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APPLICATION OF VIBRATIONAL SPECTROSCOPY TO THE ESTIMATION OF ELECTRON-DONATING PROPERTIES OF ORGANOMETALLIC GROUPS

III *. DETERMINATION OF σ-CONSTANTS OF Ph_nMX AND HX GROUPS ($X = O, S, NR$)

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Summary

It has been established that in compounds of the $Ph_nMXC_6H_6NO_2$ type good linear correlations exist between spectral characteristics and electron-donating properties of $XMPh_n$ groups, namely, the integral intensities of $\nu(Ar)$ and $\nu_s(NO_2)$, for each examined class of compounds. The intensities of $\nu_s(NO_2)$ have been found to be more sensitive to the electronic effect of substituents and solvation effects. The use of these values has made it possible to determine the σ constants which take into account the direct polar conjugation of XH and $XMPh_n$ groups with the reactive center (σ_p^+, σ_R^+). The factors affecting the solvation sensitivity of these values are discussed.

Introduction

The previous papers in this series summarized the results of measuring the intensities of $\nu(Ar)$ ($\sim 1600\ cm^{-1}$) and $\nu_s(NO_2)$ vibrations in derivatives of nitrophenols and nitrothiophenols in IR and Raman spectra [1,2]. These spectroscopic characteristics were shown to be highly sensitive to the electron-donating properties of $SMPh_n$ and $OMPh_n$ groups and dependent on the medium.

It was the purpose of the present work to use the obtained values of integral intensities in derivatives of nitrothiophenols [1] and nitrophenols [2], as well as

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* For part II see ref. 2.

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phenyl derivatives of anilines for quantitative estimation of the electronic effects of Ph_nMX groups in comparison with XH groups. Also studied was the solvation sensitivity of the determined σ constants.

As was shown earlier [1,2], the intensities of $\nu(Ar)$ and $\nu_s(NO_2)$ vibrations in IR spectra ($A(Ar)$, $A_s(NO_2)$) of nitrophenol derivatives are greater than those of the thio analogs, which agrees with the commonly accepted greater capacity for conjugation of the oxygen atom. In Raman spectra, the ratio of intensities of the Raman lines (I^{∞}_{Ar}, $I^{\infty}_{NO_2}$) is inverted ($S > O$). Earlier, some of us arrived at the conclusion, after analysis of similar data for compounds of the Ph_nX and Ph_{n-1}-XAlk types, that the values of I^{∞}_{Ar} are not applicable to the estimation of the degree of conjugation of various X heteroatoms [3]. Since one of the aims of this work was to compare the properties of MPh_n groups associated with different heteroatoms, we used only the intensities of the absorption bands in IR spectra.

Before proceeding to correlation analysis, we examined the relationship between the integral intensities of two absorption bands $A_s(NO_2)$ and $A(Ar)$ in relatively inert solvents (CH_2Cl_2 and benzene) and DMSO. The purpose of regression analysis was to select the spectral parameter that would be most sensitive to the electronic effects of substituents.

Results

As can be inferred from Table 1, good to excellent correlations (r = 0.988—0.999) exist between the values of $A(Ar)$ and $A_s(NO_2)$ in CH_2Cl_2 (C_6H_6) for each class of compounds. For all examined compounds, the $A_s(NO_2)$ intensities are the most sensitive to the electronic effect of substituents. In eqs. 1 to 4, the coefficient ρ is greater than unity and maximum in the case of nitrophenols. The linear relations for nitrophenols (eqs. 2,3) are characterized by excellent correlation factors when both the total intensity of two bands in eq. 2 and the intensity of the low-frequency component of doublet (eq. 3) are used, since the band at 1340—1330 cm^{-1} makes a small and steady contribution [2].

In DMSO, the $A(Ar)$ and $A_s(NO_2)$ intensities become more pronounced, and the slopes in the linear $A(Ar)$—$A_s(NO_2)$ relations for nitrophenol and nitro-

TABLE 1

CORRELATION EQUATIONS OF $A_s(NO_2)$—$A_{(Ar)}$ FOR COMPOUNDS $MXC_6H_4NO_2$(M = H, Ph_nM)

No	X	Relationship	r	s_0
In CH_2Cl_2				
1	S	$A_s(NO_2) = (-0.89 \pm 0.2) + (2.66 \pm 0.14)A_{Ar}$	0.999	0.12
2	O	$\Sigma A_s(NO_2)^a = (-2.20 \pm 0.5) + (3.3 \pm 0.14)A_{Ar}$	0.998	0.28
3	O	$A_{1300} = (-5.94 \pm 0.9) + (3.52 \pm 0.24)A_{Ar}$	0.997	0.48
4	NR	$\Sigma A_s(NO_2)^a = (2.33 \pm 0.6) + (1.8 \pm 0.14)A_{Ar}$	0.988	0.55
In DMSO				
5	O	$A_s(NO_2) = (-18 \pm 2.7) + (7.8 \pm 0.55)A_{Ar}$	0.993	1.1
6	NR	$A_s(NO_2) = (5.9 \pm 2.6) + (4.6 \pm 0.57)A_{Ar}$	0.985	1.9

[a] Taken as $A_s(NO_2)$ was the total intensity of two bands at 1340—1290 cm^{-1}; the factors responsible for the doublet structure of $\nu_S(NO_2)$ will be discussed in a separate publication.

TABLE 2

VALUES OF $A_s(NO_2)$ ((l mol^{-1} cm^{-2}) × 10^{-4}) AND σ CONSTANTS FOR REFERENCE COMPOUNDS OF THE $XC_6H_4NO_2$ TYPE

X	$A_s(NO_2)$	$A_s^{1/2}(NO_2)$	σ_p [5]	σ_p^+ [6]	σ_R^0 [7]	σ_R [7]	σ_R^+ [7]	σ_R^+ [8]	σ_I [7]	σ^0 [8b]
Cl	2.53	1.59	0.227	0.114	−0.23	−0.23	−0.36	−0.19	0.46	0.25
Ph	3.3	1.82	0.01	−0.179	−0.11	−0.11	−0.30	−0.26	0.1	0.035
H	1.92	1.38	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.009
CH_3	2.96	1.72	−0.17	−0.311	−0.11	−0.11	−0.25	−0.22	−0.04	−0.105
OCH_3	4.9	2.21	−0.268	−0.778	−0.45	−0.61	−1.02	−0.71	0.27	−0.078
$N(CH_3)_2$	13.2	3.63	−0.83	−1.7	−0.52	−0.83	−1.75	−1.43	0.06	−0.163

TABLE 3

CORRELATION EQUATIONS OF $A_s^{1/2}(NO_2)$—σ_i

σ_i	Relationship	r	S_0	N
σ_R^0	$A_s^{1/2}(NO_2) = (1.27 \pm 0.3) + (-3.34 \pm 1.06)\sigma_R^0$	0.845	0.49	7
σ_R	$A_s^{1/2}(NO_2) = (1.35 \pm 0.27) + (-2.60 \pm 0.51)\sigma_R$	0.910	0.38	8
σ_P	$A_s^{1/2}(NO_2) = (1.70 \pm 0.14) + (-2.10 \pm 0.37)\sigma_P$	0.937	0.30	9
σ_P^+	$A_s^{1/2}(NO_2) = (1.49 \pm 0.10) + (-1.18 \pm 0.13)\sigma_P^+$	0.976	0.20	10
σ_R^+(T) [7]	$A_s^{1/2}(NO_2) = (1.31 \pm 0.14) + (-1.21 \pm 0.16)\sigma_R^+$	0.967	0.23	11
σ_R^+(P) [8]	$A_s^{1/2}(NO_2) = (1.34 \pm 0.05) + (-1.54 \pm 0.05)\sigma_R^+$	0.990	0.08	12

aniline derivatives increase almost 2.5-fold (eqs. 5 and 6, Table 1). The values of ρ are 7.83 and 4.61, respectively, with the correlation factors remaining good. The band intensities in nitrothiophenol derivatives are less dependent on the solvent. Hence, the $A_s(NO_2)$ intensity is more sensitive to electronic effects and the influence of the medium than the A(Ar) intensities. This is precisely why we used it to determine the σ constants of Ph_nMx groups.

For correlation analysis we selected a number of reference compounds for which the values of $A_s(NO_2)$ are practically independent of the solvent, as was shown by us and in ref. 4, while the σ constants of the substituents vary within an adequately wide range (Table 2). As the intensity function we used the square root of this value ($A^{1/2}$). In the correlation analysis use was made of different σ constants (σ_p [5]; σ_p^+ [6]; σ_R, σ_R^0, σ_R^+ (T) [7] *, σ_R^+ (P) [8] **). Induction constants σ_I and σ^0 were not considered because, as can be seen from Table 2, they do not vary symbatically with $A_s(NO_2)$. The parameters of the correlation equations are listed in Table 3. The worst correlation factors were derived for the equations including σ_R^0 *** and σ_R (0.845 and 0.910, respectively), the relationships between $A^{1/2}$ and these σ constants being rather approximate. A somewhat better correlation is observed between $A^{1/2}$ and σ_p constants ($r = 0.937$, $S_0 = 0.3$). As is shown by the analysis results, good correlations exist between $A^{1/2}$ and the σ constants taking into account direct polar conjugation (correlation factors $r = 0.97$—0.99). Using eqs. 10 to 12 and the experimental values of $A_s(NO_2)$ in two media (CH_2Cl_2 and DMSO), we determined the values of σ_p^+ and σ_R^+ [7,8] of the $XMPh_n$ and XH groups (Table 4).

An indication of the applicability of the correlation equations is the good agreement with the published values of the σ constants of weakly solvated groups. Thus, in spite of the approximate nature of the correlation between

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* $\sigma_R^+(T) = \sigma_p^+ - \sigma_I$ [7].

** $\sigma_R^+(P) = \sigma_p^+ - \sigma^0$ [8].

*** Katritsky proposed a general approach to determine σ_R^0 from A(Ar) for all aromatic compounds except for the NO_2-substituted ones in which, in the author's opinion, ν(Ar) and $\nu_s(NO_2)$ interact [9]. However, as we showed earlier [10], the values of σ_R^0 cannot be determined in carbonyl-containing compounds with n-OMR_n groups either. It seems that the method proposed by Katritsky is not applicable to compounds with pronounced donor—acceptor interaction between the substituents.

the values of σ_p and $A_s^{1/2}(NO_2)$, determined with the aid of eq. 9, the values of σ_p for charged substituents (S^- and O^-) are consistent with those obtained from electrochemical measurements in DMP (—1.21 and —1.86, respectively) [11]. The values of σ_p determined by us in CH_3CN and DMSO are —1.24 and —1.32 (S^-) and —1.62 and —2.10 (O^-).

The published values of σ_p for the $NHCH_3$ and SH groups (—0.84 and +0.15, respectively) [5] practically coincide with those determined by us (—0.87 and +0.15).

The data in Table 4 indicate that all examined groups with the exception of the SH group, whose σ constants approach zero, are electron-donating ones. The values of σ_p^+ and σ_R^+ vary within wide limits. For example, in the most inert solvent, the range of variations in σ_p^+ is from 0.09 to —1.81, while σ_R^+ (T) varies from —0.06 to —1.98. In DMSO, the range is extended further, shifting toward the region of more pronounced donating capacity: σ_p^+ from —0.03 to —3.9 and σ_R^+ from —0.17 to —3.98. Comparison with the values of σ_R^0 obtained for analogous F-substituted species by the NMR ^{19}F technique [12] indicates that the range of variations in σ_p^+ and σ_R^+ observed by us is much wider for the groups under consideration. This permits a more detailed discussion of the change in the capacity for conjugation of both Ph_nMX and XH groups. As can be seen from Table 4, all three classes of compounds are characterized by σ constants of organometallic groups much greater in absolute value than those of XH

TABLE 4

CONSTANTS OF SUBSTITUENTS, DETERMINED FROM eqs. 10—12 AND VALUES OF $A^{1/2}$ FOR COMPOUNDS OF THE $XC_6H_4NO_2$ TYPE

X	CH_2Cl_2				DMSO			
	$A^{1/2}$ $\times 10^{-2}$	σ_P^+	σ_R^+(P)	σ_R^+(T)	$A^{1/2}$ $\times 10^{-2}$	σ_P^+	σ_R^+(P)	σ_R^+(T)
SH	1.38	0.09	—0.03	—0.06	1.52	—0.03	—0.12	—0.17
$SSnPh_3$	1.58	—0.08	—0.16	—0.22	1.90	—0.35	—0.36	—0.49
SHgPh	1.95	—0.39	—0.40	—0.53	2.03	—0.46	—0.45	—0.60
$SPbPh_3$	1.82	—0.28	—0.31	—0.42	2.10	—0.52	—0.49	—0.65
$SSbPh_4$	2.24	—0.64	—0.58	—0.77	4.58	—2.62	—2.10	—2.60
S^-	4.31 [a]	—2.39	—1.93	—2.48	4.58	—2.62	—2.10	—2.60
OH [b]	2.21	—0.61	—0.56	—0.74	2.90	—1.19	—1.01	—1.31
$OSnPh_3$	3.32	—1.55	—1.29	—1.66	4.25	—2.34	—1.89	—2.43
OHgPh	2.83	—1.14	—0.97	—1.26	4.70	—2.72	—2.18	—2.80
$OPbPh_3$	3.60	—1.79	—1.47	—1.89	5.18	—3.13	—2.49	—3.20
$OSbPh_4$	3.70	—1.87	—1.53	—1.98	5.29	—3.92	—2.56	—3.29
O^-	5.10 [a]	—3.06	—2.44	—3.13	6.12	—3.92	—3.10	—3.98
$NHSO_2Ph$	2.55	—0.90	—0.79	—1.02	2.65	—0.98	—0.85	—1.11
$NHgPhSO_2Ph$	2.58	—0.92	—0.81	—1.05	2.76	—1.07	—0.92	—1.20
NH_2 [c]	3.03	—1.31	—1.10	—1.42	3.54	—1.74	—1.43	—1.84
$NHCH_3$	3.52	—1.72	—1.42	—1.83	3.62	—1.81	—1.48	—1.91
NHHgPh	3.63	—1.81	—1.49	—1.92	5.14	—3.09	—2.47	—3.16
$NHCOCH_3$ [d]	2.02	—0.45	—0.44	—0.59	2.17	—0.58	—0.54	—0.71
NH^-	7.03 [a]	—4.70	—3.69	—4.73				

[a] In CH_3CN. [b] $\sigma_P^+ = —0.9$ [6], $\sigma_R^+ = —0.79$ [8]. [c] $\sigma_P^+ = —1.3$ [6], $\sigma_R^+(T) = —1.4$ [7]. [d] $\sigma_P^+ = —0.6$ [6], $\sigma_R^+ = —0.86$ [7].

groups. Among the nitrophenol and nitrothiophenol derivatives, the Ph_4SbX groups have the maximum values of σ_p^+ and σ_R^+, while the XH groups have the minimum values of these constants. The electron-donating properties of the Ph_nMX groups in DMSO become less pronounced depending on the metal species in the following series: Sb > Pb > Hg > Sn. In an inert solvent, some differences appear depending on the heteroatom; for example, for X = 0: Pb > Sn > Hg, whereas for X = S: Hg > Pb > Sn.

Analysis of the variations in the constants depending on the heteroatom indicates that in the case of similar MPh_n groups, just as in the case of the hydrogen atom, their values decrease in the same sequence, determined by the capacity of the X atom for conjugation:

$HNMPh_n > OMPh_n > SMPh_n$

$H_2N > OH > SH$

In this case, the values of σ_p^+ and σ_R^+ for all $OMPh_n$ groups are higher than those for $SMPh_n$. The ranges of variation in the σ constants do not overlap, with the exception of the $SSbPh_4$ group, whose electron-donating properties are more pronounced than those of OH.

As far as nitroaniline derivatives are concerned, it is possible to introduce an additional substituent at the heteroatom. The introduction of an electron-accepting substituent such as the SO_2Ph group suppresses the donating capacity of the amino groups to such an extent that the values of σ_p^+ and σ_R^+ for the $NHgPhSO_2Ph$ group become lower than for all $OMPh_n$ groups.

It can be seen from Table 4 that the σ constants of the XH and $XMPh_n$ groups are to a great extent dependent on the solvent. σ_p^+ and σ_R^+ in DMSO increase symbatically with the capacity to form hydrogen bonds, which is known to vary as follows: $OH > NH_2 > SH$. For example, when DMSO is used instead of CH_2Cl_2, the σ constants become twice as high for OH, the values of these constants in water and aqueous acetone [5—8] being intermediate. In the case of the NH_2 group, the constants increase at least 1.3-fold, while the SH group exhibits a low capacity for direct polar conjugation, varying only insignificantly depending on the medium ($\sigma_p^+ = 0.09$ in CH_2Cl_2 and -0.03 in DMSO). Unlike XH groups, the solvation sensitivity of $XMPh_n$ groups is not determined by their capacity for coordination interactions with the solvent. Comparison of the changes in the σ constants for the $XMPh_n$ groups involved as one goes from CH_2Cl_2 to DMSO, and the constants K_k for complexing with this solvent, determined by us earlier [13,14], indicates that these values do not vary symbatically. For example, the values of K_k for Ph_4SbX groups (X = O, S) are minimal, probably because of steric hindrance, while the solvation sensitivity of the electronic effect is maximal (Table 4). The Ph_3SnO group forms stable complexes with DMSO, as opposed to PhHgO [13]; however, the values of the σ constant for this group in the above solvent are lower. A strong dependence of the electronic effect on the solvent is observed in the case of charged substituents that do not form any complexes (O^- and S^-). Interestingly, in the case of more polar O—M bonds one can notice symbatic variations in the σ constants and dissociation constants in DMSO [13], associated with the ionic character of these bonds. These results suggest that along with coordination interactions a major role in DMSO is played by dipole—dipole and dispersion interactions. In the case of compounds with polar XM bonds, charged substituents, and readily polarizable large Ph_nMX groups, the contribution of such interactions with solvents increases and may become decisive. Such concepts provide an explanation for the high solvation sensitivity of the electronic effects of Ph_4SbX, PhHgO, PhHgNH, and X^- groups.

Thus, we have shown that the values of integral intensities of the $\nu_s(NO_2)$ bands in IR spectra can be used to determine the factors characterizing the capacity of $XMPh_n$ and XH groups for direct polar conjugation. The changes in the electron-donating properties of such groups have been found to be strongly dependent on the solvent. The basic factor responsible for solvation sensitivity of the electronic effects of XH groups is their capacity to form hydrogen bonds with the solvent. In the case of $XMPh_n$ groups, the role of interactions associated with the polarity and polarizability of solvents increases. Estimation of the relative contributions of coordination, dispersion and dipole—dipole interactions calls for additional studies.

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