4j	H	H	-CH=CH-CH=CH-	

3-Formylchromones **5a–5i** were synthesized according to the method of Nohara [15, 16] by reaction of 2-hydroxyacetophenones (**1**) with Vilsmeier reagent (*DMF*-POCl₃). 3-Formylchromone (**5j**) was synthesized by reaction of 3-chloro-2-hydroxy-5-methyl-acetophenone with Vilsmeier reagent, as described previously [17].

	R¹	R²	R³	R⁴
5a	H	H	H	H
5b	H	CH₃	H	H
5c	H	Cl	H	H
5d	H	Br	H	H
5e	H	OH	H	H
5f	H	NO₂	H	H
5g	H	Cl	H	Cl
5h	H	CH₃	CH₃	H
5i	-CH=CH-CH=CH-		H	H
5j	H	CH₃	H	Cl

3-Acetyl-2-methylchromones **6a–6i** were prepared by reaction of β-dicarbonyl compounds **2** with acetic anhydride and sodium acetate as described previously [18].

	R¹	R²	R³	R⁴
6a	H	H	H	H
6b	H	CH₃	H	H
6c	H	Cl	H	H
6d	H	Br	H	H
6e	H	Cl	CH₃	H
6f	H	Cl	H	Cl
6g	H	CH₃	CH₃	H
6h	-CH=CH-CH=CH-		H	H
6i	H	H	-CH=CH-CH=CH-	

The reaction of β-dicarbonyl compounds **2** ($R^1 = R^3 = R^4 = H$, $R^2 = CH_3$) with Vilsmeier reagent gave 3-(2,2-diformyl-1-chlorovinyl)-6-methylchromone (**7**).
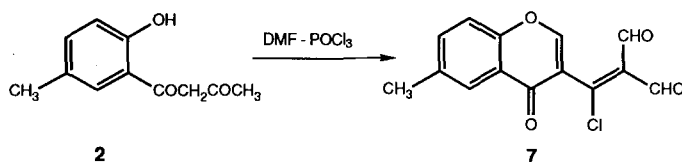
Dipole moments, infrared carbonyl stretching frequencies and relative basicities caused by hydrogen bonding interaction with phenol in the series of substituted 3-formylchromones were investigated earlier by Tsukerman and his coworkers [19, 20]. They concluded that the most favourable conformation of 3-formylchromones is the *s-cis* conformation with respect to the restricted rotation around the C_{ring}–CHO single bond. The existence of this conformation was confirmed on the basis of dipole moment investigations and the authors tried to prove it also by the

existence of a hydrogen bond between the pyrone-ring. C=O group and the formyl group hydrogen atom using infrared spectra.

In order to investigate the conformation and the transmission of electronic effects through the pyrone-ring system we decided to measure the infrared carbonyl streching frequencies of a series of substituted 2-methyl-chromones **3a–3j**, 2-formyl-chromones **4a–4j**, 3-formylchromones **5a–5j** and 3-acetyl-2-methylchromones **6a–6i** and compared them with those of related compounds. To study low energy conformations and electronic structures of the investigated compounds, the semiempirical AM1 method was used for the parent compounds of the individual series.

Experimental Part

. The preparation of 2-formylchromones **4a–4j**, 3-formylchromone (**5j**) and 3-acetyle-2-methylchromones **6a–6i** has been described in our previous reports [14, 17, 18]. 2-Methylchromones **3a–3d** and 3-formyl-chromones **5a–5i** were prepared by published methods [4–8] and [15, 16], respectively. Compounds **3i** and **3j** were synthesized in a different way as before in Ref. [12] and substances **3e–3h** and **7** have not yet been reported.

2-Methylchromones 3e–3h

To a solution of 2-hydroxyacetophenones (**1**) (10 g) in dry ethyl acetate (55 cm³) sodium metal (4 g, small pieces) was added. The reaction mixture was heated under reflux for 2 hr and left overnight at room temperature. The mixture was poured over crushed ice (70 g) and the yellow sodium salt was collected, washed with ice-cold water, then ether and decomposed by treatment with acetic acid (12 cm³), diluted with water and filtered off to obtain β-dicarbonyl compounds **2**. The compounds **2** were cyclized by solution in a minimum amount of conc. H_2SO_4 and diluted by water. The products **3e–3h** were crystallized from cyclohexane. For **3e**: yield = 97%, m.p. = 145–147 °C, $C_{11}H_9ClO_2$ ($M = 208.64$) calculated: 63.32 C, 4.35 H, 16.99 Cl, found: 63.28 C, 4.37 H, 16.67 Cl; ¹H-NMR (*DMSO*), δ/ppm: 7.88 (1 H, s, H-5), 7.63 (1 H, s, H-8), 6.24 (1 H, s, H-3), 2.44 (3 H, s, CH₃), 2.38 (3 H, s, CH₃); **3f** yield = 80%, m.p. = 141–143 °C, $C_{11}H_9ClO_2$ ($M = 208.64$) calculated: 63.32 C, 4.35 H, 16.99 Cl, found: 63.65 C, 4.33 H, 17.04 Cl; ¹H-NMR (CDCl₃), δ/ppm: 7.85 (1 H, brs, H-5), 7.50 (1 H, d, $J = 1.95$ Hz, H-7), 6.17 (1 H, s, H-3), 2.40 (6 H, brs, 2CH₃); or **3g** yield = 80%, m.p. 141–143 °C, $C_{10}H_6Cl_2O_2$ ($M = 229.06$) calculated: 52.44 C, 2.64 H, 30.95 Cl, found: 52.90 C, 2.67 H, 31.08 Cl; ¹H-NMR (*DMSO*), δ/ppm: 8.05 (1 H, s, H-5), 8.03 (1 H, s, H-8), 6.31 (1 H, s, H-3), 2.40 (3 H, s, CH₃); for **3h** yield = 85%, m.p. = 145–147 °C, $C_{10}H_6Cl_2O_2$ ($M = 229.06$) calculated: 52.44 C, 2.64 H, 30.95 Cl, found: 52.70 C, 2.65 H, 30.65 Cl; ¹H-NMR (*DMSO*) δ/ppm: 8.12 (1 H, d, $J = 2.56$ Hz, H-5), 7.87 (1 H, d, $J = 2.56$ Hz, H-7), 6.39 (1 H, s, H-3), 2.46 (3 H, s, CH₃).

2-Methylchromones 3i and 3j

To a solution of 2-hydroxyacetophenones (**1**) (10 g) in dry ethyl acetate (55 cm³) sodium metal (4 g, small pieces) was added. The reaction mixture was heated under reflux for 3 h and left overnight at room temperature. The mixture was concentrated to the half amount by distillation and after cooling it was poured over crushed ice (70 g). The solution of sodium salt was acidified by acetic acid and filtered off to give β-dicarbonyl compounds **2**; these were cyclized by solution in the minimum amount of conc. H_2SO_4 and diluted by water. The products **3i** and **3j** were purrified by crystallization from ethanol. For **3i** ¹H-NMR (CDCl₃), δ/ppm: 10.00 (1 H, d, $J = 7.67$ Hz, H-9), 8.00–7.26 (5 H, m, *Ar*-H), 6.24(1 H, s, H-3), 2.33(3 H, s, CH₃); for **3j** 8.46–7.56(6 H, m, *Ar*-H), 6.30(1 H, s, H-3), 2.49 (3 H, s, CH₃).

3-(2,2-Diformyl-1-chlorovinyl)-6-methylchromone (**7**)

$POCl_3$ (3.8 cm^3, 0.041 mol) was added dropwise to dimethylformamide (10.4 cm^3, 0.135 mol) with stirring at 30–35 °C. The mixture was stirred at 50–60 °C for 30 min. The solution of the β-dicarbonyl compound **2** ($R^1 = R^3 = R^4 = $ H, $R^2 = CH_3$) (2 g, 0.01 mol) in the minimum amount of dimethylformamide was added to the mixture dropwise with stirring at 30–35 °C and the mixture was stirred at 50–60 °C for 3 h, poured over cold water and stirred at room temperature for additional 1 h. The product was filtered off and recrystallized from ethanol. Yield = 12%. m.p. = 173–175 °C. For $C_{14}H_9ClO_4$ ($M = 276.68$) calculated: 60.78 C, 3.28 H; 12.81 Cl, found: 61.11 C, 3.25 H, 12.65 Cl; ^{1}H-NMR (CDCl$_3$), δ/ppm: 8.69(1 H, s, H-2), 7.70 (1 H, brs, H-5), 7.55 (1 H, d, $J = 8.90$ Hz, H-7), 7.40 (1 H, d, $J = 8.90$ Hz, H-8), 10.29 (2 H, s, CHO), 2.50 (3 H, s, CH$_3$); IR (CHCl$_3$), $\tilde{v}$/cm^{-1}: 1640 (v(CO), pyrone), 1668 (v(CO), CHO).

The ^{1}H-NMR spectra were measured on a Tesla BS 487A (80 MHz) spectrometer in *DMSO* and CDCl$_3$ solutions using tetramethylsilane as internal standard. The infrared spectra of CCl$_4$ and CHCl$_3$ solutions in the region of 1800–1600 cm^{-1} were recorded on a Zeiss M-80 spectrometer at room temperature, using NaCl cells of 0.1, 1.0 and 5.0 mm in thickness. The concentrations of the measured solutions were chosen to give maximal absorption between 70–75%. Solvents of the purity p.a. purified and dried in usual manner were used. Peak positions were determined with an accuracy of ±0.1 cm^{-1} against the polystyrene standard spectra.

Results and Discussion

The composition of the newly prepared compounds **3e–3h** and **7** was proved by elemental analysis and their structures were determined by ^{1}H-NMR and IR spectra. The melting points of compounds **3i** and **3j** prepared by a new method are in a good agreement with those reported [12].

The C=O stretching frequencies v(C=O)^P belonging to the pyrone-ring carbonyl group and v(C=O)^A caused by side-chain formyl or acetyl group for series of compounds **3–6** were measured in CCl$_4$ and CHCl$_3$ (Tables 1–4).

The preference of the *s-cis* conformation (**8**) of 3-formylchromones **5** has been supported recently [14] by the results of a theoretical study.

Table 1. Substituted 2-Methylchromones

Compound	v(CO)^P, cm^{-1}	
	CCl$_4$	CHCl$_3$
3a	1665.5^a	1649.1
3b	1662.5	1646.8
3c	1669.0	1652.5
3d	1669.3	1652.3
3e	1666.2	1651.0
3f	1661.4	1652.9
3g	1673.5	1656.1
3h	1671.0	1657.5
3i	1659.9	1657.2
3j	1660.9	1653.0

^{a} The value of 1665.0 cm^{-1} was reported in [21]

8   **9**   **10**
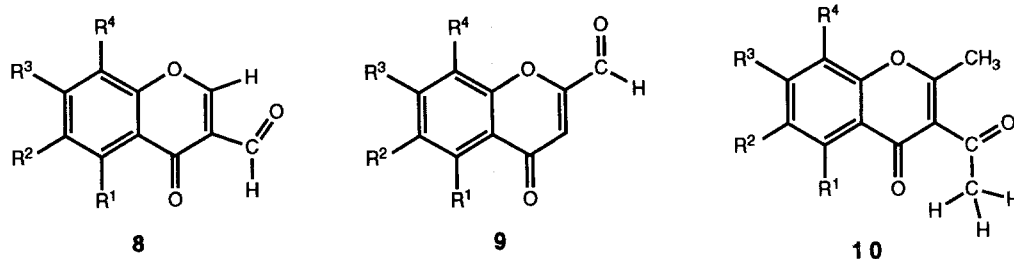
Table 2. Substituted 2-Formylchromones

Compounds	$\nu(C=O)^P$, cm^{-1}		$\nu(C=O)^A$, cm^{-1}	
	CCl$_4$	CHCl$_3$	CCl$_4$	CHCl$_3$
4a	1668.0	1656.0	1728.0	1724.0
4b	1664.6	1654.9	1721.8	1718.6
4c	1669.6	1658.2	1730.7	1730.0
4d	1670.6	1658.8	1730.0	1727.5
4e	1669.0	1658.4	1729.2	1725.0
4f	1666.4	1656.2	1726.0	1722.3
4g	1674.1	1662.9	1731.2	1730.1
4h	1677.8	1664.2	1733.7	1732.1
4i	1653.3	1647.1	1721.7	1718.2
4j	1661.3	1625.5	1723.8	1721.1

Table 3. Substituted 3-Formylchromones

Compounds	$\nu(C=O)^P$, cm^{-1}		$\nu(C=O)^A$, cm^{-1}	
	CCl$_4$	CHCl$_3$	CCl$_4$	CHCl$_3$
5a	1670.0	1662.1	1713.1	1711.0
5b	1666.7	1661.5	1704.8	1700.0
5c	1673.2	1669.0	1703.8	1700.0
5d	1671.8	1668.9	1705.0	1699.5
5e	$-^a$	$\sim 1645.0^b$	$-^a$	1700.0
5f	1682.0	1675.2	1708.5	1704.9
5g	1680.0	1674.0	1707.5	1703.4
5h	1668.5	1658.1	1710.0	1696.5
5i	1656.0	1651.4	1706.2	1703.0
5j	1671.5	1661.8	1718.2	1704.2

[a] Low solubility
[b] Intramolecular hydrogen bonding

Table 4. Substituted 3-Acetyl-2-methylchromones

Compounds	$v(C=O)^P$, cm^{-1}		$v(C=O)^A$, cm^{-1}	
	CCl$_4$	CHCl$_3$	CCl$_4$	CHCl$_3$
6a	1653.5	1645.2	1698.7	1694.0
6b	1653.5	1644.8	1697.1	1693.6
6c	1659.5	1651.2	1700.7	1695.2
6d	1657.9	1650.0	1700.3	1694.8
6e	1655.0	1649.5	1700.7	1693.9
6f	1659.9	1650.4	1701.9	1699.2
6g	1653.5	1644.7	1696.7	1692.3
6h	1647.1	1643.6	1701.5	1694.8
6i	1651.5	1646.0	1700.3	1693.8

The stretching frequencies of the pyrone-ring carbonyl group $v(C=O)^P$ of 3-formylchromones **5** in both CCl$_4$ and CHCl$_3$ solutions are shifted to higher values compared to 2-methylchromones **3**. The comparison of data (in CCl$_4$) from Table 3 and from [20, 22, 23] also shows that the introduction of a formyl group into the position 3 of the fundamental chromone skeleton causes an increase of 5 cm^{-1} in the pyrone-ring carbonyl frequency. This result is opposite from that reported by Tsukerman and coworkers [19], who compared by mistake infrared data measured in CCl$_4$ with those obtained in solid state (KBr discs). The effect of the increase of the pyrone-ring carbonyl stretching frequency caused by a formyl group in position 3 can be explained by the electron-withdrawing effect of this group and this excludes the existence of an intramolecular hydrogen bond between the pyrone-ring C=O group and formyl group hydrogen atom as claimed earlier [19].

On the other hand the results of the theoretical investigation using the semiempirical AM1 method [14] showed that in 3-formylchromone **(5a)** the formation of a weak intramolecular hydrogen bond is probably between the formyl group oxygen atom and the hydrogen atom of the chromone-ring in position 2, which is much more acidic than that of the CHO group. The relatively low values measured for the carbonyl stretching frequency of a formyl group in compounds **5** (1703.8–1718.2 cm^{-1} in CCl$_4$) can be also seen as a support of that.

Passing from 3-formylchromones **5** to 2-formylchromones **4** a slight decrease in the values of stretching frequencies of the pyrone-ring carbonyl group is observed which is connected with an increase of conjugation in the multiple bond system. On the other hand a significant increase occurrs in the $v(C=O)^A$ values of the formyl group (1721.7–1733.7 cm^{-1} in CCl$_4$) which is also reflected by the values of the calculated charge densities on the oxygen atom of the formyl group [14].

This effect can be explained by the existence of 2-formylchromones **4** in *s-trans* conformation **9** with respect of restricted rotation about the C$_{ring}$–CHO single bond, which must be free of intramolecular hydrogen bonding.

In this conformation, besides other factors, a significant contribution to the increase of the stretching frequency of the formyl group is caused by a strong field

effect (through-space interaction) operating between the ring-oxygen atom in position 1 and the C=O group of formyl moiety. It is also evident from some examples that 2-formylfuran derivatives [24, 25], which resemble compounds **5**, exist exclusively in *s-cis* conformation. The results of a theoretical investigation [14] showed only a small difference between the energies ($\Delta E \sim 4\,\mathrm{kJ\,mol^{-1}}$) of two alternative conformations (*s-cis* and *s-trans*) of 2-formylchromones **4**.

The value of the carbonyl stretching frequency of the pyrone-ring C=O group is nearly the same for 3-acetylchromone [19], unsubstituted chromone [20, 22, 23] and 2-methylchromone (**3a**) i.e. $\sim 1665\,\mathrm{cm^{-1}}$ (in CCl_4), which is probably caused by a non-coplanar conformation of the acetyl group with respect to the plane of the chromone ring. This was also proved by the results of a theoretical study which showed that the optimal rotation angle about the C_{ring}–$COCH_3$ single bond is 50° out of the planar *s-cis* arrangement.

Passing from 3-acetylchromone to 3-acetyl-2-methylchromones **6** the carbonyl stretching frequencies of pyrone-ring C=O) group markedly decreases to the values of 1647.1–$1659.9\,\mathrm{cm^{-1}}$ (in CCl_4). This significant change is caused by steric effects and can be explained only as a twisting of the acetyl group about the C_{ring}–$COCH_3$ single bond towards the *s-cis* conformation **10**.

The theoretical calculation shows that the acetyl group in compounds **6** is twisted out of the plane of the chromone ring by 60°.

For the series of compounds **3–6** the pyrone-ring carbonyl group stretching frequencies, $v(C=O)^P$, were correlated with the sum of σ^+ constants of substituents R^1, R^2, R^3, and R^4. For substituents R^2 and R^4 σ_m^+ constants and for substituents R^3 σ_p^+ constants were used. In the case of $R^1(R^2) = -CH=CH-CH=CH-$ (i.e. 5,6,-benzo) and $R^3(R^4) = -CH=CH-CH=CH-$ (i.e. 7,8-benzo) substituents the σ_α constants of 1-naphthyl and 2-naphthyl groups were employed. In the case of $v(C=O)^A$ vs. σ^+ correlations for series **4**, for substituents R^2 and R^4 σ_p^+ constants and for R^3 σ_m^+ constants were used; for $R^1(R^2) = -CH=CH-CH=CH-$ σ_α of 2-naphthyl and for $R^3(R^4) = -CH=CH-CH=CH-$ σ_α of 1-naphthyl group was

Table 5. Statistical treatment of linear correlations $v(C=P) = \rho\sigma^+ + v(C=O)^H$

Series	Carbonyl group	Solvent	ρ^a	$v(C=O)^{Hb}$	n^c	r^d	s^e	Compounds omitted
3	P	CCl_4	9.55 ± 0.98	1664.5	8	0.970	1.1	**3f, 3g**
3	P	$CHCl_3$	10.80 ± 1.28	1648.7	7	0.966	0.9	**3f, 3h**
4	P	CCl_4	16.68 ± 1.85	1665.1	9	0.954	2.2	**4f**
4	P	$CHCl_3$	12.06 ± 1.34	1655.2	9	0.959	1.6	**4f**
5	P	CCl_4	13.34 ± 2.13	1668.1	6	0.952	1.5	**5f, 5h, 5i**
5	P	$CHCl_3$	17.88 ± 1.42	1662.4	7	0.985	1.5	**5e, 5g, 5j**
6	P	CCl_4	9.42 ± 0.99	1653.5	7	0.973	1.0	**6c, 6g**
6	P	$CHCl_3$	7.62 ± 1.59	1647.2	8	0.890	1.4	**6f**
4	A	CCl_4	20.30 ± 1.97	1728.3	8	0.973	1.1	**4b, 4f**
4	A	$CHCl_3$	23.58 ± 2.96	1725.5	8	0.956	1.6	**4b, 4f**

[a] Slope; [b] Intercept; [c] Number of compounds used in correlation; [d] Correlation coefficient; [e] Standard deviation

employed. All substituent constants were taken from Ref. [26]. The results of a statistical treatment of linear correlations are listed in Table 5.

It is evident from the comparison of the slopes of correlations (ρ) obtained for data measured in CCl_4 that the pyrone-ring C=O group of 2-formylchromones **4** is most sensitive to substituent effects ($\rho = 16.68\,\text{cm}^{-1}$), which is probably caused by a strong electron-withdrawing effect of the formyl group in position 2 of the pyrone-ring. In the case of 3-formylchromones **5** the electron-withdrawing effect of the CHO group decreases and therefore the transmission of substituent effects is less effective ($\rho = 13.44\,\text{cm}^{-1}$) in the comparison with 2-formylchromones **4**. Finally, in 2-methylchromones **3**, in which the activation effect of the formyl group is missing, the efficiency of the transmission of electronic effects drops to the lowest value ($\rho = 9.55\,\text{cm}^{-1}$). It must be also mentioned that the last value is nearly the same as that of $\nu(\text{C=O})^P$ vs. σ^+ correlation for 3-acetyl-2-methylchromones $\sigma(\rho = 9.42\,\text{cm}^{-1})$, which can be regarded as an evidence that the acetyl group is twisted out of the plane of the chromone-ring and the conjugation between the two C=O groups is perturbed.

Among the series investigated, only in 2-formylchromones **4** the substituent effects are significantly transmitted to the C=O group of the sidechain attached to the chromone system. Therefore, the values of slopes of $\nu(\text{C=O})^A$ vs. σ^+ correlations for series **4** ($\rho(4)$) were used in comparison with those of similar correlations for substituted benzaldehydes $\rho(BzA) = 9.16\,\text{cm}^{-1}$ in CCl_4 and $\rho(BzA) = 15.87\,\text{cm}^{-1}$ in $CHCl_3$ (calculated using the data reported in Ref. [27, 28]) to determine the transmission factor $\gamma(2\text{-}Chrom)$ for the 2-chromone ring system according to the definition of Charton, Eq. (1).

$$\gamma(2\text{-}Chrom) = \rho(4)/\rho(BzA). \tag{1}$$

Using Eq. (1) the values $\gamma(Chrom) = 2.22$ (in CCl_4) and $\gamma(Chrom) = 0.93$ (in $CHCl_3$) were obtained. The transmission ability of the pyrone-ring C=O group markedly decreases passing from CCl_4 to $CHCl_3$, which can be explained similarly as in the case of other heterocyclic systems [27] by an additional hydrogen bonding with other sites except the formyl group.

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References

[1] Ellis G. P. (1977) Chromenes, Chromanones and Chromones. J. Wiley, New York
[2] Jerome F. F. (1964) Phyton (Buenas Aires) **21**: 133, (1965) CA **62**: 13718
[3] Klutchko S, Kaminsky D. Von Strandtmann M (1978) US 4.098.799, (1979) CA **90**: 22813C
[4] Baker W. (1933) J. Chem. Soc. Faraday Trans.: 1381
[5] Virkar V. V., Shah R. C. (1949) Proc. Indian Acad. Sci. **A30**: 57
[6] Wittig G. (1924) Bericht **57**: 88
[7] Mozingo H. (1941) Org. Synthesis **21**: 42
[8] Sami S. M., Ibrahim S. S., Abdel-Halim A. M., Aly Y. L. (1986) Ind. J. Chem. **B25**: 384

[9] Sethan S. M., Shah R. C. (1940) J. Ind. Chem. Soc. **17**: 249
[10] Heilborn I. M., Hey D. H., Lythgoe B. (1934) J. Chem. Soc. Faraday Trans.: 1581
[11] Wittig G, Bangert F., Richter H. E. (1926) Ann. **446**: 170
[12] Simonis H, Lehmann A. C. B. (1914) Bericht **47**: 697
[13] van Allan J. A., Stenberg, J. F., Reynolds G. A. (1979) J. Heterocycl. Chem. **16**: 1663
[14] El-Shaaer H. M. M., Zahradník P., Lácová M., Matulavoá M. (1992) Monatsh. Chem., to be published
[15] Nohara A., Umetani T., Sanno Y. (1974) Tetrahedron **30**: 3553
[16] von Harnish H. (1972) Liebigs Ann. Chem. **765**: 8
[17] El-Shaaer H. M. M. (1992) Thesis Comenius University, Bratislava
[18] El-Shaaer H. M. M., Matulová M., Lácová M. (1992) Collect. Czechslov. Chem. Commun., to be published
[19] Poliakow V. K., Shewtsowa R. G., Tsukerman S. V. (1979) Zh. Obsch. Khim. **49**: 1560
[20] Poliakow V. K., Surow J. P., Shewtsowa R. G., Tsukerman S. V. (1978) Zh. Obsch. Khim. **48**: 2273
[21] Murray R. D. M., McCabe P. H., Hogg T. C. (1969) Tetrahedron **25**: 5839
[22] Tolmachew A. I., Papp L. V., Riltsew E. V., Jegorow J. P. (1974) Zh. Obsch. Khim. **44**: 2747
[23] Looker J. H., Hanneman W. W. (1962) J. Org. Chem. **27**: 381
[24] Perjéssy A., Krutošíková A., Olejnik A. F. (1975) Tetrahedron **31**: 2936
[25] Chadwick D. J., Meakins G. D. (1970) J. Chem. Soc., Dalton Trans.: 637
[26] Perjéssy A. (1973) Tetrahedron **29**: 3189
[27] Perjéssy A., Frimm R., Hrnčiar P. (1972) Collect. Czechoslov. Chem. Commun. **37**: 3302
[28] Laurence Ch., Berthelot M. (1979) J. Chem. Soc. Perkin. **II**: 98