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ELECTRONIC SUBSTITUENT EFFECTS AND CARBONYL STRETCHING FREQUENCIES OF 2-ARYLMETHYLENE-1,3-INDANDIONES

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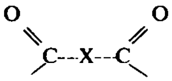
Abstract—The CO stretching frequencies of 2-arylidene-1.3-indandiones are highly sensitive to electronic substituent effects. The slopes of the correlations $\tilde{\nu}_{CO} - \sigma^+$ found are comparable with those for benzaldehydes. A linear correlation between the electronic substituent effects and the value of the CO splitting is observed, the latter becoming larger with increasing electron donor properties of the substituent. The existence of such a correlation is an indication of an electronic mechanism of interaction between the carbonyl groups. Thus the existence of coupling of unconjugated groups in a π-electronic system is emphasised.

DICARBONYL compounds of the type



where X is sp^2, sp^3 or a differently hybridized atom show in general two absorption bands in the CO stretching region. Both these bands have been assigned to the stretching vibrations of the C=O groups.[1] The band in the higher frequency region is in general less intensive and has been assigned to the symmetric stretching vibration of the dicarbonyl group O=C—X—C=O. The second band has been attributed to the asymmetric stretching vibration of the same group.[1,2]

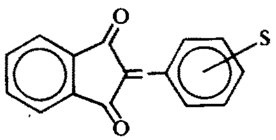
A number of interpretations of this CO splitting have been suggested. The opinion that the splitting is due to H-bonding[3] has been rejected.[4] The CO splitting of substituted diacylimides and dicarboxylic esters e.g. when X = NR, CH_2 or $(CH_2)_2$ has been interpreted as a result of mechanical resonance coupling of the CO groups.[5] Similar considerations have been expressed for the case of acid anhydrides[6]—X = 0, cyclic imides,[7] β-diketones[8] and a series of other compounds.[6,9] Fermi resonance has been found in aliphatic cyclic imides and phtalimides.[10] The influence of electronic factors on the CO splitting has also been considered.[11] The high intensity of the asymmetric absorption shown by the compounds of the maleic anhydride type has been interpreted as due to resonance stabilization of the asymmetric oscillation $\overrightarrow{O{=}C}{-}O{-}\overrightarrow{C{=}O} \leftrightarrow O{=}C{-}\overset{+}{O}{=}C{-}\overset{-}{O}$. This interpretation has been extended later to a number of compounds with X = NH, NR[10] and has been generalized for systems with X = sp^2-hybridized atom or atoms.[11] If an electronic interaction of such a nature is actually one of the reasons for the observed phenomena every change in the electronic properties of the bridge atom X will affect correspondingly the CO frequencies. There are some indications confirming the opinion that substituents attached to X have a considerable influence on the mutual and absolute positions of both CO absorption maxima.[11,13]

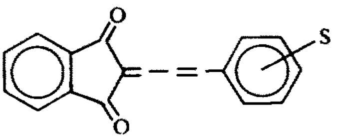
The relative intensity of the CO bands has been considered from the view of the mechanical coupling—for cyclic imides[9]—as well as from the view of an electronic nature of the interaction[11,14]—for aliphatic and aromatic cyclic anhydrides. In the last case it was found that enlarging the conjugated system decreases the ratio of intensity of the asymmetric and symmetric absorptions. This ratio is less than unity for very large conjugated systems. Hence, for aromatic and unsaturated dicarbonyl compounds electronic interactions through the corresponding π-systems have to be considered. The conclusion, resulting from the above discussion, is that the observed CO splitting and the ratio of intensities for cyclic imides cannot be explained only by mechanical coupling.[11] An additional interaction constant has to be introduced to correlate the result of the normal coordinate analysis with the experimental. This interaction constant can be assumed to express the electronic coupling through the bridge atom X.[11]

Studies of polar substituent effects on the frequencies considered have not been reported in the literature. There is a single indication that the Hammett equation is applicable for correlating CO stretching frequencies of aryl substituted N-arylimides.[13] Such an empirical approach to the problem is reasonable because of the independence of the CO stretching frequencies on the mass effect of the substituents.[15] Hence the electronic structure determines unambiguously the observed vibration frequencies[16] and a linear Hammett type correlation between these frequency values and the electronic effects of the substituents attached to the bridge atom X[17] is anticipated. The existence of a similar correlation for 2-arylmethylene-1,3-indandiones, the subject of the present study, is of particular interest as it could be used as a basis for more rigorous quantitative treatment. The elucidation of the origin and the factors influencing the position of the CO doublet could be useful for generalization of the above discussion. In our case non-equivalent CO groups are present[18] and this fact has to be taken into account before commencing the discussion.

RESULTS AND DISCUSSION

Compounds from the following two series were investigated:





where S is a *meta*- or a *para*-substituent (Table 1). It is known that the CO stretching frequencies of some dicarbonyl compounds may be correlated with Hammett constants. The relation $\tilde{\nu}_{CO}$-σ is of the same character as that observed for the corresponding carboxylic acids.[6,13] In the cases considered[6,13] this relation is not linear. The CO stretching frequencies found for aryl-substituted 2-arylmethylene-1,3-indandiones (Table 1) and Hammett σ-constants[19] show a non-linear dependence with low correlation coefficients; for $\tilde{\nu}_{sym}$ and $\tilde{\nu}_{as}$ r = 0·865 and r = 0·888 respectively.

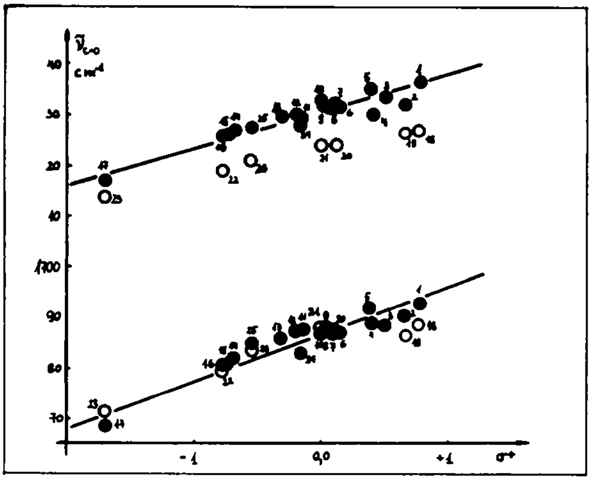


FIG 1. Plot of the carbonyl stretching frequencies vs. σ^+-values (for the numbering see Table 1)

It is reasonable to search for a relationship between $\tilde{\nu}_{CO}$ and Brown and Okamoto's σ^+ constants[20] because of the electron withdrawing properties of the carbonyl groups (Table 1, Fig 1). The inclusion of a polar conjugative effect in the σ^+-constants improves the linearity of the relation $\tilde{\nu}_{CO}$-σ^+:

$$\tilde{\nu}_{sym} = (7{\cdot}24\sigma^+ + 1730{\cdot}3)\,\mathrm{cm}^{-1}$$

$$r = 0{\cdot}931 \text{ and mean deviation } S_0 = 1{\cdot}7\,\mathrm{cm}^{-1}$$

$$\tilde{\nu}_{as} = (9{\cdot}19\sigma^+ + 1686{\cdot}5)\,\mathrm{cm}^{-1}$$
$$r = 0{\cdot}951 \text{ and mean deviation } S_0 = 1{\cdot}8\,\mathrm{cm}^{-1}$$

for the benzylidene derivatives. For the compounds including one additional double bond in the conjugated system (cinnamylidene-indandiones) a linear dependence $\tilde{\nu}_{CO} - \sigma^+$ is also observed:

$$\tilde{\nu}_{sym} = (5{\cdot}28\sigma^+ + 1723{\cdot}2)\,\mathrm{cm}^{-1}$$
$r = 0{\cdot}996$; $S_0 = 1{\cdot}3\,\mathrm{cm}^{-1}$ and transmission factor of the double bond[21] $\pi' = \rho_c : \rho_b$, where ρ_c and ρ_b are the slopes of the correlations $\tilde{\nu}_{CO}$-σ^+ for cinnamylidene and benzylidene derivatives respectively $-\pi' = 0{\cdot}721$

$$\tilde{\nu}_{as} = (7{\cdot}00\sigma^+ + 1684{\cdot}8)\,\mathrm{cm}^{-1}$$
$$r = 0{\cdot}960;\ S_0 = 1{\cdot}8\,\mathrm{cm}^{-1} \text{ and } \pi' = 0{\cdot}762$$

The values of the transmission factors found are in general higher than those for chemical reactivity but are close to those found in investigations of substituent effects on the IR-frequencies of several types of carbonyl (aldehydes, acids, esters) and nitrile groups.[22,23] The rather large values of the transmission factors as well as the high sensitivity of the frequencies to substituent effects are probably due to the strong electron withdrawing properties of the 5-membered diketone fragment.

TABLE 1. CARBONYL STRETCHING FREQUENCIES AND CORRESPONDING SIGMA- AND F-VALUES FOR ARYL-SUBSTITUTI 2-ARYLMETHYLENE-1,3-INDANDIONES; 1–17 = BENZYLIDENE DERIVATIVES; 18–23 = CINNAMYLIDENE DERIVATIVES; 24 2-THIENYL-; 25 = 2-FURYL-; 26 = 2-(2-FURYL)-ETHENYL-METHYLENE DERIVATIVES

No.	S	ν_{sym}	ν_{as}	$\Delta\nu$	σ	σ^+	σ°	$\sigma^+ - \sigma^\circ$	5·8 F/
1	4—O_2N--	1736·5	1693·0	43·5	+0·778	+0·790	0·73	0·06	1·24
2	3—O_2N--	1732·0	1690·5	41·5	+0·710	+0·674	0·70	0·03	1·16
3	3,4--Cl_2--	1733·5	1688·5	45·0	+0·600[a]	+0·513[a]	0·64[a]	−0·13	—
4	3-Br--	1730·0	1689·0	41·0	+0·391	+0·405	0·38	+0·02	0·63
5	3-Cl--	1735·0	1692·0	43·0	+0·373	+0·399	0·37	0·02	0·61
6	4-Br—	1731·5	1687·0	44·5	+0·232	+0·150	0·26	−0·11	0·68
7	4-Cl--	1732·0	1687·0	45·0	+0·227	+0·114	0·27	−0·16	0·65
8	3,5-$(CH_3O)_2$[d]	1731·5	1687·5	44·0	+0·230[a]	+0·094[a]	—	—	—
9	3-CH_3O--	1732·0	1688·0	44·0	+0·115	+0·047	0·13	−0·08	0·17
10	H—	1732·5	1687·0	45·5	0·00	0·00	0·0	0·0	0·0
11	3,4-C_4H_4--[e]	1729·5	1687·5	42·0	+0·042	−0·135	—	—	—
12	4-C_6H_5—	1730·5	1687·5	43·0	−0·01	−0·179	—	—	—
13	4-CH_3—	1729·5	1686·0	43·5	−0·170	−0·311	−0·15	−0·16	−0·12
14	3,4,5-$(CH_3O)_3$	1727·0	1682·0	45·0	−0·044[a]	−0·684[a]	0·10[a]	−0·78[a]	—
15	3,4-CH_2O_2—	1726·0	1681·0	45·0	−0·159[b]	−0·731[a]	−0·03[a]	−0·70[a]	—
16	4-CH_3O—	1726·0	1680·5	45·5	−0·268	−0·778	−0·16	−0·62	0·20
17	4-$(CH_3)_2N$--	1717·0	1668·5	48·5	−0·83	−1·7	−0·44	−1·26	−0·28
18	4-O_2N--	1727·0	1688·5	38·5	+0·778	+0·790	0·73	0·06	—
19	3-O_2N—	1726·5	1688·0	38·5	+0·710	+0·674	0·70	0·03	—
20	4-Cl—	1724·0	1687·5	36·5	+0·227	+0·114	0·27	−0·16	—
21	H--	1724·0	1687·5	36·5	0·00	0·00	0·0	0·0	—
22	4-CH_3O—	1719·0	1679·5	39·5	−0·268	−0·778	−0·16	−0·62	—
23	4-$(CH_3)_2N$—	1714·0	1671·5	42·5	−0·83	−1·7	−0·44	−1·26	—
24		1728·0	1683·0	45·0	—	−0·16[c]	—	—	—
25		1727·5	1685·0	42·5	—	−0·55[c]	—	—	—
26		1721·0	1684·5	36·5	—	−0·55[c]	—	—	—

[a] additive constant

[b] Ref. 21

[c] Ref. 27

[d] m.p. 191–192°; (Found: C, 73·35; H, 480; calc. for $C_{18}H_{14}O_4$: C, 73·50; H, 4·77%).

[e] β-naphtyl

The influence of polar substituent effects on the CO splitting can be determined by subtracting the equations for $\tilde{\nu}_{as}$-σ^+ from these for $\tilde{\nu}_{sym}$-σ^+:

$\Delta\tilde{\nu} = (43·8 - 1·95\sigma^+)\ cm^{-1}$ for the benzylidene derivatives and

$\Delta\tilde{\nu} = (38·4 - 1·72\sigma^+)\ cm^{-1}$ for the cinnamylidene derivatives. Thus the influence of polar substituent effects on the mutual position of the CO bands results an increase in the interaction between the characteristic groups and the splitting with increasing of electron donor properties of the substituents.

The mechanism of influence of the substituents on the CO stretching frequencies can be elucidated by separation of the electronic effects according to the F, M-scheme.[24] By this approach the influence of the field effect of the substituents on the frequencies of the C═O groups could be defined. In our case a rather poor correlation between the F-values and the stretching frequencies was observed (Table 1). Increasing the F-value tends to increase the frequency. The inadequacy of this dependence is probably due to the insufficient accuracy of measuring the frequencies as well as of the F-values determining the field effect. A similar result was obtained for the relation $\tilde{\nu}_{CO}$-σ°. In this case two separate satisfactorily linear parts of the dependence were found for weak and strong electron donating substituents respectively (Table 1).

It is convenient to use the values $(\sigma^{+} - \sigma^{\circ})$ to define the influence of the "pure polar conjugation" on CO stretching frequencies. The Taft-constants σ° are "free of polar conjugation"[25] and by means of these constants the +C-effect may be separated. This effect is described by the $(\sigma^{+} - \sigma^{\circ})$ values.[26] The relations $\tilde{\nu}_{CO} - (\sigma^{+} - \sigma^{\circ})$ considered are as follows:

$$\tilde{\nu}_{sym} = 12{\cdot}44(\sigma^{+} - \sigma^{\circ}) + 1733{\cdot}1\ \text{cm}^{-1}; \quad r = 0{\cdot}911$$

$$\tilde{\nu}_{as} = 15{\cdot}29(\sigma^{+} - \sigma^{\circ}) + 1690{\cdot}0\ \text{cm}^{-1}: \quad r = 0{\cdot}926$$

for the benzylidene derivatives and

$$\tilde{\nu}_{sym} = \{\ 9{\cdot}40(\sigma^{+} - \sigma^{\circ}) + 1725{\cdot}5\}\ \text{cm}^{-1}; \quad r = 0{\cdot}983$$

$$\tilde{\nu}_{as} = \{13{\cdot}06(\sigma^{+} - \sigma^{\circ}) + 1688{\cdot}0\}\ \text{cm}^{-1}; \quad r = 0{\cdot}993$$

and transmission factors $\pi'_{sym} = 0{\cdot}756$ and $\pi'_{as} = 0{\cdot}854$ respectively for the cinnamylidene derivatives. As can be seen the correlation coefficients are lower than those obtained for the relations $\tilde{\nu}_{CO} - \sigma^{+}$. This fact may be also due to the insufficient accuracy of the $(\sigma^{+} - \sigma^{\circ})$ values. These empirical values unfortunately can only be determined at present with an error of not less than $\pm 0{\cdot}05$. In spite of this the following conclusions can be drawn. The +C-effect is the main effect determining the value of the CO splitting whereas the F-effect (or inductive effects) have a less significant influence on the frequencies.

The high sensitivity of the CO stretching frequencies to substituent effects, in particular to the +C-effect, may be interpreted as an indication of increased polarity of the CO groups in the compounds considered.[26, 28] The slopes of the correlation straight lines observed are comparable with those for benzaldehydes, compounds with one double bond less in the conjugated system.[23] This fact shows that considerable charge transfer to the CO groups is present in the ground state of the molecules. This same conclusion is reached by a series of results for other physical properties of arylidene-indandiones.[29, 30] It is noteworthy that a definite dependence between the solvent effect and substituent effects on the CO stretching frequencies may be observed. For the change from CCl_4 to $CHCl_3$ the shift to lower values of the CO frequencies shows a tendency to linearity between the solvent shift and σ^{+} or $(\sigma^{+} - \sigma^{\circ})$. A least square treatment gives the following correlation equations for the frequencies measured in CCl_4:[29]

$$\tilde{\nu}_{sym} = (3{\cdot}21\sigma^{+} + 1733{\cdot}1)\ \text{cm}^{-1}$$

$$\tilde{\nu}_{as} = (8{\cdot}64\sigma^{+} + 1692{\cdot}0)\ \text{cm}^{-1}$$

$$r = 0{\cdot}960\ (14\ \text{compounds})$$

$$\Delta\tilde{\nu} = (41{\cdot}1 - 5{\cdot}43\sigma^{+})\ \text{cm}^{-1}$$

The solvent shifts for the change from CCl_4[29] to $CHCl_3$ (this work) are given by the equations:

$\Delta\tilde{\nu}_{sym} = (4{\cdot}03\sigma^{+} - 2{\cdot}8)\ \text{cm}^{-1}$ for the symmetric vibration and $\Delta\tilde{\nu}_{as} =$

$(0{\cdot}55\sigma^+ - 5{\cdot}5)$ cm^{-1} for the asymmetric one. It is obvious that the CO splitting in CCl_4 is smaller than in $CHCl_3$ but appreciably more sensitive to substituent effects.

Regarding the mechanism of the CO splitting, the electronic coupling between the characteristic groups is responsible for a considerable part of this splitting. This coupling is in accordance with the scheme given by Mirone and Chiorboli[12] for resonance stabilization of the asymmetric vibration. This conclusion is supported by the larger sensitivity of the asymmetric vibration to substituent effects and by the lesser sensitivity of the same vibration to the solvent effects.

EXPERIMENTAL

The IR absorption spectra in the region 1600–1800 cm^{-1} were measured on a Carl Zeiss UR-10 spectrophotometer. The spectrophotometer was callibrated by the spectrum of atmospheric water vapour.[31] The accuracy of the frequencies registered is about ±1 cm^{-1}. 0·2% solns of the compounds in $CHCl_3$ were used.

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