^{13}C-NMR STUDY 3-(X-BENZAL)PHTHALIDES AND 2-(X-BENZAL)-1,3-INDANEDIONES

Eva SOLČÁNIOVÁ[a], Pavol HRNČIAR[b] and Tibor LIPTAJ[c]

[a] *Institute of Chemistry,*
[b] *Department of Organic Chemistry,*
Comenius University, 816 00 Bratislava and
[c] *Central Laboratory of NMR Spectroscopy,*
Slovak Institute of Technology, 880 37 Bratislava

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^{13}C-NMR spectra of 14 derivatives of 3-(X-benzal)phthalides (*I*) and 10 derivatives of 2-(X-benzal)-1,3-indanediones (*II*) were investigated. The correlation of ^{13}C chemical shifts of carbon atoms of the phthalide ring with σ-constants showed that the electronic effect of substituents was transmitted from the benzylidene group of 3-(X-benzal)phthalides on the chemical shift of the carbonyl group not only through oxygen, but also through the aromatic ring of the phthalide moiety. The transmission of substituent effects in 2-(X-benzal)-1,3-indanediones on the chemical shift of the carbonyl groups was more pronounced on the carbonyl, which is in the *trans*-arrangement with respect to the aryl group. This phenomenon was also observed at carbon atoms of the benzene ring of the indanedione moiety closer to the *trans*-CO group.

The transmission of electronic effects of substituents to the carbonyl group of 3-(X-benzal)phthalides and their heterocyclic analogues[1-5], and 2-(X-benzal)-1,3-indanediones[6,7] have been studied by IR and ^{1}H-NMR spectroscopies, and also ^{13}C-NMR spectroscopy was employed. ^{13}C-NMR spectra of 1,3- and 1,2-indanediones and their heterocyclic analogues have already been studied[8,9].

All quaternary carbons $C_{(1)}$, $C_{(1')}$, $C_{(3)}$, $C_{(8)}$ and $C_{(9)}$ of 3-(X-benzal)phthalides (*I*) were distinguished from protonated carbons by $^{13}C\{^1H\}$ off-resonance spectra and their specific assignment (Table I) was done by comparison of the spectra and by qualitative arguments. The signal in the lowest field corresponds to carbonyl carbon $C_{(1)}$. The relatively low value of the chemical shift of carbonyl carbon is mainly due to a $-I$ effect of the lactone ring oxygen, which lowers the polarity of the carbonyl π-bond by its electron-accepting effect. This value was also in agreement with that reported[8] for phthalic anhydride. The relatively high value of chemical shift of $C_{(3)}$ and the low one of $C_{(10)}$ indicated a considerable polarization of the C=C double bond due to an effective cross-conjugation of the lone electron pairs of the lactone ring oxygen. The unambiguous assignment of chemical shift of carbons $C_{(8)}$ and $C_{(9)}$ was adduced from the spectra of 5-bromo-3-benzalphthalide and 6-bromo-3-benzalphthalide, which were synthesized for this purpose. The best accordance of the anticipated values with the experimental ones was achieved from comparison of the effect of bromine[10] on the chemical shifts of $C_{(8)}$ and $C_{(9)}$, when $\delta C_{(8)} < C_{(9)}$.

Signals of aromatic carbons of the phthalide skeleton $C_{(4)}$—$C_{(7)}$ were assigned by application of the qualitative arguments. Chemical shifts of $C_{(4)}$ and $C_{(7)}$ are in a higher field than those of $C_{(5)}$ and $C_{(6)}$ in accordance with the literature[8]. The assignment $\delta C_{(6)} < \delta C_{(5)}$ followed from the fact that $C_{(5)}$ is in *para*-position in respect to the carbonyl group. Moreover, the unambiguity of this assignment was again evidenced by the spectra of 3-bromo- and 6-bromo-3-benzalphthalides (Table I). Signals of aromatic carbons $C_{(1')}$—$C_{(6')}$ were assigned by comparison of the spectra and by application of the additive constants of substituents at the aromatic ring[10]. 1,3-Indanedione[8] displayed in the ^{13}C-NMR spectra only one signal for both carbonyl groups, since the molecule is symmetric. Derivatives of 2-(X-benzal)-1,3-indanediones (*II*) have their molecules asymmetric and consequently, both carbonyl groups are unequal. The non-bonding interactions of benzylidene aromatic ring with one carbonyl group caused that the chemical shifts $C_{(1)}$ and $C_{(3)}$ differ from each other. Their signals appeared in the region of higher frequencies when compared with other carbons and therefore, their identification was unequivocal. Since the difference in chemical shift of carbonyl carbons is small, approximately 1 ppm, it was impossible to make assignment, and, as a consequence, neither to determine the configuration at the ethylenic bond.

As found, the vicinal coupling constants ^{13}C, ^{1}H $^{3}J(trans)$ were greater than $^{3}J(cis)$ in mono-, di- and trisubstituted alkenes. This criterion was used for the configurational assignment especially in those compounds, where the difference in chemical shifts of two isomers was not significant, or where only one isomer was available. The 2-(X-benzal)-1,3-indanediones constitutted a special case, where one carbonyl group in the molecule is in a *trans*-arrangement and the other in a *cis*-arrangement with respect to the vicinal vinyl proton. The stereochemical assignment and thereby the assignment of chemical shifts to both carbons was proved by high resolution ^{13}C-NMR spectra with proton interaction measured in the region of carbonyl frequencies. We found the values of vicinal coupling constants of 2-benzal-1,3-indanedione ^{3}J (CO, H) to be 10 Hz for the signal of the carbonyl group in the higher field and 6 Hz for that in the lower field. These values are in line with those reported[11] for α, β unsaturated carboxylic acids ^{3}J(COOH, H; *trans*) 14·5 – 12·8 Hz and ^{3}J(COOH, H; *cis*) 7·5 – 6·5 Hz. The decrease of values of vicinal C, H coupling constants might be due to various structural factors as *e.g.* are the nature of the functional group (CO), steric interactions between the functional group (CO) and the *cis*-oriented substituent (C_6H_5), substitution of the double bond by electronegative groups (CO, C_6H_5). The lower value of the chemical shift was assigned to the carbonyl, which is *cis*-oriented with regard to the phenyl ring of the benzylidene grouping.

TABLE I

^{13}C Chemical Shifts (ppm) of 3-(X-Benzal)phthalides (*I*) in $CDCl_3$

X	$C_{(1)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	$C_{(1')}$	$C_{(2')}$	$C_{(3')}$	$C_{(4')}$	$C_{(5')}$	$C_{(6')}$
H	166·8	144·4	119·7	134·3	129·6	125·2	123·1	140·4	106·9	133·0	130·0	128·6	128·2	128·6	130·0
4′-NH_2	167·5	142·2	119·3	134·2	128·9	125·5	122·9	141·0	107·7	123·6	131·9	115·1	147·0	115·1	131·9
4′-OCH_3^{d}	167·2	143·0	119·5	134·3	129·2	125·4	123·0	140·7	106·9	125·9	131·6	114·2	159·7	114·2	131·6
4′-F^{e}	166·8	144·1	119·7	134·5	129·7	125·5	123·2	140·4	105·8	129·3	131·8	115·8	162·4	115·8	131·8
4′-Cl	166·7	144·8	119·8	134·6	130·0	125·5	123·3	140·2	105·6	131·6	131·2	128·9	134·1	128·9	131·2
4′-Br	166·6	145·0	119·8	134·5	130·0	125·6	123·4	140·3	105·7	131·9	131·4	131·9	122·5	131·9	131·4
4′-I	166·5	145·1	119·8	134·5	129·9	125·6	123·4	140·2	105·7	132·5	131·5	137·8	94·3	137·8	131·4
4′-NO_2	166·1	146·8	120·3	134·9	130·4	125·9	123·7	139·9^{a}	104·2	139·6^{a}	130·9	124·0	147·4	124·0	130·9
3′-CH_3^{f}	167·0	144·4	119·7	134·4	129·6	125·5	123·4	140·7	107·2	133·0	130·6	138·3	128·6	127·3	129·3
3′-OCH_3^{g}	166·8	144·7	119·8	134·4	129·7	125·6	123·5	140·6	106·9	134·4	115·1	159·8	114·5	129·6	122·8
3′-F^{h}	166·5	145·3	119·9	134·6	130·1	125·5	123·4	140·1	105·6	135·1	116·4	162·8	115·2	130·0	125·8
3′-Cl	166·5	145·4	119·9	134·5	130·1	125·6	123·5	140·2	105·3	134·6^{a}	129·8^{b}	134·8^{a}	128·2^{c}	129·6^{b}	128·1^{c}
3′-Br	166·4	145·4	119·9	134·5	130·1	125·6	123·4	140·1	105·2	135·1	132·5	122·7	131·1	130·1	128·4
3′-I	166·4	145·3	119·9	134·5	130·0	125·6	123·4	140·1	105·1	135·2	138·4	94·5	137·0	130·3	129·0
5-Br	166·0	143·1	123·0	129·8	133·0	126·8	122·1	142·1	108·3	132·6	130·2	128·9	128·9	128·9	130·2
6-Br	165·5	143·8	121·2	137·6	123·7	128·5	125·1	139·2	108·0	132·8	130·3	128·9	128·9	128·9	130·3

[a,b,c] Values of the same lettering can be interchanged; [d] OCH_3 55·2 ppm; [e] coupling constants in Hz, $^1J(CF) = 250·0$, $^2J(CF) = 22·1$, $^3J(CF) = 8·1$, $^4J(CF) = 2·9$; [f] CH_3 21·3 ppm; [g] OCH_3 55·3 ppm; [h] coupling constants in Hz, $^1J(CF) = 244·9$, $^2J(CF) = 22·4$, $^3J(CF) = 8·8$, $^4J(CF) = 2·9$.

TABLE II

^{13}C Chemical Shifts (ppm) of 2-(X-Benzal)-1,3-indanediones (*II*) in $CDCl_3$

X	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}{}^a$	$C_{(5)}{}^b$	$C_{(6)}{}^b$	$C_{(7)}{}^a$	$C_{(8)}{}^c$	$C_{(9)}{}^c$	$C_{(10)}$	$C_{(1')}$	$C_{(2')}$	$C_{(3')}$	$C_{(4')}$	$C_{(5')}$	$C_{(6')}$
H	190·2	129·2	188·9	123·3	135·2	135·4	123·4	142·6	140·1	146·9	133·2	134·2	128·8	133·2	128·8	134·2
4'-OCH_3^{d}	190·7	126·6	189·5	123·1	134·8	135·0	123·1	142·4	140·0	146·8	126·5	137·2	114·4	164·1	114·4	137·2
4'-CH_3^{d}	190·4	128·3	189·1	123·3	135·1	135·3	123·3	142·6	140·1	147·2	130·7	134·5	129·7	144·7	129·7	134·5
4'-Cl	189·8	129·4	188·9	123·4	135·3	135·5	123·4	142·5	140·1	145·1	131·5	135·3	129·1	139·5	129·1	135·3
4'-Br	189·8	129·6	188·9	124·4	135·4	135·5	123·4	142·5	140·1	145·2	131·9	135·4	132·1	128·4	132·1	135·4
4'-NO_2	189·1	132·3	188·4	123·8	135·9	136·0	123·8	142·7	140·4	142·7	138·5	134·3	123·7	156·5	123·7	134·3
3'-OCH_3^{d}	190·0	129·1	189·0	123·3	135·1	135·3	123·3	142·5	139·9	147·0	134·3	120·7	159·7	116·8	129·5	127·7
3'-Cl	189·7	130·4	188·7	123·5	135·5	135·7	123·6	142·7	140·2	144·9	134·8	133·3	134·7	132·8	130·0	132·1
3'-Br	189·7	130·3	188·8	123·5	135·5	135·7	123·5	142·6	140·2	144·8	134·9	136·3	122·8	135·7	130·2	132·5
3'-I	189·7	130·3	188·7	123·5	135·4	135·6	123·5	142·6	140·2	144·7	135·0	142·2	94·2	141·5	130·3	133·0

^{a,b,c} Values of the same lettering can be interchanged; ^{d} chemical shifts of other groups: 4'-OCH_3 = 55·6, 4'-CH_3 = 21·9, 3'-OCH_3 = 55·5.

The chemical shifts of carbons $C_{(8)}$ and $C_{(9)}$ were little influenced by substituents and therefore, they could be unambiguously identified. Signals of protonated carbons were assigned by $^{13}C\ \{^1H\}$ off-resonance experiments and ascribed to individual atoms on the basis of spectral comparison (Table II). Nonetheless, the unequivocal assignment to the symmetrically equivalent carbons $C_{(8)} \leftrightarrow C_{(9)}$, $C_{(4)} \leftrightarrow C_{(7)}$ and $C_{(5)} \leftrightarrow C_{(6)}$ was impossible on the basis of ^{13}C-NMR spectral analysis. Signals of $C_{(1')}$—$C_{(6')}$ were assigned by comparing the spectra with respect to the effect of substituents[10].

The comparison of slopes of linear correlation of chemical shifts with σ-constants[12] (Table III) for $C_{(3)}$ and $C_{(10)}$ of phthalides and $C_{(2)}$ and $C_{(10)}$ of 1,3-indanediones

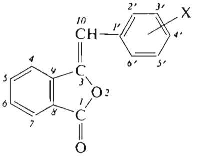
TABLE III

Results of Correlations of ^{13}C Chemical Shifts of 3-(X-Benzal)phthalides (*I*) and 2-(X-Benzal)-1,3-indanediones (*II*) with σ-Constants of Substituents

Series	Parameter	δ_0[a]	Q[b]	r[c]	n[d]	s.d.[e]	t[f]
I	$C_{(1)}$	0·059	—1·019	0·988	14	0·059	22·09
	$C_{(3)}$	—0·183	3·151	0·989	14	0·179	22·99
	$C_{(4)}$	—0·012	0·629	0·975	14	0·052	15·26
	$C_{(5)}$	0·112	0·425	0·886	14	0·081	6·62
	$C_{(6)}$	0·033	1·117	0·985	14	0·071	19·70
	$C_{(7)}$		does not correlate				
	$C_{(8)}$	0·143	0·547	0·896	14	0·098	6·99
	$C_{(9)}$	0·078	—0·822	0·946	14	0·104	10·11
	$C_{(10)}$	—0·516	—2·559	0·910	14	0·423	7·60
	$C_{(1')}$	—2·177	10·675	0·917	14	1·685	7·97
II	$C_{(1)}$	—0·002	—1·412	0·996	10	0·040	31·50
	$C_{(2)}$	—0·597	4·642	0·973	10	0·363	11·95
	$C_{(3)}$	0·167	—0·868	0·942	10	0·103	7·93
	$C_{(4)}$	—0·006	0·570	0·962	10	0·054	9·94
	$C_{(5)}$	—0·067	0·917	0·964	10	0·084	10·23
	$C_{(6)}$	—0·072	0·844	0·960	10	0·081	9·66
	$C_{(7)}$	—0·085	0·565	0·936	10	0·070	7·52
	$C_{(8,9)}$		does not correlate				
	$C_{(10)}$	—0·515	—4·189	0·917	10	0·603	6·50
	$C_{(1')}$	—1·785	9·469	0·919	9[g]	1·440	6·60

[a] δ_0 the intercept; [b] the slope of linear relation $\Delta\delta = \delta_0 + Q\sigma$; [c] r correlation coefficient; [d] n number of correlated derivatives; [e] standard deviation; [f] Student's t-test; [g] without 4'-Br derivative.

showed that the values of slopes for phthalides were substantially lower (approximately by 1/3), the reason being that the phthalide moiety of 3-(X-benzal)-phthalides (*I*) acts as an electron donor, whilst with 2-(X-benzal)-1,3-indandiones (*II*) the indanedione moiety acts as an electron acceptor.



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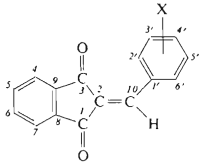

II

It has been ascertained[1] on the basis of results of correlation $\nu(CO)$ with σ-constants and the same values of line slopes of transmission of substituent effect from the benzylidene group to the carbonyl group of 3-(X-benzal)phthalides and 2-(X-benzal)-6-azaphthalides that the effects of substituents were transmitted mainly through lone electron pairs of lactone ring oxygen. The correlation of the ^{13}C-NMR chemical shifts of the individual carbon atoms with σ-constants (Table III) showed that the transmission of substituent effects from the benzylidene group to the carbonyl group proceeds in two ways: through oxygen of the lactone ring and through the aromatic ring of phthalide moiety. The transmission of substituent effect also through the aromatic ring of the phthalide moiety was evidenced by the high value of the line slope for $C_{(6)}$, which is, with respect to the benzylidene group, in *para*-position and consequently, the transmission to $\delta C_{(6)}$ is most effective. The finding that $\delta C_{(7)}$ does not correlate with σ-constants could be rationalized by the fact that the final substituent effect is the difference of the effect transmitted through the carbonyl group and aromatic ring of the phthalide moiety.

The electronic effects of substituents were transmitted in molecules of 2-(X-benzal)-1,3-indanediones (*II*) through the system of bonds in two ways, through atoms $C_{(1)}$ and $C_{(3)}$. The final effect in the aromatic ring is the difference of the effect transmitted through atoms $C_{(1)}$ and $C_{(3)}$. Both parts of substituent effects interferred mostly in positions $C_{(8)}$ and $C_{(9)}$ ($\delta C_{(8)}$ and $\delta C_{(9)}$ do not correlate with σ-constants) and at least in positions $C_{(5)}$ and $C_{(6)}$. The nonbonding interactions of the aromatic ring of the benzylidene grouping with one carbonyl group caused not only that the chemical shifts of carbonyl groups $C_{(1)}$ and $C_{(3)}$ are different, but this interaction was even more pronounced with transmission of substituent effect on the chemical shifts of carbons $C_{(1)}$ and $C_{(3)}$ and thereby on the remaining atoms of the indanedione skeleton. The transmission of the substituent effect from the benzylidene group to the chemical shift of the carbonyl group in a *trans*-position with regard to the phenyl ring of the benzylidene group is much more effective (by 1/3) than to the carbonyl group in *cis*-arrangement. The transmission coefficient $k = \varrho C_{(1)}/\varrho C_{(3)} = 1{\cdot}60$ is of the same value as the ratio of vicinal constants ^3J(CO, H; *trans*)/^3JCO, H; *cis*) = 1·63, this providing an evidence that both chemical shift and coupling constants affected the same structural factors.

EXPERIMENTAL

The synthesis and constants of 3-(X-benzal)phthalides (*I*) and 2-(X-benzal)-1,3-indanediones (*II*) were already reported[13,14]. The ^{13}C-NMR spectra were measured with a JEOL FX-100 FT spectrometer operating at 25·05 MHz. Chemical shifts were determined from spectra using proton noise decoupling. 8192 Data points were used to represent a spectral width of 5000 Hz. The spectra of 10% $CDCl_3$ solutions or of saturated solutions were measured at room temperature relative to internal tetramethylsilane. The deuterium signal was used as an internal lock signal. The pulse repetition was 3·6 s and the pulse width 45°. Chemical shifts were determined with an accuracy of ± 1 Hz. The ^{1}H—^{13}C coupling constants ^3J(CO, H) were determined from the high resolution ^{13}C — proton coupled spectra, spectral width 1000 Hz, with the acquisition time 2 s and the pulse repetition 2·5 s. The reproducibility of C, H coupling constants was better than ± 0·5 Hz.

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