INFRARED SPECTRA AND TRANSFER OF POLAR EFFECTS IN *ortho*-SUBSTITUTED 2-BENZYLIDENE-1,3-INDANEDIONES

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Linear correlations were studied between wavenumbers of C=O stretching vibrations (measured in tetrachloromethane and chloroform, respectively) and substituent constants in a series of *ortho*-substituted 2-benzylidene-1,3-indanediones. The results confirm the assumed spatial structure and conformation of the compounds under study. In addition to the π-induction effect, the direct field effect plays an important part in the mechanism of transfer of polar effects from the *ortho* position of the benzene ring to the carbonyl groups. In the case of compounds with substituents in both *ortho* positions, the observed departures from linear correlations confirm the assumptions of a significant perturbation of coplanarity of the system.

Infrared spectra of *para*- and *meta*-substituted 2-benzylidene-1,3-indanediones have been studied previously[1−3]. In the works[1,2] we have found that arithmetic means of wavenumbers of symmetric and asymmetric C=O stretching vibrations in series of 3- and 4-substituted 2-benzylidene-1,3-indanediones can be correlated with σ_p^+ substituent constants. Agranat and coworkers[4] have measured the wavenumbers of the C=O stretching vibrations of some *ortho*-substituted 2-benzylidene-1,3-indanediones. Based on the differences between the wavenumbers for the various derivatives and on the comparison of the spectral data for *ortho*-substituted compounds with those for the *para*- and *meta*-substituted compounds, they suggested conformation and the occurrence of steric effects in *ortho*-substituted 2-benzylidene-1,3-indanediones. More recently Yukhnovskii and Kaneti[5], who have studied linear empirical relations between the C=O or C=C bond orders and the wavenumbers of the corresponding stretching vibrations, confirmed the suggested conformation of *ortho*-substituted 2-benzylidene-1,3-indanediones and pointed out some other steric effects in those substances.

As linear correlations of the Hammett type can be often useful for the elucidation of the structure and the transfer of electronic effects, we decided to apply them in this work to the case of *ortho*-substituted 2-benzylidene-1,3-indanediones. For this purpose we measured the wavenumbers of symmetric and asymmetric C=O stretching vibrations of a series of compounds with a substituent in one *ortho* position (series *I*) and of some compounds with identical substituents in both *ortho* positions (series *II*).

The results obtained in this work are then compared with those[2] for series of *para*- and *meta*-substituted 2-benzylidene-1,3-indanediones (series *III*).

EXPERIMENTAL

The preparation and purification of the compounds of the series *I* and *II* have been described[6,7]. The wavenumbers of the C=O stretching vibrations were measured in tetrachloromethane and in chloroform solutions on a spectrophotometer Spekord IR 71 (Zeiss, Jena GDR) by applying the method reported previously[1,2]. The linear correlations were evaluated by using statistic relations of regression analysis, employing a calculator Hewlet-Packard 9100 B with a standard program.

RESULTS AND DISCUSSION

The wavenumbers of the symmetric, ν_s, and asymmetric, ν_{as}, C=O stretching vibrations for the series *I* (compounds *1−10*) and *II* (compounds *11−13*) along with their arithmetic means $\bar{\nu}\left(=(\nu_s + \nu_{as})/2\right)$ are given in Table I. Similarly as in the case of *para*- and *meta*-substituted 2-benzylidene-1,3-indanediones and their 5,6-dihydro-4,7-dithia analogues[8] as well as derivatives of those compounds containing hetero-cyclic bridge groups[2,10], the wavenumbers of the C=O stretching vibrations of the

TABLE I

Wavenumbers of the C=O Stretching Vibrations (cm^{-1}) and the Corresponding σ^+ Constants for Substituted 2-Benzylidene-1,3-indanediones *I* and *II*

No	X	CCl$_4$			CHCl$_3$			$\sigma^{+\ a}$
		ν_s	ν_{as}	$\bar{\nu}$	ν_s	ν_{as}	$\bar{\nu}$	
1	2-OCH$_3$	1735·5	1693·0	1714·0	1732·5	1688·5	1710·5	−0·78
2	2-OC$_2$H$_5$	1733·5	1692·5	1713·0	1729·5	1687·5	1708·5	−0·72
3	2-CH$_3$	1736·5	1695·5	1716·0	1735·0	1692·5	1714·0	−0·31
4	2-F	1739·5	1697·0	1718·0	1736·0	1693·5	1715·0	−0·07
5	2-Cl	1741·0	1698·5	1720·0	1737·5	1695·0	1716·0	0·11
6	2-Br	1741·0	1698·0	1720·0	1738·5	1696·5	1717·0	0·15
7	2-CHO	1740·0	1704·0	1722·0	1737·5	1700·0	1719·0	0·46
8	2-NO$_2$	1743·5	1704·5	1724·0	1742·5	1701·0	1722·0	0·79
9	2,4-Cl$_2$	1738·5	1696·5	1717·5	1733·5	1692·5	1713·0	0·22
10	2-COOH	1756·0	1723·0	1740·0	1756·0	1720·0	1738·0	0·42
11	2,6-Cl$_2$	1747·0	1708·0	1728·0	1745·0	1706·0	1725·0	0·22
12	2,3,4,5,6-F$_2$	1746·0	1709·5	1728·0	1743·0	1705·0	1724·0	0·56
13	2,4,6-(OCH$_3$)$_3$	1735·5	1697·0	1716·0	1732·5	1692·0	1712·0	− 2·34

[a] Taken from ref.[9].

compounds *I* can be satisfactorily correlated with the corresponding substituent constants. Statistic analyses of the correlations of the wavenumbers v_s, v_{as}, and $\bar{v}$ with the substituent constants σ_p or σ_p^+ show, similarly as in the case of the other analogous series[2,8−10], that the statistically most significant are the correlations of the arithmetic means of the wavenumbers of the symmetric and asymmetric C=O stretching vibrations, $\bar{v}$, with the substituent constants σ_p^+. For a comparison with the previous results we give the dependence in Table II and Fig. 1. In the linear correlations for the series *I*, the values for 2-(2-carboxybenzylidene)-1,3-indanedione (compound *10*) were not included, as they depart considerably from the regression straight line. This departure can be explained in terms of the probable occurrence of an intramolecular hydrogen bond between the hydrogen of the carboxylic group and the π-electrons of the central double bond. The fact that $\bar{v}$ can be correlated with the σ_p^+ substituent constants indicates that − despite the nonplanar structure of 2-benzylidene-1,3--indanedione itself[5] − a strong mesomeric interaction exists between the substituted benzene ring and the carbonyl groups. Furthermore it can be assumed that the π-induction effect will play an important role in the mechanism of transfer of polar effects from the *ortho* position of the benzene ring to the carbonyl groups. These ideas are in addition supported by the findings[4,5] that *ortho*-substituted 2-benzylidene--1,3-indanediones appear predominantly in a conformation such that the substituent X lies in the longest distance from the carbonyl groups. Comparing the slopes of the linear correlations, ϱ (Table II) for the substances *I* with those for the series *III* we find them different. This suggests that the mechanism of transfer of polar effects in the two series is not the same. Another situation occurs *e.g.* in the case of 3-phenyl-methylene- (*IV*) and 3-phenoxymethylenephthalides[11] (*V*), where a good common

TABLE II

Statistic Parameters of Linear Correlations Between Arithmetic Means of the Wavenumbers of Symmetric and Asymmetric C=O Stretching Vibrations and the σ^+ Constants for the Compound Series *I* and *III*

Series	Solvent	n^a	r^b	ϱ^c	q^d	s^e
I	CCl_4	8	0·992	7·01	1718·7	0·5
I	$CHCl_3$	8	0·984	7·87	1715·6	0·8
III^f	CCl_4	9	0·973	6·20	1715·5	1·4
III^f	$CHCl_3$	10	0·989	8·91	1710·5	1·2

[a] Number of compounds used for correlation; [b] correlation coefficient; [c] slope; [d] intercept on the wavenumber axis; [e] standard deviation; [f] taken from ref.[2].

correlation of $v(C{=}O)$ with σ was achieved for the *para-, meta-,* and *ortho*-substituted derivatives. A study of the Dreiding models of the compounds *I* and *III* in comparison with the systems *IV* and *V* shows that in the case of the compounds *I* and *II* the different mechanism of transfer of polar effects can be caused by the existence of a direct field effect between the substituent and the carbonyl group which lies closer to that substituent. The significance of the direct field effect in the transfer of polar effects in *ortho*-substituted *cis*-isomers of cinnamic acid, which can serve as a simple model for the compounds *I*, was pointed out by Bowden and Parkin[12], based on extensive studies.

The value of the slope, ϱ (Table II), obtained from the data in tetrachloromethane is for the *ortho*-substituted compounds *I* higher than for the series of the *para-* and *meta*-substituted compounds *III*. This can be explained by the direct field effect which participates significantly, in addition to the π-induction effect, in the mechanism of transfer of polar effects. In chloroform, the carbonyl groups form hydrogen bonds with the hydrogen atoms of the solvent, so the direct field effect acts to a lower extent and the π-induction effect predominates in the mechanism of the transfer. The latter effect is more pronounced for substituents in the *para* position than for those in the *ortho* position, the slope being for the series *III* higher than for the series *I*.

Based on the study of departures from linear relations (Fig. 1) we can come to additional useful findings on the spatial structure of the substances *I* and *II*. The
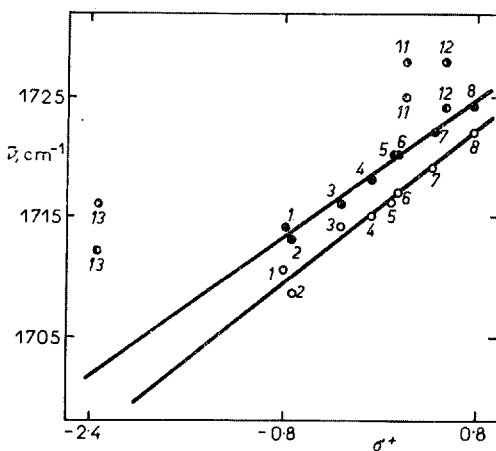

FIG. 1

Dependence between the Arithmetic Means of the Wavenumbers of Symmetric and Asymmetric C=O Stretching Vibrations and the σ^+ Substituent Constants

Compounds of the series *I* ● in tetrachloromethane, ○ in chloroform; compounds of the series *II* not included in the correlation ◖ in tetrachloromethane, ◐ in chloroform.

substances of the series *II* (compounds *11 — 13*) which have identical substituents in the two *ortho* positions, display in tetrachloromethane as well as in chloroform much higher $\bar{v}$ values than as would correspond to the linear relations valid for the series *I*. The departures increase in the order F < Cl < OCH$_3$, hence with the bulk of the substituent. This confirms the conclusions of Agranat and coworkers[4] as well as of Yukhnovskii and Kaneti[5], who suggest that compounds of the type *II* occur in a conformation, where the coplanarity of the substituted benzene ring and the carbonyl groups is appreciably perturbed as a result of steric interaction between the other substituent in the *ortho* position and the carbonyl group near the substituent. The angle of departure from the coplanarity in such compounds makes, according to the results obtained by Yukhnovskii and Kaneti, 20 to 75°. These results are in accordance with those obtained from ^{1}H NMR studies[7] of the compounds of the types *I* and *II*.

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