IR SPECTROSCOPIC STUDY OF THE STRUCTURE AND CAPACITY FOR INTERMOLECULAR COORDINATION OF ORGANOMERCURY, ORGANOLEAD, AND ORGANOTIN DERIVATIVES OF p-CARBONYL-CONTAINING PHENOLS

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We have already shown [1] that IR spectroscopy can be used to detect the presence of and semiquantitatively assess the strength of the intramolecular coordination bonds in HgPh- and $SnPh_3$- substituted o-formylphenols. We have now used IR spectroscopy to examine the strucutre, capacity for self-association, association with unlike molecules, and intermolecular coordination with solvents of substituted p-carbonyl-containing phenols and phenolates of the type $R_nMOC_6H_4COR'$ (R_nM = H, PhHg, Ph_3Pb, Ph_3Sn, and Et_3Sn, R' = H, CH_3, OCH_3).

To examine the relative capacity for self-association we measured the IR spectra in the region of the carbonyl modes in the solid state and in solution in nonpolar solvents (C_6H_6, CCl_4) and examined their concentration and temperature dependence. Table 1 shows that the νCO bands of all these compounds lie at lower frequency in the solid state.* In many cases the band is split into two components, while in the case of the PhHg derivatives considerable low-frequency asymmetry is apparent.

Since the low-frequency solid-state bands (or the asymmetry) disappear in dilute solutions in a nonpolar solvent we assign them as associated carbonyl modes. We made a reliable assignment of the two bands found for solutions with reasonably high concentrations on the basis of the temperature and concentration dependences. Figure 1 shows that, as exemplified by $p\text{-}CH_3OOCC_6H_4OSnEt_3$ (I), the intensity of the low-frequency band sharply increases when the temperature is reduced to −60°C, i.e., it belongs to the associated carbonyl groups and at this temperature (I) exists mainly as associates. At high temperatures (70°C) (I) is only slightly associated, since the high-frequency component predominates.

Qualitative comparison of the change in the relative intensity of the two bands as a function of concentration not only supports the assignment but also reveals that the capacity for self-association in solution increases in the order $PbPh_3 < SnEt_3 < H$ (Fig. 2). Unfortunately, the poor solubility of the PhHg derivatives in nonpolar media precluded their inclusion in this study. Quantitative evaluation of the capacity for self-association was possible only for the $SnEt_3$ derivatives and the corresponding phenols. Table 2 shows that the organotin derivatives are less associated than the phenols and that the capacity for association falls in the order $CHO > COCH_3 > COOCH_3$, which is the same as in the phenol derivatives ($COCH_3 > COOCH_3$).

The νCO frequency shifts in the solid state relative to solution ($\Delta\nu$, Table 1) do not vary in the same sense as the association constants; they are similar for the phenols and tin phenolates with $COCH_3$ and $COOCH_3$ substituents and are 40-48 cm^{-1}. Consequently, to decide whether $\Delta\nu$ can act as a measure of the capacity for self-association in the solid state, we need additional, information, most probably x-ray structure analyses. However, the substantial reduction of the shifts for the phenylmercury derivatives ($\Delta\nu$ = 10-15 cm^{-1}) together with the existence of low-frequency asymmetry in the solid state suggest that these compounds are less susceptible to self-association.

Comparison of the self-association with association with unlike molecules gave interesting results. The capacity for heteroassociation is much lower than that for self-asssociation. Figure 3 shows that the IR

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*The values of $\Delta\nu$ (THF − solid state) for $Et_3SnOC_6H_4COR$, where R = H and OCH_3, have been reported by others [2].

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TABLE 1. νCO Absorption Bands of MOC_6H_4X in the Solid State and C_6H_6 Solution

M	X=CHO			X=COCH₃			X=COOCH₃		
	solid	solution	Δν	solid	solution	Δν	solid	solution	Δν
H	1666	1695	29	1644	1684	40	1672	1720	48
HgPh	1680	1695	15	1673	1683	10	1702	1716	14
SnEt₃	1660	1692	35	1640	1682	42	1676	1717	41
PbPh₃	1653	1692	39	1655	1677	22	1685	1710	25

TABLE 2. Kass in CCl_4, liter/mole

Compound	X=CHO	X=COCH₃	X=COOCH₃
p-XC_6H_4OH	–	70	36±6
p-$XC_6H_4OSnEt_3$	10,7±0,5	9,4±0,3	2,0±0,2

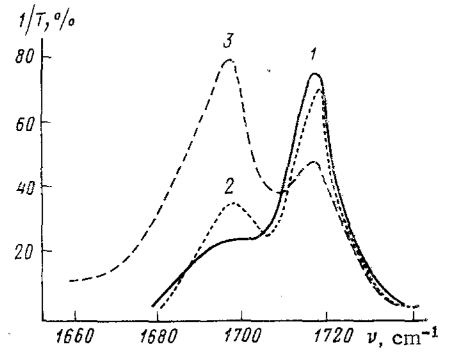
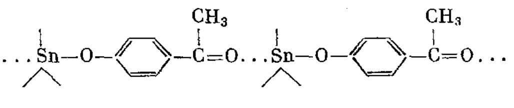


Fig. 1. Temperature dependence of νCO of $Et_3SnOC_6H_4COOCH_3$ (C 0.2 M): 1) 70°C; 2) 20°C; 3) −60°C.

spectrum of a mixture of equimolar amounts of $PhOSnEt_3$ (II) and $PhCOCH_3$ (C = 0.14 M) has no associated carbonyl band. Conversely, in a solution of $Et_3SnOC_6H_4COCH_3$ (III) with the same concentration the bound and free carbonyl bands have roughly the same intensities.

The reason for this could be that in (III) the positive charge δ^+ on the Sn atom is higher than in (II) because of the electron-accepting properties of the p-CH_3CO groups, while the negative charge δ^- on the oxygen atom in (III) is higher than in $PhCOCH_3$, since the Et_3SnO group is more electron-donating than OH [3]. To verify this, we examined the effect on the association of the introduction of electron-accepting substituents into (II) and of electron-donating substituents into acetophenone. However, even in the substituted triethyltin phenolates and substituted $PhCOCH_3$, which simulate the electron-density distribution in (III), the capacity for heteroassociation is much lower than that of association. The model compounds were p-$Me_2NC_6H_4COCH_3$ (IV) and 3,5-Br_2-4-$FC_6H_2OSnEt_3$ (V). We chose these compounds because the p-NMe_2 group is slightly more electron-donating than Et_3Sn [3], while the 3,5-Br_2-4-FC_6H_2 group ($\Sigma\sigma$ 0.84) has higher electron-accepting ability than p-$CH_3COC_6H_4$ (σ_n = 0.52) [4]. Figure 4 shows that equimolar mixtures of (IV) with both (II) and (V) have only a small low-frequency asymmetry of the νCO band and that the introduction of electron-accepting substituents into (II) slightly alters the spectral pattern. Our results point to the existence of some additional stabilizing factor that favors self-association.

One possibility is the intermolecular mesomerism in coordination associates [5]. Thus, in the linear polymer chain of the self-associate of (III)



$$\ldots Sn{-}O{-}C_6H_4{-}\overset{CH_3}{C}{=}O\ldots Sn{-}O{-}C_6H_4{-}\overset{CH_3}{C}{=}O\ldots$$

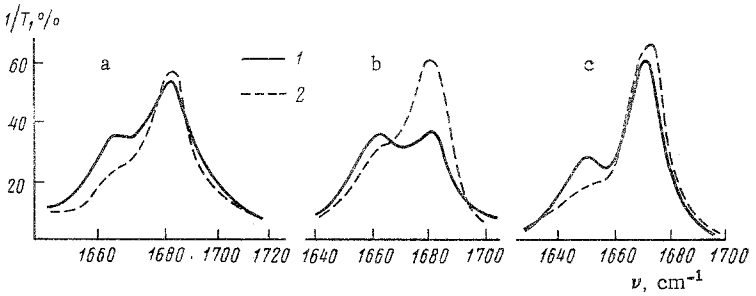


Fig. 2. Concentration dependence of νCO of $R_nMOC_6H_4COCH_3$: a) M = H, C = 0.006 (1) and 0.03 mole/liter (2); b) M = $SnEt_3$, C = 0.15 (1) and 0.02 mole/liter (2); c) M = $PbPh_3$, C = 0.15 (1) and 0.02 mole/liter (2).

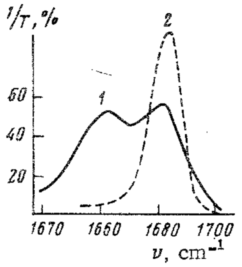


Fig. 3

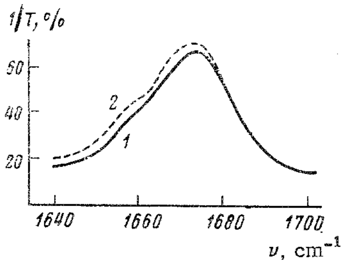
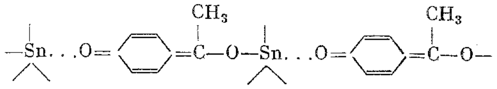


Fig. 4

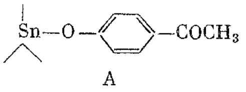
Fig. 3. Absorption in the νCO region: 1) $Et_3SnOC_6H_4COCH_3$ (C 0.14 mole/liter); 2) mixture of $Et_3SnOC_6H_5$ + $C_6H_5COCH_3$ (C 0.14 mole/liter).

Fig. 4. Absorption in the νCO region: 1) mixture of $Me_2NC_6H_4COCH_3$ (0.12 mole/liter); 2) mixture of $Me_2NC_6H_4COCH_3$ + $Et_3SnOC_6H_2$-Br_2-3,5-F-4 (0.13 mole/liter each).

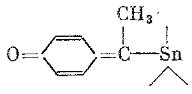
the Sn−O bond is polarized as a result of the formation of the C=O...Sn coordination bond and a contribution from the isomeric state appears



Thus, in terms of the structure of the organic residue the structure of the self-associate is intermediate between the two possible limiting forms

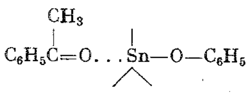


A



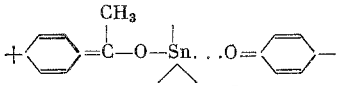
B

As a result of the breakup of the aromatic system of the benzene ring form B should be energetically less preferred than A and its contribution to the mesomeric structure of the associate should be much lower. Nevertheless, it can make a definite contribution to the stabilization of the associate, since the energy of the mesomeric state is known to be less than that of the limiting states [6]. In the association of unlike molecules



$$C_6H_5\overset{CH_3}{C}{=}O\ldots Sn{-}O{-}C_6H_5$$

the second possible form is structure C, in which both breakup of the aromaticity of the benzene rings and considerable charge separation occur



C

TABLE 3. Spectral Characteristics of the νCO Bands in MOC_6H_4X

X	Solvent	M=H		M=HgPh		$M=SnPh_3$		$M=PbPh_3$	
		ν, cm^{-1}	A*	ν, cm^{-1}	A*	ν, cm^{-1}	A*	ν, cm^{-1}	A*
CHO	C_6H_6	1695	3,0	1695	3,0	1695	3,4†	1692	3,4
	THF	1692	3,3	1693	3,5			1685	3,5
	DMSO	1685	3,5	1683	4,1			1670	4,3
$COCH_3$	C_6H_6	1684	2,5	1683		1682	3,3†	1677	3,4
	THF	1683	2,4	1673	2,6	1682	2,5	1670	3,9
	DMSO	1671	2,6	1663	3,4	1663	3,2	1658	3,6
$COOCH_3$	C_6H_6	1720	3,7	1716		1717	3,0†	1710	3,7
	THF	1721	3,6	1714	2,7	1714		1710	3,7
	DMSO	1710	4,4					1698	4,6

*$A \cdot 10^{-4}$, liter/mole · cm^2.
†$SnEt_3$ in CCl_4.

TABLE 4. Integral Intensities ($A \times 10^{-4}$, liter/mole · cm^2) of the Benzene Ring Absorption Bands (1580-1610 cm^{-1}) of MOC_6H_4X

X	Solvent	M=H	M=HgPh	$M=SnPh_3$	$M=PbPh_3$
CHO	C_6H_6	3,7		5,5*	6,2
	THF	4,0			6,3
	DMSO	5,3			7,3
$COCH_3$	C_6H_6	3,9	–	6,3*	6,2
	THF	3,4	4,6	3,7	6,2
	DMSO	4,4	4,7	4,4	6,2
$COOCH_3$	C_6H_6	1,7	–	2,6*	3,3
	THF	2,2	2,7	–	3,5
	DMSO	3,2	–	–	4,9

*$SnEt_3$ in CCl_4.

Consequently, the energy difference between forms C and A should be much higher than that between forms A and B. At the same time, the resonance energy will increase as the difference between the energies of the limiting structures falls [7]. The effect of these factors seems to be that intermolecular mesomerism enhances the intermolecular coordinate interactions more in the case of self-association than in the association of unlike molecules containing the same interacting groups. In this case when intermolecular mesomerism is eliminated because of the specific nature of the molecular structure, no additional stabilization favors self-association relative to the association of unlike molecules. This is indicated by, for example, the absence of the associated carbonyl band in 0.14 M solution of $m\text{-}CH_3OOCC_6H_4OSnEt_3$ in CCl_4.

We then examined the capacity of these compounds for intermolecular coordination with the solvent. The measured νCO frequencies and integrated intensities in noncoordinating (C_6H_6) and coordinating solvents (THF, DMSO) are summarized in Table 3. This shows that νCO is shifted 15-20 cm^{-1} in DMSO relative to C_6H_6 both for the phenols that form strong hydrogen bonds with DMSO and for the organometallic derivatives. The integrated intensities are slightly higher. These spectral changes point to intermolecular coordination with DMSO, but they are so small that we could not use them for a comparative estimate of the capacity for coordination of the phenols and organometallic derivatives.

Minkin et al. have stated [8] on the basis of the UV spectra that the phenylmercury derivatives of p- and o-benzaldehydes have the benzenoid structure in nonpolar solvent but the quinonoid structure in DMSO. Glocking and Mahale [9] cast doubts on the existence of this sort of tautomerism in $o\text{-}CHOC_6H_4OHgMe$, but they recorded the PMR, IR, and UV spectra of this compound only in C_6H_6 and $CDCl_3$. Our work has shown that in the case of all these p- and o-carbonyl organometallic compounds [1] replacement of the inert solvent by DMSO does not cause changes in the IR and UV spectra that would demonstrate the occurrence of tautomeric rearrangements.* Thus, the bands of the quinonoid carbonyl group are missing from the 1620-1640 cm^{-1}

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*The long-wavelength UV bands are apparent only after inadequate purification of DMSO from traces of water.

TABLE 5. σ_R° of the OMR_n Groups in XC_6H_4OM Derived from A_{Ar}

X	Solvent	M=H	M=HgPh	M=SnPh₃	M=PbPh₃
CHO	C_6H_6	−0,382		−0,446 *	−0,509
	THF	−0,415			−0,517
	DMSO	−0,545			−0,600
$COCH_3$	C_6H_6	−0,485		−0,640 *	−0,632
	THF	−0,411	−0,483	−0,387	−0,632
	DMSO	−0,538	−0,493	−0,463	−0,632
$COOCH_3$	C_6H_6	−0,259		−0,252 *	−0,417
	THF	−0,337	−0,341		−0,440
	DMSO	−0,470			−0,588

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*$SnEt_3$ in CCl_4.

TABLE 6. Yields, Melting Points, and Elemental Analyses of Organometallic Derivatives of Substituted Phenols

Compound	Yield, %	mp, °C	Found, %		Formula	Calculated, %	
			C	H		C	H
$Ph_3SnOC_6H_4CHO$-4	84	140—142 (from heptane)	64,05	4,45	$C_{25}H_{20}O_2Sn$	63,70	4.29
$Ph_3SnOC_6H_4COCH_3$-4	75	132—133 (from C_6H_6)	64,81	4,63	$C_{26}H_{22}O_2Sn$	64,53	4,54
$Ph_3SnOC_6H_4COOCH_3$-4	84	120—122 (from heptane)	62,69	4,38	$C_{26}H_{22}O_3Sn$	62,27	4,37
$Ph_3PbOC_6H_4CHO$-4	81	168—171 (from cyclohexane)	53,83	3,68	$C_{25}H_{20}O_2Pb$	53,66	3,64
$Ph_3PbOC_6H_4COCH_3$-4	75	184—185 (from C_6H_6)	54,45	3,87	$C_{26}H_{22}O_2Pb$	54,90	3,92
$Ph_3PbOC_6H_4COOCH_3$-4	78	160—169 (from cyclohexane)	53,18	3,81	$C_{26}H_{22}O_3Pb$	52,92	3,76
$Et_3SnOC_6H_4COCH_3$-4	84	69—70 (from heptane)	49,21	6,47	$C_{14}H_{22}O_2Sn$	49,30	6,49
$Ph_3HgOC_6H_4CHO$-4	61	144—145 (from toluene)	39,42	2,68	$C_{13}H_{10}HgO_2$	39,19	2,51
$PhHgOC_6H_4COCH_3$-4	60	147—148 (from toluene)	40,86	2,80	$C_{14}H_{12}HgO_2$	40,77	2,91
$PhHgOC_6H_4COOCH_3$-4	74	150—151 (from toluene)	39,66	2,82	$C_{14}H_{12}HgO_3$	39,25	2,80

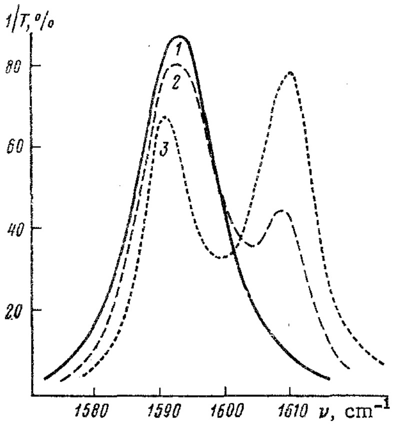

Fig. 5. νAr bands in $R_nMOC_6H_4CHO$; MR_n = 1) H, 2) Et_3Sn, and 3) PhHg.

region and there are no substantial changes in the intensities of the (1600-1580 cm^{-1}) and carbonyl stretching modes in DMSO relative to C_6H_6 (Tables 3 and 4). Consequently, all these compounds have the benzenoid structure in both solvents.

The intensities of the two bands in this region are redistributed in the organometallic derivatives by comparison with the hydroxy compounds. Figure 5 shows that the contribution of the low-frequency component characterizing the conjugated nature of the system is higher (~1580 cm^{-1}). The overall intensity is also higher (Table 4), demonstrating the increase in donor properties in the order OH < $OSnPh_3$ < $OPbPh_3$. This ordering represents a series of changes in the electron-donating properties of the OMR_n group, which have been measured by the ^{19}F NMR method [3], and also by IR [10] and UV [11] spectroscopy for the p-NO_2-substituted compounds.

Katritzky and Topsin in a series of works generalized in a review [12] have suggested a method for measuring the resonance interaction of the substituent with the aromatic ring σ_R° from the intensities of the bands of the benzene ring stretching modes in the 1600 cm^{-1} region. We attempted to use a similar approach with these compounds. We calculated σ_R° from the equation for the p-disubstituted compounds with allowance for the donor–acceptor interaction between the substituents

$$A_p = 15{,}000\ [\sigma_R^\circ(R_nM) - \sigma_R^\circ(\mathrm{COR}) + \lambda]^2 + 170$$

where A_p is the intensity of the ν Ar band in the 1600 cm^{-1} region and λ are corrections for the donor–acceptor interactions between the substituents. We used the donor corrections for the OH group in the calculation of λ for all these compounds [12].

The figures of Table 5 suggest that σ_R° is not a constant but depends to a considerable extent on which acceptor group is para to the OMR_n group. The difference in σ_R° in $COCH_3$, $COOCH_3$, and F relative to CHO are greater than the range of variation of σ_R° measured by the ^{19}F NMR method (OH = −0.43; $OPbPh_3$ = −0.52). The figures for the OH and $OPbPh_3$ groups in C_6H_6, THF, and DMSO reveal that σ_R° is strongly solvent-dependent.

Consequently, this approach cannot be used to isolate from the overall effect of direct polar conjugation a constant contribution from the resonance interaction of the substituent with the aromatic ring and is not applicable to compounds containing strong donor and acceptor groups capable of interacting via conjugated system. We do not think this sort of conclusion unexpected, since the electron density redistribution within the molecule depends on the donor and acceptor abilities of the groups involved in conjugation and the isolation of a constant resonance component is not justified.

EXPERIMENTAL

The IR spectra were measured on a UR-20 in the 1550-1750 cm^{-1} region (NaCl and LiF prisms). The mean rate was 25 cm^{-1}/min and the chart scale 1-10 cm^{-1}. The spectral slit width was 6-6.5 cm^{-1} with the NaCl prism and 3.4-4 cm^{-1} with the LiF prism. Integrated intensities were measured by the procedure of [13]; the accuracy of measurement was 10%.

The substituted phenols were synthesized by published procedures and characterized by their melting points; purity was monitored from the PMR spectra.

Phenylmercury derivatives of substituted phenols were prepared by a general method. To a hot solution of PhHgCH (5 mmoles) in MeOH (40 ml) was added a hot solution of the substituted phenol (5 mmoles) in MeOH (10 ml). After removal of the solvent under vacuum the residue was recrystallized from an appropriate solvent. The $RC_6H_4OMPh_3$ (M = Sn, Pb) derivatives of the substituted phenols were prepared in the same way by the action of Ph_3SnOH and Ph_3PbOH on a methanolic solution of the substituted phenol.

The yields, elemental analyses, and melting points of the organometallic derivatives of the substituted phenols are summarized in Table 6.

CONCLUSIONS

1. We have examined the spectral characteristics of the absorption bands in the 1550-1750 cm^{-1} region of p-carbonyl-containing phenols and the corresponding organometallic derivatives in nonpolar and polar solvents.

2. The capacity for self-association of p-carbonyl-containing compounds falls in the order H > $SnPh_3$ > $PbPh_3$ > HgPh for different classes of compounds.

3. When conjugation between the R_3SnO group and the CH_3CO substituent is possible self-association of p-$R_3SnOC_6H_4COCH_3$ is more facile than association of R_3SnOAr and $ArCOCH_3$.

4. These compounds have the benzenoid structure in polar and nonpolar solvents. The intensity of the benzene ring modes varies in an order corresponding to the change in the electron-donating properties of the R_nM groups: $Ph_3Pb \geq SnEt_3 > HgPh > SnPh_3 > H$.

5. The magnitudes of σ_R° of these groups calculated from the ν Ar intensity by Katritzky's method are not constant but depend on the p-substituent and the solvent.

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INTRAMOLECULAR HYDROGEN BOND ENERGIES

2. THE ETHANOL HALIDES

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The belief persists that the energy of intramolecular hydrogen bonding (E_{IHB}) can be obtained by measuring ΔE_{exp}, the difference in the energies of two conformers, one with, and the other without, intramolecular hydrogen bonds (IHB). It has been shown, however, that ΔE_{exp} is not identical with E_{IHB}, the two quantities being related through an equation of the form

$$-E_{IHB} = \Delta E_{exp} - \Delta E_{conf} \quad (1)$$

in which ΔE_{exp} is determined from the van't Hoff equation covering the temperature variation of the equilibrium constant, and ΔE_{conf} is the energy difference between the two conformers after IHB elimination [1]. This last is a hypothetical quantity whose value is to be obtained through theoretical calculations, or through modeling with IHB-free compounds having similar molecular structures. The absence of IHB can be readily modeled in terms of the atom–atom potential functions (AAPF) introduced in [1] for ΔE_{conf} calculations. It can be seen from Eq. (1) that the IHB energy will be equal to the measured difference in the energies of two conformers, one with and the other without IHB, provided the conformational energies are equal, i.e., provided $\Delta E_{conf} = 0$, a hypothetical situation. Since ΔE_{conf} is not generally equal to zero, and can even be comparable to ΔE_{exp} itself [1], a correction for this factor must be introduced into the calculation. This definition of the IHB energy is "nonphysical" insofar as it rests on the modeling of the situation which would exist were IHB to be eliminated. Nevertheless, it is, in our opinion, entirely logical.

Equation (1) was used in [1] for calculating $-E_{IHB}$ values for the phenol o-halides; there it was shown that the IHB energy differs from ΔE_{exp} insofar as it varies in parallel with $\Delta\nu$ OH, the shift in OH group

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