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^{1}H-NMR SPECTRA AND SUBSTITUENT EFFECTS IN 3-ARYLMETHYLENEPHTHALIDES AND 3-ARYLTHIOMETHYLENEPHTHALIDES

A.PERJÉSSY[a], M.VIDA[b], P.HRNČIAR[a] and M.LÁCOVÁ[a]

[a] *Department of Organic Chemistry, Komenský University, and*
[b] *Department of Physical Chemistry, Slovak Institute of Technology, Bratislava*

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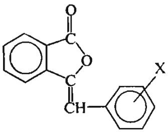
Signals of central methine group C—H proton in ^{1}H-NMR spectra of 22 substituted *trans*-3-phenylmethylenephthalides and *trans*-3-phenylthiomethylenephthalides were studied. In both series of the phthalides the chemical shifts of methine proton correlated well with σ constants of substituents. Serious deviations from the linear dependence of τ on σ observed in the case of halogeno substituted 3-arylmethylenephthalides were accounted for by steric effect of the bulky halogeno substituents. It was found that transmission of electronic effects of substituents on methine proton proceeds better in 3-arylthiomethylenephthalides than in 3-arylmethylenephthalides. For this positive bridge effect the transmissive factor of electronic effects of substituents through sulphur atom $\bar{\pi}$ (s) = 1·29 was calculated.

In previous works[1-3] we have studied electronic effects of substituents and their transmission in *trans*-3-arylmethylenephthalides and *trans*-3-arylthiomethylenephthalides by means of IR spectra in the region of the C=O stretching vibrations.

Within the framework of this study, in the present work we have examined transmission of electronic effects in 3- and 4-substituted *trans*-3-phenylmethylenephthalides (*I*) and *trans*-3-phenylthiomethylenephthalides (*II*) by ^{1}H-NMR spectroscopy, studying signals of central methine group C—H protons. The ^{1}H-NMR spectra of these compounds have not so far been reported.



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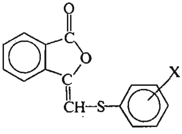

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EXPERIMENTAL

Preparation of *trans*-3-arylmethylenephthalides (*I*) and *trans*-3-arylthiomethylenephthalides (*II*) was reported elsewhere[4,5]. Melting points of the studied compounds agreed well with literature data. All the compounds were recrystallized prior to their application, and their purity was checked by IR and UV spectroscopy.

Proton high resolution NMR spectra were measured on Tesla BS 487 spectrometer, working at 80 MHz. The measurements were made in frequency sweep mode, using $5 . 10^{-2}$M solutions of the compounds in hexadeuterioacetone, or saturated solutions, when a given compound was less soluble. The temperature was 24 ± 1°C. The solvent, hexadeuterioacetone (isotopic purity 98·4% at., supplied by Isocomerz), contained 3 w.% of tetramethylsilane which was used as internal standard. The chemical shifts were read with accuracy of $\pm 0{\cdot}02$ p.p.m. The concentration dependence of the C—H proton chemical shift was measured with 3-phenylmethylenephthalide in the range of concentrations 10^{-2}—$5 . 10^{-2}$M.

The chemical shifts were correlated with constants σ reported by McDaniel and Brown[6]. Parameters of linear correlations were computed on a digital computer, using statistical relations given in ref.[7].

RESULTS AND DISCUSSION

In the NMR spectra of 3-arylmethylenephthalides (*I*) and 3-arylthiomethylenephthalides (*II*) we have observed the two overlapping, complex multiplets corresponding to protons of aromatic rings. The AA′XX′ system of the phthalide aromatic ring is located at τ 1·63–2·15 and the multiplet of phenyl protons at τ 2·15–3·34. In addition, the spectra show the line of central methine C—H proton, which lies

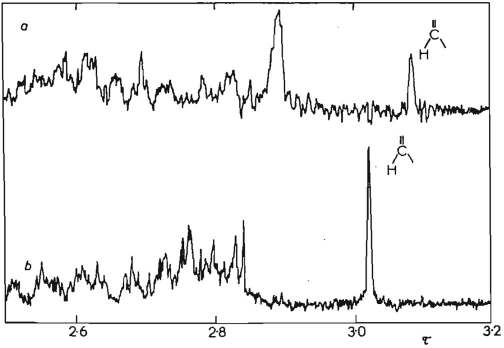

FIG. 1

^{1}H-NMR Spectrum of $5 . 10^{-2}$M 3-Phenylmethylenephthalide (*a*) and $5 . 10^{-2}$M 3-Phenylthiomethylenephthalide (*b*) in Hexadeuterioacetone at τ 3·04 – 3·38 in the phthalides *I*, while in the thio-derivatives *II* it is located in the region of τ 2·85 – 3·25. The corresponding part of the spectra of both parent compounds of the studied series is shown in Fig. 1. As follows from the figure the line of C—H proton, the determination of chemical shift of which was one of the aims of this study, is a singlet, more or less isolated from other lines. The assignment of the line of C—H proton is in all the compounds studied quite unequivocal, except 3-(4-aminophenylmethylene)phthalide (Fig. 2). In the latter case, in the region of the C—H proton line there occur also other lines belonging to the part of AA'XX' system of the substituted phenyl group. As it is seen from Fig. 2, the problem of the assignment reduced to the decision which of the three lines corresponds to the C—H proton. By comparing with the other part of AA'XX' system we have found that the line of C—H proton lies at highest field, *i.e.* at the right side of the discussed system of the lines. This assignment was also proved by Indor method (Fig. 2).

The bridge sulphur atom in 3-arylthiomethylenephthalides (*II*) makes the protons of substituted phenyl group less shielded, while the protons of the phthalide aromatic ring are not significantly affected. Furthermore, also long-range interaction between the C—H proton and the phenyl group is markedly reduced. The above effects can be seen *e.g.* in the spectra of 3-phenylmethylenephthalide and 3-phenylthiomethylenephthalide shown in Fig. 1.

With the aim to evaluate the effect of a decreased concentration of some compounds (when measuring their saturated solutions) on the C—H proton chemical

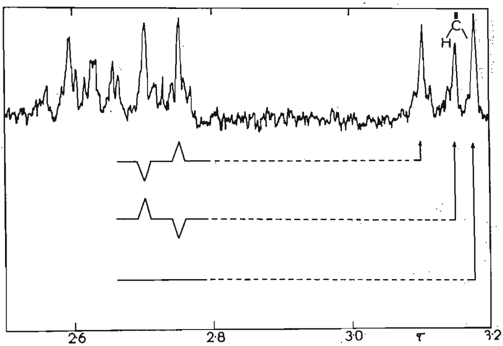

FIG. 2

^{1}H-NMR Spectrum and Indor Spectrum of 3-(4-Aminophenylmethylene)phthalide in Saturated Solution in Hexadeuterioacetone shift, we measured concentration dependence of this line in the range of concentrations which must be considered for these solutions. We have found that the change of the chemical shift upon changing concentration within the given range is lesser than the experimental error. The values of chemical shifts of C—H proton obtained by measuring saturated solutions can be thus used in correlations with structure. A lower field shift of the line on diluting by non-aromatic solvent is caused by magnetic anisotropy of studied compounds.

As seen from Tables I and II, in both series the substituents with electronacceptor properties shift the signal of the C—H proton to the higher, and those acting as electrondonors to the lower field, relative to the corresponding signal of the parent compounds. This indicates that a correlation between C—H proton chemical shift and substituent effects could be detected in both series of the studied compounds.

TABLE I

Chemical Shifts of C—H Proton in 3-Arylmethylenephthalides (*I*) and σ Substituent Constants

Compound	X	σ	τ	Compound	X	σ	τ
1	4-NH_2	−0·66	3·38[a]	*8*	4-I	0·18	3·25[a]
2	4-OCH_3	−0·27	3·26	*9*	4-Cl	0·23	3·21
3	4-CH_3	−0·17	3·26	*10*	4-Br	0·23	3·23[a]
4	3-CH_3	−0·07	3·25	*11*	3-F	0·34	3·18
5	H	0·00	3·21	*12*	3-I	0·35	3·26
6	4-F	0·06	3·21	*13*	4-NO_2	0·78	3·04[a]
7	3-OCH_3	0·12	3·23				

[a] Measured in saturated solutions of the compounds (see Experimental).

TABLE II

Chemical Shifts of C—H Proton in 3-Arylthiomethylenephthalides (*II*) and σ Substituent Constants

Compound	X	σ	τ	Compound	X	σ	τ
14	4-NH_2	−0·66	3·25[a]	*19*	4-Cl	0·23	3·06[a]
15	4-CH_3	−0·17	3·14	*20*	3-Cl	0·37	2·99[a]
16	H	0·00	3·09	*21*	3-NO_2	0·71	2·89[a]
17	4-I	0·18	3·06	*22*	4-NO_2	0·78	2·85[a]
18	4-Br	0·23	3·06				

[a] Measured in saturated solutions of the compounds (see Experimental).

In the series of 3-arylmethylenephthalides (*I*), 10 of the measured values of C—H proton chemical shifts can be well correlated with σ constants of substituents (Eq. (*1*), Fig. 3), correlation coefficient $r = 0{\cdot}969$, standard deviation $s = \pm 0{\cdot}02$.

$$\tau = (-0{\cdot}213 \pm 0{\cdot}019)\,\sigma + (3{\cdot}23 \pm 0{\cdot}00)\,. \qquad (1)$$

As seen in Fig. 3, the values of the chemical shifts for 3-iodo, 4-iodo, and 4-bromo derivatives were not included into correlation as their deviations (toward higher values of τ) are greater than experimental error. When all the 4-halogeno derivatives and 3-iodo derivative are excluded, the slope of the so obtained correlation is nearly the same as that found in the preceding case (Eq, (*2*); Fig. 4), $r = 0{\cdot}976$, $s = \pm 0{\cdot}02$.

$$\tau = (-0{\cdot}220 \pm 0{\cdot}018)\,\sigma + (3{\cdot}22 \pm 0{\cdot}00)\,. \qquad (2)$$

The inspection of the chemical shifts of the 4-halogeno derivatives (Fig. 4) reveals that their deviations from the regression line towards higher values of τ increase in the order Cl < Br < I, the chemical shift in the fluoro derivative being almost on the line. The calculated deviations of the C—H proton chemical shifts of the halogeno derivatives from the regression line are given in Table III. Fig. 5 shows that these deviations can be well correlated with Van der Waals atom radii of the halogens. An analogous, nearly linear dependence is also obtained by the use of covalent radii of halogen atoms. On the other hand, there is no linear relationship between the above deviations and mass of the substituents. As follows from the foregoing discussion, the deviations of the chemical shifts of C—H proton of the above halogeno-

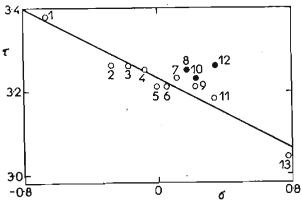

FIG. 3

Dependence of Chemical Shift of C—H Proton of 3-Arylmethylenephthalides (*I*) on σ

○ The points included into correlation, ● the points not included. Numbering of compounds see Table I.

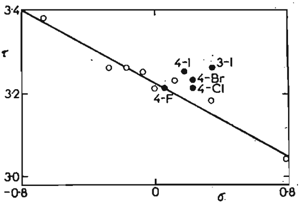

FIG. 4

Dependence of Chemical Shift of C—H Proton of 3-Arylmethylenephthalides (*I*) on σ

For designation of points see Fig. 3.

TABLE III

Deviations of Chemical Shifts of C—H Proton from the Linear Dependence of τ on σ and Van der Waals Atom Radii for 3-(4-Halogenophenylmethylene)phthalides *I*

X	Δτ, p.p.m.	r, Å	X	Δτ, p.p.m.	r, Å
4-F	0·000	1·35	4-Br	0·058	1·95
4-Cl	0·038	1·80	4-I	0·066	2·15

phenylmethylenephthalides are probably due to steric effect of bulky halogen atoms on the shielding constant of the C—H proton. The deviation from the τ–σ plot of the chemical shift of the C—H proton of 3-(3-iodophenylmethylene)phthalide is about twice as great (Δτ = 0·114 p.p.m.) as that of 3-(4-iodophenylmethylene)phthalide (Δτ = 0·066 p.p.m.). Similarly, also the value for 3-(3-fluorophenylmethylene)phthalide does not lie on the regression line, in contrast to 3-(4-fluorophenylmethylene)phthalide. The above findings indicate that the mentioned steric effect on the shielding constants increases about twice when halogen is attached to the position closer to the methine group, *i.e.* to position 3 of the phenyl ring.

The chemical shifts for all nine 3-arylthiomethylenephthalides studied (*II*) correlate well with σ values (Eq. (*3*), Fig. 6), $r = 0·984$, $s = \pm 0·02$.

$$\tau = (-0·275 \pm 0·017)\,\sigma + (3·09 \pm 0·01)\,. \qquad (3)$$

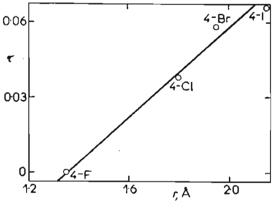

FIG. 5

Correlation of the Deviation of C—H Proton Chemical Shifts from the τ–σ Plot with Van der Waals Radii for 3-(4-Halogenophenylmethylene)phthalides

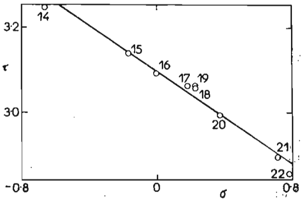

FIG. 6

Dependence of Chemical Shift of C—H Proton of 3-Arylthiomethylenephthalides (*II*) on σ

Numbering of compounds see Table II.

In Fig. 6 it is seen that the values of chemical shifts even in the derivatives with bulky halogeno substituents deviate from the regression line only within the experimental error. This can probably be accounted for by the fact that, due to sulphur bridge, the methine group is more remote from the substituents on phenyl group, which minimizes steric effect of substituents on the shielding constant.

The greater value of the slope of the τ–σ plot observed in the case of 3-arylthiomethylenephthalides (*II*), relative to the compounds *I*, indicates that the introduction of bridge sulphur atom "improves" the transmission of electronic effects of substituents from the substituted phenyl group on the methine hydrogen. A similar effect has already been reported by Litvinenko[8,9] in a study of the kinetics of reactions of substituted diphenyl sulphides and diphenyls and called "positive bridge effect", in contradistinction to "negative bridge effect", *i.e.* the case when the electronic effects are transmitted to a lesser extent upon introduction of a bridge atom. If, in the studied systems *I* and *II*, the reaction center is the methine hydrogen, then the observed positive bridge effect relates to the transmission of electronic effects in the arylthiomethylene part of 3-arylthiomethylenephthalide (*II*). This effect can be expressed by the transmissive factor of substituent effects through sulphur bridge: $\acute{\pi}(\mathrm{S}) = \varrho(II)/\varrho(I) = 1{\cdot}29$.

Quite different situation arises, however, when the carbonyl group becomes reaction center. In a study of substituents effects in the above systems by means of the C=O stretching frequency shifts it has been found[2] that the introduction of bridge sulphur atom into the structure of 3-arylmethylenephthalides brings about the negative bridge effect (the transmissive factor $\acute{\pi}(\mathrm{S}) = 0{\cdot}62$).

An entirely analogous situation has also been observed[10] in a study of half-wave potentials of polarographic reduction of the central double bond in series *I* and *II*. From the foregoing it follows that bridge sulphur atom in 3-arylthiomethylenephthalides affects transmission of electronic effects on reaction center in two different ways, depending on the relative position of the bridge and the center. It is well known that in planar systems negative bridge effects are more frequent than the positive effects. In the case of diphenyl sulphide and diphenyl derivatives[8,9] the positive bridge effects of sulphur can be explained by distorted coplanarity of the aromatic rings in diphenyl derivatives, which results in less efficient transmission of substituent effects in these compounds, relative to diphenylsulphide derivatives. According to current ideas the substituted benzene ring and the central double bond in 3-arylmethylenephthalides are more coplanar than the benzene rings in the diphenyl system. Hence, the positive bridge effect of sulphur bridge observed in the system under study can probably be explained in terms of non-bonding interaction between the orbitals of sulphur atom and of the methine hydrogen (these are located in the close vicinity to each other) which facilitates the transmission of electronic effects on the methine proton. In the case of substituted toluenes and thioanisols, which were studied by Marcus and coworkers[11] by means of chemical shifts of the methyl proton, this non-bonding interaction is probably suppressed due to hyperconjugation effect of the methyl group, the result being the observed negative bridge effect of sulphur bridge.

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