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Preliminary communication

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

II*. ORGANOMETALLIC DERIVATIVES OF *p*-NITROPHENOL

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Summary

The IR and Raman spectra of organometallic derivatives of *p*-nitrophenol in the region of aromatic ring and nitro group stretching vibrations have been studied. Assignment of two bands in the region of symmetric vibrations of the nitro group is proposed. Considerable sensitivity of ν(Ar) and $\nu(NO_2)$ intensities to the electron-donating capacity of the OMR_n group and solvation sensitivity of the electronic effect have been established.

In this paper we report the IR and Raman spectra of *p*-nitrophenol derivatives of the general formula $ArOMR_n$ (where Ar = p-$O_2NC_6H_4$; OMR_n = H, HgC_6H_5, $Sn(C_6H_5)_3$, $Pb(C_6H_5)_3$ and $Sb(C_6H_5)_4$) in benzene, methylene chloride, pyridine (Py) and dimethyl sulphoxide (DMSO). Only the regions of symmetric NO_2 stretchings ($\nu^s(NO_2)$) and benzene ring stretchings are considered. Asymmetric vibrations of the NO_2 group practically do not vary in organometallic derivatives ($\nu^{as}(NO_2)$ 1490 ± 2 cm^{-1}).

Spectral characteristics of the compounds studied are listed in Tables 1 and 2. Vibration intensity increases with the electron-donating effects of the OM group in the sequence: $OH < OSnPh_3 < OHgPh < OPbPh_3 < OSbPh_4$ [1,2]. However, the intensity of the 1340 cm^{-1} band does not increase, as in the case of *p*-nitrothiophenol derivatives but. in contrast, decreases in the same sequence. In the spectra of all oxygen-containing compounds (with exception of the Raman spectrum of *p*-nitrophenol) an additional strong band is displayed at 1280—1300 cm^{-1}. Its intensity both in IR and Raman spectra substantially in-

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*For part I see ref. 7.

TABLE 1 CHARACTERISTICS OF THE IR SPECTRA FOR THE COMPOUNDS p-$O_2NC_6H_4OMR_n$

OMR_n	Solvent	$\nu_1^S(NO_2)$ (cm^{-1})	$A \times 10^{-4}$	$\nu_2^S(NO_2)$ (cm^{-1})	$A \times 10^{-4}$	$\nu(Ar)$ (cm^{-1})	$A \times 10^{-4}$
OH	Benzene	1280	1.6	1342	3.3	1602	2.2
OH	Pyridine	1296	4.0	1339	3.0		
OH	DMSO	1294	4.7	1339	3.7	1593—1614	3.3
$OHgC_6H_5$	CH_2Cl_2	1283—1292	5.4	1338	2.6	1587	3.1
$OHgC_6H_5$	Pyridine	1300	15.8	1334	2.0		
$OHgC_6H_5$	DMSO	1300	19.8	1337	2.3	1584	5.0
$OSn(C_6H_5)_3$	Benzene	1277—1288	7.6	1340	3.4	1587	3.9
$OSn(C_6H_5)_3$	Pyridine	1305	12.0	1340	2.7		
$OSn(C_6H_5)_3$	DMSO	1302	17.4	1337	0.7	1584	4.8
$OPb(C_6H_5)_3$	Benzene	1277—1288	10.1	1336	2.9	1587	3.6
$OPb(C_6H_5)_3$	Pyridine	1302	16.7	1332	0.7		
$OPb(C_6H_5)_3$	DMSO	1302	26.8			1582	5.7
$OSb(C_6H_5)_4$	Benzene	1300	11.3	1338	2.4	1588	4.9
$OSb(C_6H_5)_4$	Pyridine	1300	15.0	1332	0.9		
$OSb(C_6H_5)_4$	DMSO	1300	28.0				
		1277	37.4			1585	5.8
$OSb(C_6H_5)_4$ + $(CH_3)_3COK$	DMSO	1277	37.4			1586	10.9

[a] A = integral intensities in l mol^{-1} cm^{-2}.

TABLE 2 FREQUENCIES AND INTERNAL INTENSITIES (J^∞) OF THE RAMAN SPECTRA FOR THE COMPOUNDS p-$O_2NC_6H_4OMR_n$

OMR_n	Solvent	$\nu_1^S(NO_2)$ (cm^{-1})	$J^\infty \times 10^{-4}$	$\nu_2^S(NO_2)$ (cm^{-1})	$J^\infty \times 10^{-4}$	$\nu(Ar)$ (cm^{-1})	$J^\infty \times 10^{-4}$
OH	CH_2Cl_2			1345	2.9	1599	0.5
OH	DMSO	1295	0.6	1336	3.2	1592	0.6
$OSn(C_6H_5)_3$	CH_2Cl_2	1290	0.7	1339	2.5	1586	1.0
$OSn(C_6H_5)_3$	DMSO	1300	6.7	1335	2.6	1582	1.3
$OHgC_6H_5$	CH_2Cl_2	1294	1.5	1340	5.4	1585	1.2
$OHgC_6H_5$	DMSO	1298	5.8	1335	2.6	1585	1.1
$OPb(C_6H_5)_3$	CH_2Cl_2	1291	3.9	1336	5.2	1583	1.7
$OPb(C_6H_5)_3$	DMSO	1298	11.5	1336	2.0	1580	0.1
$OSb(C_6H_5)_4$	CH_2Cl_2	1298	9.4	1334	5.7	1582	1.9
$OSb(C_6H_5)_4$	DMSO	1296	9.0	1334	2.6	1583	1.5
		1278	2.3				
$OSb(C_6H_5)_4$ + $(CH_3)_3COK$	DMSO	1278	30.0				

creases with the donor properties of the substituents, while its position is slightly shifted to higher frequencies.

In coordinating solvents the low-frequency band is much stronger and the 1340 cm^{-1} band is weaker both in IR and Raman spectra. These changes increase with the coordinating capacity of the solvent: Py < DMSO. Thus, the IR spectra of $OPbPh_3$ and $OSbPh_4$ derivatives in Py display the 1340 cm^{-1} band, although it is very weak, whereas in DMSO this band is not observed at all. The intensity of the low-frequency band increases in Py as compared with nonpolar solvents by a factor of 1.5 and in DMSO the increase is nearly three-fold. This is accompanied by a shift of the low-frequency band to 1300 cm^{-1}.

The assignment of the two bands in the 1280—1350 cm^{-1} region observed in the spectra of *p*-nitrophenol [3] and of aromatic nitroamines [4] have been discussed in the literature. The authors of [3] consider the low-frequency band not associated with NO_2 vibrations, whereas in [4,5] a strong involvement of the NO_2 group in both vibrations, which are modified under the effect of the medium and have a non-localized complex character, is postulated.

Quantitative estimation of the participation of various bonds and angles in these vibrations undoubtedly requires analysis of the normal vibrations. However, in our opinion study of a series of nitrophenol and nitrothiophenol derivatives, in which the electron-donating properties of OMR_n and SMR_n groups vary in a wide range, provides additional information about the nature of the low-frequency band.

The low-frequency band is displayed in the spectra of nitrophenol derivatives and is not observed in the spectra of nitrothiophenol derivatives in which the SMR_n group is a weaker donor. Intensity of the ~ 1290 cm^{-1} band increases in the same series as the electron-donating properties of the OMR_n group, accompanied by decrease of the intensity of the 1340 cm^{-1} band in the IR spectra. In the Raman spectra the intensity of this band slightly increases, since polarizability of the organometallic groups increases in the same series, but increase of the intensity of the ~ 1290 cm^{-1} band is stronger (in *p*-nitrophenol this band is absent, whereas in the spectrum of the $OSbPh_4$ derivative it is stronger than the 1334 cm^{-1} line). Increase of the intensity of the low-frequency band and its shift towards higher frequencies may be due not only to intramolecular processes but also to the effect of coordinating solvents. The intensity of the high-frequency band decreases both in the IR and Raman spectra, although in the former the effect is more marked. Therefore the ~ 1290 cm^{-1} band corresponds to a vibration with considerable contribution of the NO_2 group. Presumably with increase of the donating capacity of the substituents and of the multiplicity of the CN bond the vibrations involving the CN and NO bonds draw closer together (contribution of the angles into these vibrations may also vary). For compounds containing OMR_n and NHR groups there are two vibrations of the CNO_2 group with different participation of the CN and NO bonds. With increase of the donating capacity of the substituent the low-frequency vibration probably delocalizes, leading to a sharp rise of its intensity. The strongest electron-donor effect of the *p*-substituent should be displayed in anions. In the case of *p*-nitrophenolate anion, absorption has been observed at 1295 cm^{-1} in Py [6] in the IR spectrum and in the Raman spectra at 1289 cm^{-1} in alkaline aqueous solution [4]. For the *p*-nitrothiophenolate anion a doublet band appears at 1278—1288 cm^{-1} in DMSO. In all cases one exceedingly strong low-frequency band appears, which corresponds to a complex vibration of the CNO_2 group of the anion.

In DMSO solutions an additional low-frequency band is displayed at 1277—1278 cm^{-1} in the spectra of the most dissociated derivative (UV data), $OSbPh_4$. In additional experiments (with addition of potassium t-butylate which causes complete dissociation of the compound) the anionic nature of this band was proved and its IR and Raman intensities were determined. Concentrations of the free ions calculated according to the intensity of the 1277 cm^{-1} band coincide with the values obtained from K_{diss}.

References

1 A.N. Nesmeyanov, D.N. Kravtsov, E.M. Rokhlina, V.M. Pachevskaya, L.S. Golovchenko and E.I. Fedin, J. Organometal. Chem., 38 (1972) 307.

2 D.M. Kravtsov, B.A. Kvasov, S.I. Pombrik and E.I. Fedin, J. Organometal. Chem., 86 (1975) 383.

3 A.V. Iogansen and G.D. Litovchenko, Zh. Prikl. Spektr., 2 (1965) 243.

4 P.P. Shorygin and B.V. Lopatin, Zh. Fiz. Khim., 39 (1965) 2868.

5 K. Kumoc and P.R. Carey, J. Chem. Phys., 63 (1975) 3697.

6 B.V. Lopatin and T.E. Kuznetsova, Izv. Akad. Nauk SSSR, Ser. Khim., (1970) 713.

7 L.M. Epstein, V.L. Beloborodov, L.D. Ashkinadze, E.M. Rokhlina, S.I. Pombrik, D.N. Kravtsov and L.A. Kazitsyna, J. Organometal. Chem., 162 (1978) C1.