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Preliminary communication

APPLICATION OF VIBRATIONAL SPECTROSCOPY FOR ESTIMATION OF ELECTRON-DONATING PROPERTIES OF ORGANOMETALLIC GROUPS

I. ORGANOMETALLIC DERIVATIVES OF *p*-NITROTHIOPHENOL

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Summary

The IR and Raman spectra of several derivatives of *p*-nitrothiophenol in the region of aromatic ring and nitro group stretching vibrations have been studied. Variation of the band intensities conforms with the electron-donating capacity of SMR_n groups obtained on the basis of ^{19}F NMR spectroscopy. Appreciable solvation sensitivity of the electronic effect of the substituents is established.

The use of IR and Raman spectroscopy in the study of mutual influence of X and NO_2 groups in p-$XC_6H_4NO_2$ systems provides valuable information on the transfer of electronic influence via the system of π-bonds of the benzene ring [1—3].

In the present work we describe the possibility of using vibrational spectroscopy for studying electron-donating effects of R_nMS fragments (R_nM = H, HgC_6H_5, $Sn(C_6H_5)_3$, $Pb(C_6H_5)_3$, $Sb(C_6H_5)_2$ and $Sb(C_6H_5)_4$ groups) in compounds of the type p-$(R_nMS)C_6H_4NO_2$ and the solvation sensitivity of these compounds. IR and Raman spectra were recorded in the regions of symmetric NO_2 stretchings ($\nu^S(NO_2)$) and stretching vibrations of the benzene ring ($\nu(Ar)$) in benzene, methylene chloride, pyridine (Py) and dimethyl sulphoxide (DMSO). The frequencies and intensities of asymmetric NO_2 stretchings are much less sensitive to the electronic effects of substituents and to the effect of solvents and are not considered here.

The spectral characteristics of the compounds studied are listed in Table 1. A strong absorption band in the 1343—1329 cm^{-1} region, $\nu^S(NO_2)$, is observed in the IR and Raman spectra recorded in nonpolar solvents.

Substitution of a H atom with a MR_n fragment increases the intensity of

TABLE 1

SPECTRAL CHARACTERISTICS OF THE COMPOUNDS p-$O_2NC_6H_4SMR_n$

SMR_n	Solvent	IR			
		$\nu^S(NO_2)$ (cm^{-1})	$A(NO_2) \times 10^{-4}$	$\nu(Ar)$ (cm^{-1})	$A(Ar) \times 10^{-4}$
SH	CH_2Cl_2 [a]	1345	1.9	1580—1600	1.02
SH	Pyridine	1342	5.5		
SH	DMSO	1343	2.3	1579—1597	1.7
$SSn(C_6H_5)_3$	CH_2Cl_2	1344	2.5	1575—1597	1.3
$SSn(C_6H_5)_3$	Pyridine	1340	5.1		
$SSn(C_6H_5)_3$	DMSO	1337	3.6	1573—1590	2.2
$SHgC_6H_5$	CH_2Cl_2	1344	3.8		
$SHgC_6H_5$	Pyridine	1335	5.9		
$SHgC_6H_5$	DMSO	1339	4.1	1575—1590	2.6
$SPb(C_6H_5)_3$	CH_2Cl_2	1344	3.3	1575—1597	1.6
$SPb(C_6H_5)_3$	Pyridine	1337	5.7		
$SPb(C_6H_5)_3$	DMSO	1337	4.4	1572—1588	3.3
$SSb(C_6H_5)_2$	CH_2Cl_2				
$SSb(C_6H_5)_2$	DMSO				
$SSb(C_6H_5)_4$	CH_2Cl_2	1331	5.0	1572—1587	2.2
$SSb(C_6H_5)_4$	Pyridine	1330	7.8		
		1310	17.0		
$SSb(C_6H_5)_4$	DMSO	1279—1290	21.0	1567	4.2
$\cdot SSb(C_6H_5)_4$ + $(CH_3)_3COK$	DMSO	1279—1290	21.0		

[a] Except for the PhHg derivative the IR spectra were taken in benzene; A = intensity (in l mol^{-1} cm^{-2})

benzene ring stretchings. The $\nu(Ar)$ intensity depends on the degree of conjugation of substituents with the ring, and for p-disubstituted compounds may also characterize the influence of substituents through the system of aromatic π-bonds [3,5]. Of considerable interest is the fact that $\nu^S(NO_2)$ intensity increases in both IR and Raman spectra in the same sequence (the effect being stronger for $\nu(Ar)$): $ArSH < ArSSnPh_3 < ArSSbPh_2 < ArSPbPh_3 < ArSHgPh < ArSSbPh_4$. This series is similar to the series of electron-donating capacity determined by ^{19}F NMR [6,7] and electronic spectroscopy: $SSbPh_2 < SSnPh_3 < SPbPh_3 < SH < SHgPh < SSbPh_4$.

The fact that the intensities observed for p-nitrothiophenol are lower than expected may be explained by the lower polarity and polarizability of the hydrogen-sulphur bond as compared with the metal—sulphur bond. It should be noted that the vibrational spectra are much more sensitive to the electronic effect of organometallic groups than ^{19}F NMR and electronic spectroscopy.

In coordinating solvents an approximately two-fold increase of $\nu^S(NO_2)$ intensity is observed in IR and Raman spectra; increase of the intensity of benzene ring stretchings is more noticeable in the IR spectra (2—3 fold). Three compounds ($ArSSbPh_4$, $ArSSnPh_3$ and ArSH) display a new low-frequency band represented by a doublet with maxima at 1278 and 1288 cm^{-1} in Raman spectra recorded in DMSO. In the IR spectra this band is observed only for the $SSbPh_4$ derivative, and, in both the IR and Raman spectra of this compound the band at 1340 cm^{-1} is absent.

Raman			
$\nu^S(NO_2)$ (cm^{-1})	$J^\infty(NO_2) \times 10^{-4}$	$\nu(Ar)$ (cm^{-1})	$J^\infty(Ar) \times 10^{-4}$
1343	3.4	1580	1.2
1342	3.2		
1278—1288	1.1	1580	1.3
1343	4.5	1577	2.1
1334	7.6	1575	2.3
1278—1288	4.2		
1341	5.9	1575	2.5
1334	9.6	1573	2.8
1341	5.8	1575	2.7
1334	9.0	1573	2.6
1315	0.8		
1344	5.7	1575	2.5
1336	7.1	1578	2.1
1315	2.2		
1329	25.0	1569	5.7
1278—1288	130.0	1567	6.1
1278—1288	230.0	1570	190.0

By UV spectroscopy we have previously established that in DMSO solutions these compounds are partially dissociated. The highest capacity to dissociation is displayed by the three compounds that exhibit the low-frequency band in the Raman spectra, and dissociation decreases in the order $\text{ArSSbPh}_4 \gg \text{ArSSnPh}_3$ ArSH (K_{diss} 3×10^{-3}, 2×10^{-5} and 5×10^{-6} l mol^{-1}, respectively). Therefore it may be assumed that the new band is due to $\nu^S(NO_2)$ vibrations in the anion. To verify this assumption we added an excess of potassium t-butylate, which causes complete dissociation of the compound, to a solution of ArSSbPh_4 in DMSO. The position of the band of the anion in the Raman spectrum coincided with the low-frequency band at 1278—1288 cm^{-1} displayed in the spectra of partially dissociated compounds. The intensity of this band is exceedingly high, 2.3×10^6. This is probably connected with resonance excitation due to the frequencies of electronic transition and the excitation frequency drawing closer to each other.

We calculated the concentrations of ions from the intensity of J^∞_{1285} in the anion and from the effective values of J^∞_{1285} for partially dissociated compounds. The obtained values are in complete agreement with calculations based on K_{diss}. This confirms the assignment of the low-frequency band at 1285 cm^{-1} to the $\nu^S(NO_2)$ vibrations of the anion. It is noteworthy that the exceedingly high intensity of the anion band makes it possible to determine even 0.5% of dissociated species in DMSO solutions (for example, for *p*-nitrothiophenol at *c* 0.19 m/l).

Experimental

Raman spectra were recorded with a Coderg PH_0 spectrometer using a He-Ne laser (λ_{excit} 6328 Å, 20 mW). J^{∞} were determined by the internal reference method (1420 cm^{-1} line of DMSO or methylene chloride). J^{∞}(DMSO) and J^{∞}(CH_2Cl_2) are 320 and 130 units, respectively, on the cyclohexane scale. IR spectra were recorded with a UR-20 spectrophotometer. Integral intensities were determined from 5—7 measurements according to ref. 8.

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