THE *ortho* EFFECT IN *ortho*-SUBSTITUTED 2-(X-BENZAL)-1,3-INDANEDIONES, 3-(2-X-BENZAL)PHTHALIDES AND 3-(2-X-BENZAL)-5,6-DIHYDRO-4,7-DITHIAPHTHALIDES: A ^{1}H-NMR STUDY

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The ^{1}H-NMR spectra of *ortho*-substituted 2-(X-benzal)-1,3-indanediones, 3-(2-X-benzal)-phthalides and 3-(2-X-benzal)-5,6-dihydro-4,7-dithiaphthalides have been studied. The chemical shifts observed for the methine proton were correlated with various constants of the substituents. In addition to simple correlations, two- and three-parameter correlations were also made. Statistically most important one-parameter correlations were observed for σ_p-constants. Apart from the common electronic effects, in the transfer of effects of the substituents from the *ortho*-position upon the chemical shift of the methine proton the field effect plays also an important role. The deviations observed in the case of substances substituted in both *ortho*-positions confirm the assumed considerable distortion of the coplanarity of the studied systems.

The transfer of effects of the substituents upon the chemical shift of the methine proton in *meta*- and *para*-substituted 3-benzalphthalides has been studied[1,2] and after having made corrections taking into account the magnetic anisotropy, good correlations with the $\sigma_{p,m}$ constants were observed. Since *ortho*- and *para*-positions comprise a conjugated system the various *ortho*-substituted derivatives were predominantly correlated only with σ_p constants. The portion of the effect which is carried over through π bonds is approximately the same for both positions. The mechanism of the transfer of the effects of substituents in *ortho*-substituted 2-(X-benzal)-1,3-indanediones *I*, 3-(2-X-benzal)phthalides *II* and 3-(2-X-benzal)-5,6-dihydro-4,7-dithiaphthalides *III* has been studied by IR (ref.[3]) and UV (refs[4,5]) spectroscopy. Indanedione itself and some *p*-X-indanediones were studied by ^{1}H-NMR spectroscopy[10]. A series of 265 *ortho*-substituted substances of this class, of which 210 well correlated with the Hammett equation

$$Q_X = \alpha\sigma_{I,X} + \beta\delta_{R,X} + h$$

was studied by Charton. The successful correlations with the equation which takes into account only the electronic effects shows that the data are independent of the sterical effects. Some substituents, such as iodine and phenyl, often show spatial effects and a tert-butyl group shows it always but, according to Charton[6], the effect of the *ortho*-substituents is independent of it. The factors upon which the electronic effect depends[7], given by $\varepsilon = \beta/\alpha$, vary markedly from zero to infinity, *viz.* from a purely inductive to purely mesomeric effect. This variability makes it impossible to determine simple, universal σ_0 constants. Hammet's correlations are applicable to *ortho*-substituted series where the reaction center and the substituent are well separated. The possibility of correlating well *ortho* with otherwise substituted, derivatives indicates that, virtually, no sterical effect exists.

The objective of the present work was to study the transfer of the effects of the substituents upon the chemical shift in ^{1}H-NMR spectra of the methine proton of X-indandiones *I*, *ortho*-X-phthalides *II* and *ortho*-X-dithiaphthalides *III*. The chemical shifts of the methine proton of the three series of compounds were correlated with various constants of the substituents. Coplanarity and steric effects in X-indanediones *I* have also been studied within this work.

EXPERIMENTAL

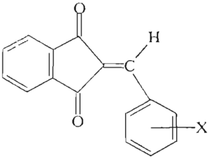
The syntheses and properties of *ortho*-X-indanediones *I* (ref.[4,8]), *ortho*-X-phthalides *II* (ref.[9]) and *ortho*-X-dithiaphthalides *III* (ref.[4,8]) have been described. The ^{1}H-NMR spectra (80 MHz) for 10% solutions in $CDCl_3$ with tetramethylsilane as the internal standard were obtained with a Tesla BS 487 instrument. For less soluble substances the measurements were run with saturated solutions. Linear correlations were calculated with a Hewlett–Packard, Model 9100 B electronic desk calculator using statistical equations for regressive analysis. Two- and three-parameter correlations were calculated with a Siemens 4004/150 computer.

RESULTS AND DISCUSSION

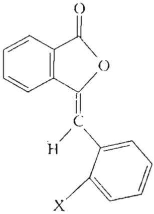
In contrast to benzalphthalides, in the spectra of which the *o*-protons on the phenyl ring are overlapped by other aromatic protons and form one multiplet, the *ortho*-protons of 2-benzal-1,3-indanedione and his derivatives show a marked downfield shift and appear as a separate multiplet at δ 8·45 – 8·93. The pronounced deshielding observed can be explained by a diamagnetic anisotropy of the carbonyl group. A similar effect was observed by Agranat and coworkers[10]. At δ 7·8 – 8·5 there is a sharp singlet of the methine proton (Table I).

In an attempt to correlate the chemical shift of the methine proton of indandiones with the σ constants no statistically important results were obtained even when corrections taking into account the magnetical anisotropy were made. This, obviously, is caused by two pronounced phenomena upon which the chemical shift of the methine proton depends, namely the effects of the substituents and that of the neighbouring carbonyl group. Owing to different structure of phthalides the effect of the carbonyl group does not operate in these substances, which is confirmed by good correlation with σ constants in the case of *o*-*X*-phthalides *II*.

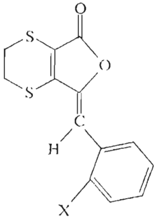
Two overlapped multiplets of aromatic protons (δ 6·8 – 8·4) were observed in the ^{1}H-NMR spectra of *o*-X-phthalides. The singlet of the methine proton appears at δ 6·48 – 6·92 (Table II). In the spectra of *o*-X-dithiophthalides *III* CH_2 groups appear as a singlet at ~δ 3·3 and their chemical shift is independent of the surrounding substituents. In addition, the spectra show at δ 5·86 – 6·45 a singlet of the methine proton (Table II). The upfield shift observed with dithiaphthalides, compared with the spectra of benzalphthalimides and constant (Δ ppm ~ 0·5) for all derivatives under investigation, is caused by different structure of the basic skeleton of the two types of derivatives (different type of conjugation). Also, the multiplet of aromatic protons at δ 6·8 – 8·3 is less complicated as in the spectra of benzalphthalides.



I



II



III

A comparison of the relative chemical shift of the methine proton in the spectra of 2-benzal-1,3-indanedione and its *o*-methoxy derivative with those in the spectra of benzalphthalides and benzaldithiaphthalides shows that owing to the presence of the methoxy group the signal of the methine proton is in all three series of substances (*I*, *II*, *III*) shifted downfield ($\delta_{(CH)}$ = 0·616, −0·552 and −0·590, respectively). This phenomenon can be accounted for the pronounced field effect operating between the oxygen atom of the methoxy group and a methine proton. The presence of a bulkier group at the same position (ethoxy, isopropoxy) does not alter the chemical shift of the methine proton showing, that the shift of the methine proton is influenced by polar interactions and is independent of the bulkiness of the substituent. The same follows from a reasonable correlability of the methyl group where there is no possibility of polar interactions. With *p*-X-phthalides *II* and *p*-X-dithiaphthalides *III* the data observed for the methoxy derivatives show no deviation from the linear dependence. A comparison of the chemical shift of the methine proton of 2-(2,4-dichlorobenzal)-1,3-indanedione and 2-(2,6-dichlorobenzal)-1,3-indanedione shows that the 6-substituent on the phenyl ring causes a pronounced upfield shift, since it noticeably makes the ring bend out of the plane of the molecule (steric factors) shortening thus the conjugation. At the same time, the field effect of the substituent upon the

TABLE I

The Chemical Shifts Found for 2-(X-Benzal)-1,3-indanediones *I*

Compound	X	δ(CH)	Δδ(CH)[a]
1	2-OC_2H_5	8·508	0·645
2	2-$OCH(CH_3)_2$	8·490	0·627
3	2,5-$(OCH_3)_2$	8·483	0·620
4	2-OCH_3	8·479	0·616
5	2,4-$(OCH_3)_2$	8·470	0·607
6	2-Cl	8·313	0·450
7	2-NO_2	8·275	0·412
8	2,4-Cl_2	8·252	0·389
9	2-Br	8·246	0·383
10	2-CH_3	8·230	0·367
11	2-F	8·196	0·333
12	2,4,6-$(OCH_3)_3$	8·020	0·157
13	2,3,4,5,6-F_5	7·931	0·068
14	2-COOH	7·885	0·022
15	H	7·863	0·0
16	2,6-Cl_2	7·840	—0·023

[a] Δδ(CH) = relative chemical shift, $\delta(CH)_X - \delta(CH)_H$.

TABLE II

The Chemical Shifts Found for 3-(2-X-Benzal)phthalides *II* and 3-(2-X-Benzal)-5,6-dihydro-4,7-dithiaphthalides *III*

Compound	X	Series *II*		Series *III*		
		δ(CH)	Δδ(CH)[a]	δ(CH)	Δδ(CH)[a]	$\delta(CH_2)$
1	2-OCH_3	6·920	—0·552	6·450	—0·590	3·327
2	2-CH_3	6·588	—0·220	6·080	—0·220	3·320
3	2-NH_2	6·485	—0·117	—	—	—
4	H	6·368	0	5·860	0	3·297
5	2-F	6·670	0·302	6·195	0·335	3·350
6	2-J	6·709	0·341	6·226	0·366	3·347
7	2-Br	6·834	0·466	—	—	—
8	2-Cl	6·853	0·485	6·383	0·523	3·351
9	2-NO_2	7·009	0·641	—	—	—

[a] Δδ(CH) = relative chemical shift, $\delta(CH)_X - \delta(CH)_H$.

methine proton becomes less pronounced. In agreement with IR and UV spectra, as well as with works of others[10,11], the above-mentioned observations were confirmed for all 2,6-substituted derivatives (2,6-dichloro-, 2,3,4,5,6-pentafluoro-, and 2,4,6-trimethoxybenzal-1,3-indanedione), whereas the phenomenon was not observed for the 2,4- and 2,5- disubstituted compounds (2,4-dichloro-, 2,4-dimethoxy-, and 2,5-dimethoxybenzal-1,3-indanedione). Thus, substitution at another position of 6-phenyl substituted compounds does not affect substantially the chemical shift of the methine proton. It can therefore be concluded that, similar to benzalphthalides, the chemical shift of the methine proton is not much influenced by polar effects of substituents. This is suggested by chemical shift values observed with 2-chloro- and 2,4-dichlorobenzal-1,3-indanediones, and 2-methoxy-, 2,4-dimethoxy and 2,5-dimethoxybenzal-1,3-indanediones which differ only slightly from each other. Chemical shifts of the methine proton observed by others[10] for some *para*-substituted derivatives, differing only slightly from that of unsubstituted 2-benzal-1,3-indanedione ($\sim$0·08 ppm) confirms this assumption. For none of *p*-X-phthalides and *p*-X-dithiaphthalides does the relative chemical shift exceed the value 0·1 ppm. With *o*-X-phthalides *II* and *o*-X-dithiaphthalides *III* the highest relative chemical shift is 0·65 and 0·59 ppm, respectively. It can be assumed by comparing the relative chemical shifts observed with *para*- and *ortho*-derivatives that the one of the methine proton is but slightly affected by polar effects of substituents. Thus, as far as the *o*-effect of a substituent is concerned, which according to Charton[6] consists of a common electronic and an electron field effects (proximity effect) in *o*-X-indanediones, *o*-X-phthalides and *o*-X-dithiaphthalides the field effect predominates. In other word[5], the effect of substituents is transferred through the system of linkages also by non-bonding interactions.

In the series of *o*-X-phthalides *II* the relative chemical shifts were correlated with σ_p and σ_m (ref.[12]), σ_p^+ (ref.[13]), σ_I and σ_R (ref.[14]) constants. All correlations were $>0{\cdot}93$. Best results were obtained with σ_p constants where the correlation coefficient $r = 0{\cdot}955$, and the standard deviation $s = 0{\cdot}058$.

$$\Delta\delta = (0{\cdot}386 \pm 0{\cdot}03)\,\sigma_p + 0{\cdot}332 \pm 0{\cdot}054\,, \quad n = 7$$

Since in the series of *o*-X-dithiaphthalides *III* there was only a small number of derivatives at hand, a joint correlation for the two series *II* and *III* was made ($r = 0{\cdot}932$, $s = 0{\cdot}059$, $n = 11$). It follows from the fact that for the two series an important correlation was reached, that in both series the effects of the substituents is being transferred by the same mechanism. Also, the very small change of the tangency value shows that in both series the transfer effects of the substituents are quantitatively almost the same.

In addition to the one-parameter correlations a two-parameter correlation with the extended Hammett's equation for the phthalide derivatives *II*

$$\Delta\delta = 0{\cdot}295 \pm 0{\cdot}052 + (0{\cdot}489 \pm 0{\cdot}097)\,\sigma_I + (0{\cdot}332 \pm 0{\cdot}132)\sigma_R\,,$$

$$r = 0{\cdot}945\,. \quad s = 0{\cdot}013\,, \quad n = 7$$

and a joint correlation for the series *II* and *III* were also made ($r = 0{\cdot}931$, $s = 0{\cdot}025$, $n = 11$).

For the series *II* and *III* a three-parameter correlation using constants $\mathcal{F}$ and $\mathcal{R}$ (ref.[15]) and Q (ref.[16]) was also calculated and here the obtained results were the best.

$$\Delta\delta = -0{\cdot}035 + 1{\cdot}161\mathcal{F} + 0{\cdot}189\mathcal{R} - 0{\cdot}009Q\,,$$

$$r = 0{\cdot}965\,, \quad s = 0{\cdot}021\,, \quad n = 11$$

The equation shows that there is a pronounced effect of the inductive portion of the polar effect whereas the contribution of the steric factors is almost negligible. The methoxy derivatives were not included in any of the correlations since the values observed with these substances were detrimental to the found results.

Good correlation observed with the series of *o*-X-derivatives *II* and *III* (except methoxy derivatives) with the above-mentioned constants excludes any serious steric effects of *o*-substituents, which is in agreement with Charton's conclusions concerning the *ortho*-effect.

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