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# Solvatochromism of Heteroaromatic Compounds: XXIX.[1] Configurational Isomerism of H Complexes of Phenols with Amides and Esters

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**Abstract**—Phenol and amides and esters in carbon tetrachloride form an H complex with an OH···*n* bond, whose configurational isomers differ from each other by the direction of the hydrogen bond and, as a result, by the value of the spectral shift. Structural details of such configurational isomers and solvatochromism of their IR absorption bands are discussed.

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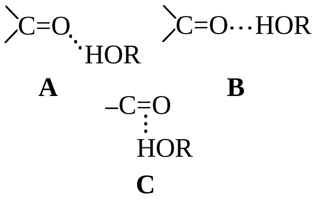
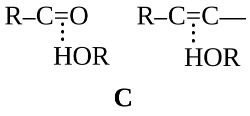
Complicated shape and asymmetry of the IR bands belonging to OH stretching vibrations of complexes of phenols with aldehydes, ketones, and quinones was explained by the fact that the complexes exist in solutions as equilibrium mixtures of stereoisomers: nonlinear (**A**), bidentate (**B**), and OH···π-bonded (**C**) [2, 3] (Scheme 1).

**Scheme 1.**



According to [2–8], stereoisomer **A** absorbs at lower frequencies than **B** or **C**. The overlap of the absorption bands of the three stereisomers results in a complex contour of the observed band. This explanation was criticized in view of the fact that local distortions of the contour may be caused by incomplete compensation of the 2ν(C=O) overtone absorption of the free and complexed molecule of the carbonyl compound [9, 10]. This is so indeed in certain cases [7]. However, with structurally diverse phenols, evidence for the composite nature of the observed band was obtained in the research on H complexes of their isotopically labeled derivatives [2, 11, 12]. As found in [13], the shifts of the high-frequency component of the absorption band of complexes of phenol with ketones and with substituted ethylenes, caused by the same alkyl group (Scheme 2), are the same. Therefore, of the two alternative forms **B** and **C** preference was given to the latter.

**Scheme 2.**



R = Me, Et, *t*-Bu.

According to [14–16], the ν(OH) band in the IR spectra of complexes of phenols and methanol with acetates and amides, too, is composite in nature. In one of the previous communications of the present series [17] we showed that the components of the observed band in the spectra of H complexes of methanol with these electron donors relate to configurational isomers of a complex of type **A** [*synperiplanar* (*sp*-**A**) and *antiperiplanar* (*ap*-**A**)] (Scheme 3, parenthesized is the fragment oriented similarly to the H bond).

In principle, with such strong H-bond donors as phenols, acetates and amides can form, apart from these configurational isomers, complexes with an OH···π bond. Moreover, there is some evidence showing that in alcohol–ester systems an H bond involving both oxygen atoms may form [18]. At the same time, no evidence is available for the presence of several bands in the IR spectra of H complexes of

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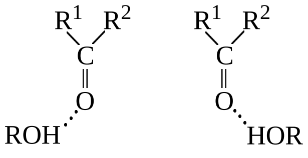
[1] For communication XXVIII, see [1].

**Scheme 3.**



*sp*-**A**(R$^1$) *ap*-**A**(R$^2$)

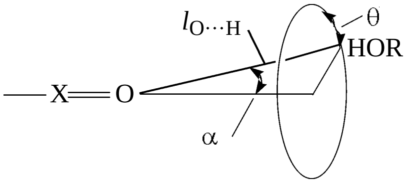
symmetrical donors of this series (ureas, carbonates) [7, 16, 19], even though such donors are also capable of forming additional H complexes. There has also been no information on the complex shape of IR absorption bands of H complexes of phenols with sulfoxides [20–23], not counting the well-defined Fermi resonance structure in the strongest of such complexes [24]. No data on the existence of one more complex for compounds with P=O or $SO_2$ groups has been reported [25–34].

In whole the IR spectral evidence shows that symmetrical ketones, quinines, and analogous electron donors form with phenols a nonlinear H complex and an OH···π(C=O) complex; reliable evidence in favor of existence in solution of a bidentate H complex is lacking; reactions of ureas, carbonates, and symmetrical sulfoxides and phosphine oxides with phenols and alcohols result in exclusive formation of complexes of type **A** whose configurational isomers are degenerate in energy; unsymmetrical carbonyl-containing electron donors can form h complexes of various structures. Thus, there has already been fairly much work on the stereoisomerism of H complexes. At the same time, most research has been qualitative and establishing in nature. Consequently, spectral manifestations of the H-bond direction call for further research.

In the present communication we discuss the results of theoretical and experimental research on 1:1 H complexes of phenol with amides and acetates, and empirical correlations between their ν(OH) absorption maximum and the Kamlet–Taft solvatochtomic parameter β that characterizes the ability of an electron donor to act as an H-bond acceptor. An ample body of general theoretical information concerning the simpler methanol H complexes is presented.

**Configurational isomerism of nonlinear H complexes.** The spatial arrangement of the bridging hydrogen atom with respect to the X=O oxygen in H complexes of any type (**A**–**C**) is defined by three geometric parameters: two angles (α and θ) and O···H distance ($l_{O\cdots H}$) (Scheme 4).

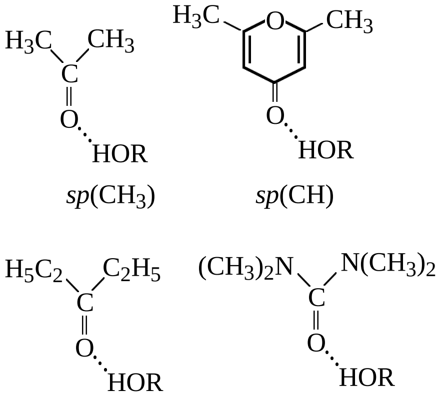
**Scheme 4.**



The calculations of isolated methanol H complexes at the B3LYP/6-311G* level [17] showed that the α angle is nonconstant and varies with the H-bond acceptor in a fairly wide range (40–80°). The θ angle, too, is variable, but in most H complexes it is no larger than 30°. On this basis the configurational isomers of H complexes of type **A** were classed as *synperiplanar* (*sp*-**A**) and *antiperiplanar* (*ap*-**A**) (Scheme 3).

Symmetrical H-bond acceptors are characterized by the degenerate configurational isomerism of H complexes of type **A**. In what follows such complexes are denoted according to the value of the α angle (Scheme 5).

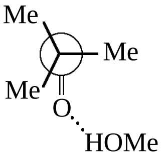
**Scheme 5.**



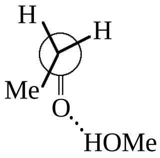
*sp*($CH_3$) *sp*(CH)

*ap*($C_2H_5$) *ap*[$N(CH_3)_2$]

No linear complexes (type **B**, α → 0) were found among the calculated structures. In this connection particular attention should be given to carbonyl compounds with *tert*-butyl and trifluoromethyl groups. According to [8], it is these groups that stabilize complex **B** with methanol. The calculation results show that this is not the case with isolated 1:1 H complexes. The *tert*-butyl substituent decreases the α angles compared with methyl, but simultaneously increases the θ angle. As a result, the α angle remains roughly the same as in complexes with electron donors with other bulky substituents.



*ap*(*t*-Bu)



*ap*(Et)

**Table 1.** Theoretical characteristics of methanol H complexes of type **A**, obtained by B3LYP/6-311G* calculations

| H-Bond acceptor | $-\Delta E_H$, kJ mol$^{-1}$ | $\Delta\nu$(OH), cm$^{-1}$ | $\alpha$, deg | $\theta$, deg |
|---|---|---|---|---|
| *sp*-**A** analogs | | | | |
| 2,6-Dimethylpyran-4-one | 46.31 | 223 | 68 | 2 |
| Trimethylphosphine oxide | 46.05 | 234 | 74 | 9 |
| DMSO | 45.76 | 211 | 68 | |
| Pyran-4-one | 43.96 | 197 | 68 | 2 |
| Acetone | 36.05 | 135 | 64 | 2 |
| Cyclopentanone | 35.13 | 139 | 68 | 14 |
| Propylene carbonate | 26.04<br>26.00 | 61<br>61 | 59<br>58 | 21<br>13 |
| | | | $\bar{\alpha}$ 66 | |
| *ap*-**A** analogs | | | | |
| 1,3-Dimethylimidazol-2-one | 45.22 | 176 | 48 | 10 |
| 1,3-Dimethylimidazolidin-2-one | 42.79 | 158 | 47 | 1 |
| 1,3-Dimethyl-3,4,5,6-tetrahydropyrimidin-2-one | 42.04 | 144 | 37 | 1 |
| Tetramethylurea | 39.86 | 131 | 42 | 30 |
| Benzophenone | 35.00 | 96 | 44 | 34 |
| Diethyl carbonate | 33.70 | 88 | 47 | 25 |
| Dimethyl carbonate | 33.41 | 86 | 48 | 32 |
| Pentane-3-one | 31.74 | 91 | 44 | 8 |
| | | | $\bar{\alpha}$ 45 | |

| H-Bond acceptor | $\alpha$, deg | $\theta$, deg |
|---|---|---|
| MeCOMe | 63.8 | 2 |
| EtCOEt | 43.9 | 9 |
| *t*-BuCOBu-*t* | 48.5 | 31 |
| PhCOPh | 44.1 | 34 |

The trifluoromethyl group shifts the configurational isomerism *sp*-**A** $\rightleftarrows$ *ap*-**A** to a form having this substituent and the hydrogen bond *trans* to each other [below are the formation energies ($\Delta E_H$) of H complexes with methanol, kJ mol$^{-1}$].

| H-Bond acceptor | Configurational isomer | $-\Delta E_H$ |
|---|---|---|
| $CF_3COMe$ | *sp*($CH_3$) | 30.15 |
| | *ap*($CF_3$) | 19.18 |
| $CF_3CONMe_2$ | *sp*($CF_3$) | 26.67 |
| | *ap*($NCH_3$) | 35.42 |

In other words, the $CF_3$ group renders the molecular system configurationally more homogeneous, which simplifies the IR spectrum.

**Regularities in variation of the ν(OH) frequency of H complexes of symmetrical electron donors.** This type of H-bond acceptors includes compounds with a symmetry plane or axis ($C_2$), as well as electron donors that form H complexes with a quasi-degenerate configurational isomerism (propylene carbonate, etc.).

Analysis of the theoretical characteristics of methanol H complexes, listed in Table 1, allows the following conclusions. At a roughly constant $\alpha$ angle, the correlation between $\Delta\nu$(OH) [complexation-induced shift of $\nu$(OH)] and $\Delta E_H$ is linear. The slope of the corresponding regression equations (1) and (2) decreases with decreasing average value of the $\alpha$ angle ($\bar{\alpha}$) of the group of H-bond acceptors.

$$\bar{\alpha}\ 66°:\ \Delta\nu(\text{OH}) = (-147 \pm 13) - (8.0 \pm 0.3)\Delta E_H, \quad (1)$$
$$r\ 0.995,\ sd\ 8,\ n\ 8,$$

$$\bar{\alpha}\ 45°:\ \Delta\nu(\text{OH}) = (-139 \pm 20) - (6.9 \pm 0.5)\Delta E_H, \quad (2)$$
$$r\ 0.984,\ sd\ 7,\ n\ 8.$$

The $\theta$ angle has no effect on the parameters of the $\Delta\nu(\text{OH})$–$\Delta E_H$ correlation, and is likely to define, to a certain extent, the formation energy of the H complex.

At $|\Delta E_H| > 0$, the $\Delta\nu$(OH) value changes sign. This result points to an appreciable and almost constant stabilizing contribution of interactions not affecting $\nu$(OH) into the total formation energy of the H complex. At $\bar{\alpha}$ ~65°, this contribution comprises ~18.4 kJ mol$^{-1}$, while at $\bar{\alpha}$ ~45°, it is ~20.1 kJ mol$^{-1}$. Let us denote this contribution into $\Delta E_H$ as $\Delta E_H^{el}$. Including $\Delta E_H^{el}$, i.e. using the difference $\Delta E_H^{c} = \Delta E_H - \Delta E_H^{el}$, we can readily obtain regression lines coming to the origin.

The H bond directed at the $\alpha$ angle of ~65° to the axis passing along the C=O group is the most favorable for specific interaction, as evidenced by the maximum slope in Eq. (1). In its turn, such $\alpha$ angle corresponds to the spacial arrangement of the maximum electron density of the lone electron pair. Since the $\alpha$ angle in the first-group H complexes varies over fairly wide range (the deviation from the mean arithmetic value is up to 8°), we can conclude that in the $58° < \alpha < 74°$ range the electron density of the lone electron pair is distributes symmetrically and varies only slightly.

The $\Delta E_H^{el}$ value sharply decreases in going from H complexes of type **A** to type **C**. Thus, as follows from Eq. (3) for H complexes of methanol with typical $\pi$-electron donors ($\alpha$ ~0°, $\theta$ ~90°), the $\Delta E_H^{el}$ for such complexes is ~9.5 kJ mol$^{-1}$.

| H-Bond acceptor | $-\Delta E_H$, kJ mol$^{-1}$ | $\Delta$(OH), cm$^{-1}$ |
|---|---|---|
| Benzene | 11.89 | 20 |
| 2-Methylpropene | 17.54 | 66 |
| 2-*tert*-Butyl-3,3-dimethylbut-1-ene | 21.02 | 96 |

$$\Delta\nu(\mathrm{OH}) = (-79 \pm 2) - (8.3 \pm 0.1)\Delta E_H, \quad (3)$$
$$r\ 0.999,\ sd\ 0.8,\ n\ 3.$$

At the same time, the sensitivity of Δν(OH) for OH···π complexes to their formation energy is nearly the same as for OH···*n* complexes at the optimal α angle (~65°).

Thus, there are several implications of the theoretical. In Badger–Bayer correlations, one should take into account the possibility of configurational isomerism in complexes of type **A**. The correlation between Δν(OH) for H complexes and the quantitative measure of specific interactions of their subunits (solvatochromic parameter β) should be described by a family of linear equations. The effect of specific interactions on the Δν(OH) values of complexes of type **C** and configurational isomers of complexes of type **A** with α ~65° is almost the same.

A series of formation heats for methanol H complexes (Δ*H*), determined by IR spectroscopy in $CCl_4$ [5, 35–37] are known. The Δ*H* values in the cited papers were estimated using the absorption bands belonging exclusively complex **A** or **B** with acetone and benzophenone at a low concentration of the latter. Thus determined Δ*H* values can be compared with $\Delta E_H^c$

| H-Bond acceptor | Type of H complex | $-\Delta E_H^*$, kJ mol$^{-1}$ | $-\Delta H(CCl_4)$, kJ mol$^{-1}$ |
|---|---|---|---|
| 2,6-Dimethylpyran-4-one | **A** | 28.1 | 23.4 ± 3.3 |
| | **C** | | 12.6 ± 3.8 |
| DMSO | **A** | 27.2 | 18.8 |
| Acetone | **A** | 17.6 | 10.5 |
| Benzophenone | **A** | 15.9 | 9.2 |
| Benzene | **C** | 2.1 | 4.6 |

As seen from the above data, even without accounting for medium effects the calculation method fairly reproduces the trend in variation of the formation heats of the H complexes in hand.

**Hydrogen complexes of unsymmetrical H-bond acceptors.** As shown in [2], the spectral shifts characteristic of stereoisomeric phenol H complexes are linearly related to each other. We considered it interesting to find out whether there is analogous correlation between the Δν(OH) values of configurational isomers *sp*-**A** and *ap*-**A**.

The B3LYP/6-311G* calculations of H complexes whose electron-donor subunit contains a constant methyl substituent (Table 2) show that the $\bar{\alpha}$ values for isomers *sp*-**A** and *ap*-**A** only slightly vary in the series of complexes of phenol and methanol (phenol: *sp*-**A** $\bar{\alpha}$ 59°, *ap*-**A** $\bar{\alpha}$ 38°; methanol: *sp*-**A** $\bar{\alpha}$ 64°, *ap*-**A** $\bar{\alpha}$ 44°). Moreover, the difference between α(*sp*-**A**) and α(*ap*-**A**) is independent of the structure of the H-bond donor and equals ~20°. By this reason, the Δν(OH)(*sp*-**A**) and Δν(OH)(*ap*-**A**) values for both donors are linearly related to each other [Eq. (4)].

$$\Delta\nu(\mathrm{OH})(ap\text{-}\mathbf{A}) = (-3 \pm 4) + (0.74 \pm 0.02)\Delta\nu(\mathrm{OH})(sp\text{-}\mathbf{A}), \quad (4)$$
$$r\ 0.996,\ sd\ 5,\ n\ 11.$$

Note that, like with the series of symmetrical H-bond acceptors, the H complexes *ap*-**A** having smaller α angles induce smaller spectral shifts. This is evidenced by the fact that the slope of Eq. (4) is less than unity.

As follows from the calculations, the spectral shift at $\Delta E_H \approx$ const depends on the orientation of the H bond. This result can be interpreted as follows. If α is smaller or larger than 65°, optimal conditions for specific interactions between subunits in the complex are disturbed, since the bridging hydrogen atom leaves the region corresponding of the maximum electron density of the lone electron pair.

Since Eq. (4) relates to H-bond donors of various structures, it can be used to determine from experimental data the nature of the second (minor) H complex. However, before using this approach one should make sure that independently determined Δν(OH) values for isomers *sp*-**A** and *ap*-**A** fit this equation. Such data are available for H complexes of methanol with MeCOX (X = Et, Ph, OAlk, $NMe_2$) in $CCl_4$ [17], and they fit Eq. (4).

Table 3 lists the experimental Δν(OH) values for H complexes of phenol and alcohols with electron donors of the MeCOX series (X = OAlk, $NR_2$), obtained by resolving the composite band into two components (solutions in $CCl_4$; data of the authors and from [2, 7, 14, 15, 17]). We chose just this series of electron donors in view of the fact that the corresponding symmetrical compounds XCOX form no other complexes than those with an OH···*n* bond. Joint treatment of the theoretical (Table 2) and experimental (Table 3) data gives Eq. (5) whose parameters are almost the same as in Eq. (4). This result suggests that the components of the observed band of H complexes of the H-bond donors listed in Table 3 relate to configurational isomers *sp*-**A** and *ap*-**A**.

**Table 2.** Theoretical characteristics of the configurational isomers of H complexes of type **A** of phenol and methanol with electron donors MeCOR, obtained by B3LYP/6-311G* calculations

| H-Bond donor | H-Bond acceptor (conformation) [a] | H Complex | $-\Delta E_H$, kJ mol$^{-1}$ | $\Delta\nu$(OH), cm$^{-1}$ | $\alpha$, deg |
|---|---|---|---|---|---|
| PhOH | MeCOEt (*sp*) | *sp*(Me) | 39.98 | 228 | 60 |
| | MeCOPh | *sp*(Me) | 0.32 | 236 | 59 |
| | $MeCONMe_2$ | *sp*(Me) | 49.82 | 319 | 59 |
| | MeCOEt (*sp*) | *ap*(Et) | 36.84 | 163 | 42 |
| | MeCOPh | *ap*(Ph) | 37.93 | 178 | 38 |
| | $MeCONMe_2$ | *ap*(NMe) | 46.22 | 231 | 35 |
| MeOH | MeCOEt (*sp*) | *sp*(Me) | 35.88 | 135 | 64 |
| | MeCOPh | *sp*(Me) | 35.96 | 138 | 62 |
| | $MeCONMe_2$ | *sp*(Me) | 42.79 | 191 | 62 |
| | MeCOOMe (*sp*) | *sp*(Me) | 35.34 | 121 | 65 |
| | MeCOOEt (*sp*, *ap*) | *sp*(Me) | 35.63 | 124 | 65 |
| | MeCOOEt (*sp*, *sc*) | *sp*(Me) | 35.42 | 124 | 65 |
| | MeCOOPr (*sp*, *ap*, *ac*) | *sp*(Me) | 35.67 | 124 | 65 |
| | MeCOCOMe (*sp*) | *sp*(Me) | 30.77 | 94 | 65 |
| | MeCOEt (*sp*) | *ap*(Et) | 31.95 | 91 | 45 |
| | MeCOPh | *ap*(Ph) | 35.29 | 98 | 40 |
| | $MeCONMe_2$ | *ap*(NMe) | 40.32 | 134 | 38 |
| | MeCOOMe (*sp*) | *ap*(OMe) | 33.79 | 90 | 46 |
| | MeCOOEt (*sp*, *ap*) | *ap*(OEt) | 34.12 | 94 | 46 |
| | MeCOOEt (*sp*, *sc*) | *ap*(OEt) | 34.33 | 90 | 42 |
| | MeCOOPr (*sp*, *ap*, *ac*) | *ap*(OPr) | 34.12 | 93 | 46 |
| | MeCOCOMe (*sp*) | *ap*(COMe) | 29.43 | 61 | 45 |

[a] The conformations of H-bond acceptors are denoted with respect to the carbonyl group.

$$\Delta\nu(\mathrm{OH})(ap\text{-}\mathbf{A}) = (-6 \pm 2) + (0.74 \pm 0.01)\Delta\nu(\mathrm{OH})(sp\text{-}\mathbf{A}), \quad (5)$$
$$r\ 0.997,\ sd\ 5,\ n\ 36.$$

Since the direction of the H bond in separate groups of H complexes does not change in going from symmetrical (XCOX) to the narrow range of unsymmetrical (MeCOX) H-bond acceptors, joint correlation between the theoretical $\Delta\nu$(OH) and $\Delta E_H$ values is possible [cf. Eqs. (1), (2), (6), and (7); for data, see Tables 1 and 2].

$$\bar{\alpha}\ 65°:\ \Delta\nu(\mathrm{OH}) = (-157 \pm 11) - (8.1 \pm 0.3)\Delta E_H, \quad (6)$$
$$r\ 0.990,\ sd\ 8,\ n\ 16,$$

$$\bar{\alpha}\ 44°:\ \Delta\nu(\mathrm{OH}) = (-137 \pm 12) - (6.8 \pm 0.3)\Delta E_H, \quad (7)$$
$$r\ 0.983,\ sd\ 6,\ n\ 16.$$

For the joint series of H complexes of methanol with MeCOX and XCOX the $\Delta E_H^{el}$ value, too, is determined by the $\alpha$ angles and equals ~19.4 and ~20.1 kJ mol$^{-1}$ for isomers *sp*-**A** and *ap*-**A**, respectively. In going to H complexes of methanol with the other unsymmetrical H-bond acceptors, the $\Delta E_H^{el}$ values in groups with $\alpha \approx$ const slightly differ from each other. Thus, for the configurational isomers with $\alpha$ ~65°, characterized in Table 4, two regression equations (8) and (9) were found, relating to different $\Delta E_H^{el}$ values.

$$\bar{\alpha}\ 62°:\ \Delta E_H^{el}\ \sim 18.1\ \mathrm{kJ\,mol^{-1}},$$
$$\Delta\nu(\mathrm{OH}) = (-139 \pm 11) - (7.7 \pm 0.4)\Delta E_H, \quad (8)$$
$$r\ 0.991,\ sd\ 6,\ n\ 9,$$

$$\bar{\alpha}\ 66°:\ \Delta E_H^{el}\ \sim 21.2\ \mathrm{kJ\,mol^{-1}},$$
$$\Delta\nu(\mathrm{OH}) = (-172 \pm 20) - (8.1 \pm 0.6)\Delta E_H, \quad (9)$$
$$r\ 0.991,\ sd\ 5,\ n\ 5.$$

Configurational isomers with $\alpha$ ~45°, too, divided into two subgroups (Table 5). They are characterized by Eqs. (10) and (11), and different $\Delta E_H^{el}$ values.

$$\bar{\alpha}\ 46°:\ \Delta E_H^{el}\ \sim 17.3\ \mathrm{kJ\,mol^{-1}},$$
$$\Delta\nu(\mathrm{OH}) = (-107 \pm 14) - (6.2 \pm 0.4)\Delta E_H, \quad (10)$$
$$r\ 0.990,\ sd\ 8,\ n\ 7,$$

$$\bar{\alpha}\ 45°:\ \Delta E_H^{el}\ \sim 21.6\ \mathrm{kJ\,mol^{-1}},$$
$$\Delta\nu(\mathrm{OH}) = (-136 \pm 12) - (6.3 \pm 0.3)\Delta E_H, \quad (11)$$
$$r\ 0.986,\ sd\ 6,\ n\ 12.$$

**Table 3.** Shifts of the O–H stretching vibration frequencies characterizing components of the observed absorption band of H complexes of phenols and alcohols with electron donors MeCOX (X = OAlk, $NR_2$) in $CCl_4$

| H-Bond donor | X | Δν(OH) (*sp*-**A**), $cm^{-1}$ [a] | Δν(OH) (*ap*-**A**), $cm^{-1}$ [a] |
|---|---|---|---|
| 4-Nitrobenzene-thiol | OEt | 48 [b] | 29 [b] |
| | $NPh_2$ | 96 [b] | 60 [b] |
| Trifloroethanol | OEt | 185 | 130 |
| | $NMe_2$ | 300 | 230 |
| 2-Methylpropan-2-ol | OEt | 105 | 75 |
| | OBu | 110 | 75 |
| | $NMe_2$ | 185 | 135 |
| Methanol | OMe | 100 | 70 |
| | OBu | 100 | 70 |
| | OEt | 110, 102 [b] | 75, 69 [b] |
| | $NMe_2$ | 205, 215 [b] | 140, 131 [b] |
| 2,6-Dimethyl-phenol | OEt | 165 | 110 |
| | $NMe_2$ | 280 | 200 |
| 3-(Dimethyl-amino)phenol | OEt | 195 | 135 |
| | $NMe_2$ | 355 | 265 |
| Phenol | OMe | 190 | 135 |
| | OBu | 210 | 145 |
| | OEt | 207, [b] 195 [b] | 145, [b] 140 [b] |
| | $OCH_2CH_2\cdot(CH_3)_2$ | 195 [b] | 145 [b] |
| | $NMe_2$ | 348 [b] | 256 [b] |
| 4-Fluorophenol | OEt | 201 [b] | 142 [b] |
| | $NMe_2$ | 363 [b] | 261 [b] |
| 2,4,6-Trichloro-phenol | OEt | 220 | 150 |
| 4-Nitrophenol | OEt | 280 | 190 |
| | $NMe_2$ | 430 | 315 |

[a] For assignment, see text. [b] Taken from [2, 7, 14, 15, 17].

**Theoretical forecast.** Analysis of experimental data in solutions (see below) was performed in terms of the Kamlet–Taft β parameter that measures the specific solvatochromic effect. For this reason, as the theoretical energetic characteristic of H complexes of type **A** we used $\Delta E^{c}_{H}$ . Using this value we could obtain a common structure–Δν(OH) correlation for all the above H complexes. As would be expected, the key feature here is that the slope of the Δν(OH) $\sim f(\Delta E^{c}_{H})$ equations depends on the direction of the H bond.

$$\bar{\alpha}\ 65°:\ \Delta\nu(OH) = (-1\pm3) - (8.2\pm0.2)\Delta E^{c}_{H} \quad (12)$$
$$r\ 0.994,\ sd\ 6,\ n\ 30,$$

$$\bar{\alpha}\ 45°:\ \Delta\nu(OH) = (1\pm4) - (6.4\pm0.2)\Delta E^{c}_{H} \quad (13)$$
$$r\ 0.980,\ sd\ 7,\ n\ 35.$$

**Table 4.** Theoretical characteristics of configurational isomers *sp*-**A** of H complexes of methanol with unsymmetrical electron donors, obtained by B3LYP/6-311G* calcualtions

| H-Bond acceptor[a] | Direction of H bond | $-\Delta E_H$, kJ $mol^{-1}$ | Δν(OH) $cm^{-1}$ [a] |
|---|---|---|---|
| $\bar{\alpha}$ 62° | | | |
| 1-Methyl-2-pyrrolidone | $CH_2$ | 41.41 | 189 |
| 1-Methyl-2-oxazolidone | $OCH_2$ | 30.86 | 91 |
| 1-Methyl-2-oxazolone | OCH | 29.48 | 83 |
| Butyrolactone | $OCH_2$ | 28.39 | 79 |
| Dimethyl carbonate (*sp*)(*ap*) | *ap*($OCH_3$) | 28.14 | 74 |
| Methyl formate (*ap*) | *ap*($OCH_3$) | 25.54 | 63 |
| 2-Methyl-2-nitropropane | NO | 24.16 | 46 |
| Nitromethane | NO | { 22.82<br>21.69 | { 40<br>37 |
| $\bar{\alpha}$ 66° | | | |
| Ethyl acetate (*ap*, *ap*) | $CH_3$ | 38.10 | 133 |
| Butyrolactone | $CH_2$ | 36.17 | 125 |
| 1,1,1-Trifluoroacetone | $CH_3$ | 30.14 | 72 |
| 1,1,1-Trifluoromethyl acetate (*sp*) | $CH_3$ | 29.89 | 64 |
| 1,1,1-Trifluorobutane-2,3-dione (*sp*) | $CH_3$ | 29.06 | 67 |
| α ≠ const | | | |
| DMF (α 79°) | H | 38.94 | 167 |
| Niromethane (α 63°) | $CH_3$ | 32.32 | 67 |
| Methylformate (*sp*) | H | 30.40 | 90 |
| (α 80°) | | | |

[a] See note to Table 2.

The parameters of Eqs. (12) and (13) allow the following forecast. On condition that we have configurational isomers of H complexes of type **A** and the α angles are constants, two linear correlations between Δν(OH) and β should exist in series of configurational isomers of the same type (*sp*-**A** and *ap*-**A**). To find these correlations, one should invoke a broad range of H-bond acceptors. In this connection a the question arises of whether this range may include unsymmetrical ketones. For H complexes of such compounds the nature of the additional band in the Δν(OH) range is unknown. It may belong both to isomer *ap*-**A** and to an OH···π complex. This uncertainty can be obviated by comparing the parameters of the correlation between Δν(OH) for the first and second components of the composite band in the

**Table 5.** Theoretical characteristics of configurational isomers *ap*-**A** of H complexes of methanol with unsymmetrical electron donors, obtained by B3LYP/6-311G* calcualtions

| H-Bond acceptor[a] | Direction of H bond | $-\Delta E_H$, kJ mol$^{-1}$ | $\Delta\nu$(OH) cm$^{-1}$ [a] |
|---|---|---|---|
| $\bar{\alpha}$ 46° | | | |
| 1-Methyl-2-pyrrolidone | $NCH_3$ | 42.24 | 157 |
| DMF | $NCH_3$ | 40.36 | 134 |
| Ethoxydiethylamine (*sp*)(*ap*) | $OC_2H_5$ | 38.18 | 125 |
| Acetoxydiethylamine (*sp*) | $OCH_3$ | 37.93 | 124 |
| Di-*tert*-butyl ketone | *sc*($t$-$C_4H_9$) | 32.36 | 107 |
| 1,1,1-Trifluoro-acetamide | $CF_3$ | 26.67 | 53 |
| 1,1,1-Trifluoroacetone | $CF_3$ | 19.18 | 9 |
| $\bar{\alpha}$ 45° | | | |
| 1-Methyl-2-oxazolone | $NCH_3$ | 40.95 | 119 |
| 1-Methyl-2-oxazolidone | $NCH_3$ | 40.03 | 119 |
| Ethoxydimethylamine (*sp*)(*ap*) | $NCH_3$ | 39.23 | 119 |
| Acetoxydimethylamine (*sp*) | $NCH_3$ | 39.02 | 118 |
| Dimethyl(phenoxy)-amine (*sp*) | $NCH_3$ | 37.76 | 102 |
| *N*,*N*-Dimethylchloro-acetamide (*sp*) | $NCH_3$ | 38.02 | 99 |
| Dimethyl carbonate (*sp*)(*ap*) | *sp*($OCH_3$) | 35.59 | 89 |
| 1,1,1-Trifluoro-acetamide | $NCH_3$ | 35.42 | 81 |
| Methyl formate (*sp*) | *sp*($OCH_3$) | 32.99 | 76 |
| 2-Methyl-2-nitropropane | *sc*($t$-$C_4H_9$) | 30.90 | 65 |
| Methyl trifluoroacetate (*sp*) | *sp*($OCH_3$) | 30.14 | 47 |
| 1,1,1-Trifluorobutane-2,3-dione (*sp*) | *sp*($COCH_3$) | 24.91 | 24 |

[a] See note to Table 2.

series of H complexes of symmetrical and unsymmetrical electron donors. Sufficient body of Δν(OH) values is presenty available for acetone, butanone, benzophenone, and acetophenone (Table 6). In the case of symmetrical electron donors, there are linear correlations between the Δν(OH) values for OH···π and OH···*n* complexes, described by Eqs. (14) (benzophenone) and (15) (acetone).

$$\Delta\nu(\mathrm{OH})(\mathrm{OH}\cdots\pi) = (12 \pm 4) + (0.59 \pm 0.02)\Delta\nu(\mathrm{OH})(\mathrm{OH}\cdots n), \quad (14)$$
$$r\ 0.992,\ sd\ 4,\ n\ 18,$$

$$\Delta\nu(\mathrm{OH})(\mathrm{OH}\cdots\pi) = (-2 \pm 6) + (0.57 \pm 0.03)\Delta\nu(\mathrm{OH})(\mathrm{OH}\cdots n), \quad (15)$$
$$r\ 0.979,\ sd\ 9,\ n\ 21.$$

These equations differ from each other by free terms only but have almost equal slopes. The difference (14 cm$^{-1}$) between the free terms is explained by the fact that the orientation of the H-bond donor in a complex of type **A** to the benzophenone benzene ring decreases the α angle, which adversely affects specific interactions. As a result, the absorption band of such complex is shifted to higher frequencies compared with complexes in which the hydrogen bond is directed to the methyl group. Thus, comparison of the parameters of the equation for symmetrical and unsymmetrical electron donors will be correct if the direction of the OH···*n* bond will be the same in both cases, which is provided by the constancy of one of the substituents. To this end, we used, as already mentioned, MeCOEt, MeCOPh, and, in addition, MeCOBu-*t* (data from [2]). For H complexes of such ketones we can theoretically admit the complex equilibrium **C** $\rightleftarrows$ *sp*-**A** $\rightleftarrows$ *ap*-**A**, with two possible particular cases: **C** $\rightleftarrows$ *sp*-**A** and *sp*-**A** **C** $\rightleftarrows$ *ap*-**A**. If the first case is realized, the parameters of the corresponding equation will coincide with those of Eq. (15), while if the second, with those of Eq. (5). In the case of the complex equilibrium, the slope will have an intermediate value. Just such value was obtained in regression analysis of the experimental shifts of the highfrequency component of the observed band [$\Delta\nu^{(2)}$(OH)] with respect to the low-frequency component [$\Delta\nu^{(1)}$(OH)(OH···*n*)] for the above unsymmetrical ketones.

$$\Delta\nu^2(\mathrm{OH}) = (-10 \pm 6) + (0.66 \pm 0.03)\Delta\nu^{(1)}(\mathrm{OH})(\mathrm{OH}\cdots n), \quad (16)$$
$$r\ 0.981,\ sd\ 6,\ n\ 25.$$

Thus, the high-frequency band of H complexes of phenols with unsymmetrical ketons is composite in nature and thus unfeasible for quantitative description of solvatochromism.

**Correlation between Δν(OH) and β.** The experimental data on the solvatochromism of the absorption band due to stretching vibrations of the O–H band in H complexes of phenol with various electron donors are listed in Table 7. Their analysis shows that Δν(OH) are related to β by a family of linear dependences, each described by correlation equation (17).

$$\Delta\nu(\mathrm{OH}) = \Delta\nu^0(\mathrm{OH}) + b\beta. \quad (17)$$

On this basis, five groups of electron donors can

**Table 6.** Spectral shifts (cm$^{-1}$) of the low-frequency [$\Delta\nu^{(1)}$(OH)] and high-frequency [$\Delta\nu^{(2)}$(OH)] components of the observed band[a] of H complexes of acetone, benzophenone, butanone, and acetophenone (solvent $CCl_4$)

| H-Bond donor | $\Delta\nu^{(1)}$(OH)(**A**) | $\Delta\nu^{(2)}$(OH)(**B**) | $\Delta\nu^{(1)}$(OH)(**A**) | $\Delta\nu^{(1)}$(OH)(?) |
|---|---|---|---|---|
| | Acetone | | | Butanone |
| 4-Nitrobenzenethiol | 66 | 36 | – | – |
| 2,6-Dimethylphenol (1-OD) | 110 | 60 | – | – |
| 2-Methylpropan-2-one | 115[b] | 75[b] | – | – |
| Methanol | 135[b] | 80[b] | – | – |
| 2,6-Diisopropyl-4-nitrophenol | 140 | 74 | – | – |
| Phenol (1-OD) | 160 | 90 | 150 | 95 |
| 2,6-Dimethylphenol | 185, 190 | 100, 100 | 178 | 100 |
| Pentachlorophenol (1-OD) | 199 | 100 | – | – |
| Trifluoroethanol | 210[b] | 110[b] | – | – |
| 2,5-Dimethylphenol | 224 | 130 | 218 | 130 |
| 2-Methylphenol | 230 | 130 | – | – |
| Phenol | 237, 235 | 133, 135 | 216, 220 | 125, 125 |
| 4-Chlorophenol | 257, 230 | 148, 130 | 242 | 148 |
| 2,4,6-Trichlorophenol | 254 | 139 | 236 | 139 |
| 2-Naphthol | 255 | 160 | – | – |
| 2-Chlorophenol | 278 | 165 | 266 | 165 |
| 3,5-Dichlorophenol | 307 | 179 | 292 | 179 |
| Pentachlorophenol | 324 | 168 | – | – |
| 4-Nitrophenol | 325 | 200 | 315[b] | 200[b] |
| | | Acetone-$d_6$ | | |
| Pentachlorophenol (1-OD) | 207 | 104 | – | – |
| Pentachlorophenol | 326 | 172 | – | – |
| | Benzophenone | | | Acetophenone |
| 2-Methylpropan-2-one | 100[b] | 75[b] | – | – |
| Methanol | 110[b] | 80[b] | – | – |
| 2,6-Dimethylphenol (1-OD) | 110 | 75 | 125 | 75 |
| Phenol (1-OD) | 135 | 85 | 150 | 90 |
| 2-Methylphenol (1-OD) | 150 | 100 | – | – |
| 2,6-Dimethylphenol | 165 | 100 | 195 | 120 |
| 2-Methoxyphenol | 170 | 119 | – | – |
| Trifluoroethanol | 175[b] | 115[b] | 200[b] | 125[b] |
| 4-Methylphenol | 180 | 120 | – | – |
| Phenol | 198, 195 | 127, 125 | 225 | 135 |
| 2-Naphthol | 205 | 130 | 230 | 130 |
| 4-Chlorophenol | 215 | 140 | 230 | 140 |
| 2-Methylphenol | 215 | 140 | – | – |
| 4-Bromophenol | 218 | 146 | – | – |
| 3,4-Dichlorophenol | 245 | 155 | – | – |
| 3-Nitrophenol | 258 | 166 | – | – |
| 3,5-Dichlorophenol | 262 | 171 | – | – |
| 3,4,5-Trichlorophenol | 291 | 180 | – | – |
| 4-Nitrophenol | – | – | 300 | 195 |

[a] Taken from [2, 6, 7, 11–13]. [b] Data of the authors.

be recognized, which is inconsistent with the forecast in the preceding section.

Apparently, in the liquid phase a finer gradation of H complexes by the specific (*b*β) and nonspecific [$\Delta\nu^0$(OH)] solvatichromic effects takes place. A similar solvatochromic behavior was observed with H complexes of other hydroxyl-containing H-bond

**Table 7.** Solvatochromism of the ν(OH) bands of phenol H complexes in $CCl_4$

| H-Bond acceptor | $\beta$ [a] | H Complex | $\Delta\nu(OH)$, [b] $cm^{-1}$ |
|---|---|---|---|
| Group I | | | |
| Chlorobenzene | 0.07 | **C** | 36 |
| Benzene | 0.10 | **C** | 49 |
| Toluene | 0.11 | **C** | 59 |
| *p*-Xylene | 0.12 | **C** | 68 |
| Acetone | 0.48 | **A** ($CH_3$) | 236 |
| Group II | | | |
| 4-Nitrobenzaldehyde | 0.32 | *sp*-**A** (H) | 150 |
| Ethyl chloroacetate | 0.35 | *sp*-**A** ($CH_2Cl$) | 150 [c] |
| Methyl acetate | 0.42 | *sp*-**A**($CH_3$) | 190 [c] |
| Benzophenone | 0.44 | **A** ($C_6H_5$) | 196 |
| Ethyl acetate | 0.45 | *sp*-**A** ($CH_3$) | 207 |
| Butyl acetate | 0.45 | *sp*-**A** ($CH_3$) | 210 [c] |
| Butanone | 0.48 | *sp*-**A** ($CH_3$) | 216 |
| 1,1,1-Trimethylpropanone | 0.48 | *sp*-**A**($CH_3$) | 228 |
| Acetophenone | 0.49 | *sp*-**A** (CH3) | 225 |
| Cyclohexanone | 0.53 | **A**($CH_2$) | 245 |
| Dimethylacetamide | 0.76 | *sp*-**A** ($CH_3$) | 348 |
| DMSO | 0.76 | **A** ($CH_3$) | 356 |
| 1-Methyl-2-pyrrolidone | 0.77 | *sp*-**A** ($CH_2$) | 355 [c] |
| Diisopropyl sulfoxide | 0.78 | **A** [$CH(CH_3)_2$] | 360 |
| 2,6-Dimethylpyran-4-one | 0.79 | **A** (CH) | 365 [d] |
| Tetramethylene sulfoxide | 0.80 | **A** ($CH_2$) | 370 |
| Dibutyl sulfoxide | 0.83 | **A** ($C_4H_9$) | 375 |
| Group III | | | |
| 1,3-Dichloropropanone | 0.34 | **A** ($CH_2Cl$) | 135 [d] |
| Butyraldehyde | 0.41 | *sp*-**A** (H) | 175 |
| Benzaldehyde | 0.44 | *sp*-**A** (H) | 185 |
| *N,N*-Dimethyltrifluoroacetamide | 0.46 | *ap*-**A** ($NCH_3$) | 185 |
| Butyrolactone | 0.49 | *sp*-**A** ($CH_2$) | 205 [c] |
| DMF | 0.69 | *sp*-**A** (H) | 285, 304 |
| Diphenyl sulfoxide | 0.70 | **A** ($C_6H_5$) | 293 |
| Ditolyl sulfoxide | 0.72 | **A** ($C_6H_4CH_3$) | 309 |
| Dibenzyl sulfoxide | 0.74 | **A** ($CH_2C_6H_5$) | 322 |
| Tetramethylurea | 0.80 | **A** ($NCH_3$) | 334 |
| Group IV | | | |
| Dimethyl carbonate | 0.38 | **A** ($OCH_3$) | 136 |
| Diethyl carbonate | 0.40 | **A** ($OC_2H_5$) | 145 |
| Propylene carbonate | 0.40 | **A** ($OCH_2$) | 149 [c] |
| Diethyl sulfite | 0.45 | **A** ($OC_2H_5$) | 158 |
| Dipropyl sulfite | 0.45 | **A** ($OC_3H_7$) | 154 |
| Dibutyl sulfite | 0.46 | **A** ($OC_4H_9$) | 162 |
| Di-*tert*-butyl ketone | 0.48 | **A** [$C(CH_3)_3$] | 186 |
| Group V | | | |
| Benzoyl chloride | 0.20 | **A** (?) | 55 |
| Nitromethane | 0.25 | *sp*-**A** ($CH_3$) | 70 [c] |
| Ethyl trichloroacetate | 0.25 | *ap*-**A** ($OC_2H_5$) | 76 [c] |
| Ethyl chloroacetate | 0.35 | *ap*-**A** ($OC_2H_5$) | 110 [c] |
| Methyl acetate | 0.42 | *ap*-**A** ($OCH_3$) | 135 [c] |
| Ethyl acetate | 0.45 | *ap*-**A** ($OC_2H_5$) | 145 |
| Butyl acetate | 0.45 | *ap*-**A** ($OC_4H_9$) | 145 [c] |
| Butyrolactone | 0.49 | *ap*-**A** ($OCH_2$) | 145 [c] |
| DMF | 0.69 | *ap*-**A** ($NCH_3$) | 209, 230 |
| Dimethylacetamide | 0.76 | *ap*-**A** ($NCH_3$) | 256 |
| 1-Methyl-2-pyrrolidone | 0.77 | *ap*-**A** ($NCH_3$) | 250 |

[a] The $\beta$ values were taken from [38, 39]. [b] Mean values [2, 4, 6, 13–15, 21, 40–53]. [c] Present communication. [d] Calculated by the equation $\Delta\nu(OH)^{obs} = (-12 \pm 6) + + (1.00 \pm 0.03)\Delta\nu(OH)(A)$, *r* 0.995, *sd* 7, *n* 14, found for the case of equilibrium between complexes of types **A** and **C**.

| Group | $\Delta\nu^0(OH)$, $cm^{-1}$ | *b*, $cm^{-1}$ | *r* | *sd* | *n* |
|---|---|---|---|---|---|
| I | $5 \pm 3$ | $483 \pm 12$ | 0.999 | 4 | 5 |
| II | $-4 \pm 4$ | $466 \pm 7$ | 0.998 | 5 | 17 |
| III | $-11 \pm 6$ | $440 \pm 11$ | 0.998 | 5 | 10 |
| IV | | ~380 | | | |
| V | $-13 \pm 4$ | $344 \pm 8$ | 0.997 | 5 | 11 |

donors. The results of this research will be reported in one of the following communications of the series.

## EXPERIMENTAL

The IR spectra were obtained on a Specord IR-75 spectrophotometer. A standard technique for resolution of composite absorption bands into Lorentz components was used.

Nonempirical calculations of the energetic and geometric parameters of 1 : 1 H complexes, as well as OH absorption frequencies were performed using the GAUSSIAN-98 program package [54].

Commercial reagents of chemical grade were used. They were purified by recrystallization from organic solvents, vacuum sublimation, or distillation. The purity was controlled by physicochemical methods.

## REFERENCES

1. Vokin, A.I., Shulunova, A.M., Aksamentova, T.N., Bozhenkov, G.V., and Turchaninov, V.K., *Russ. J. Gen. Chem.*, 2006, vol. 76, no. 4, p. 596.
2. Fritzsche, H., *Spectrochim. Acta*, 1965, vol. 21, no. 4, p. 799.
3. Fritzsche, H., *Acta Chim. Acad. Sci. Hung.*, 1964, vol. 40, no. 1, p. 31.
4. Fritzsche, H., *Ber. Bunsen-Ges. Phys. Chem.*, 1964, vol. 68, no. 5, p. 459.
5. Osawa, E., Kitamura, K., and Yoshida, Z., *J. Am. Chem. Soc.*, 1967, vol. 89, no. 15, p. 3814.
6. Thijs, R. and Zeegers-Huyskens, T., *Spectrochim. Acta, Part A*, 1984, vol. 40, no. 3, p. 307.
7. Laurence, C., Berthelot, M., and Helbert, M., *Spectrochim. Acta, Part A*, 1985, vol. 41, no. 7, p. 883.
8. Besseau, F., Lucon, M., Laurence, C., and Berthelot, M., *J. Chem. Soc., Perkin Trans. 2*, 1998, no. 1, p. 101.
9. Rassadin, B.V. and Iogansen, A.V., *Zh. Prikl. Spektrosk.*, 1967, vol. 6, no. 6, p. 801.
10. Iogansen, A.V., Rassadin, B.V., and Sultanov, B.Yu., *Zh. Prikl. Spektrosk.*, 1977, vol. 26, no. 1, p. 101.
11. Korppi-Tommola, J. and Shurvell, H.F., *Can. J. Chem.*, 1978, vol. 56, no. 23, p. 2959.
12. Korppi-Tommola, J. and Shurvell, H.F., *Can. J. Chem.*, 1979, vol. 57, no. 20, p. 2707.
13. Massat, A., Guillaume, P., Doucet, J.P., and Dubois, J.E., *J. Mol. Struct.*, 1991, vol. 244, nos. 1–3, p. 69.
14. Arnett, E.M., Joris, L., Mitchell, E., Murty, T.S.S.R., Gorrie, T.M., and Schleyer P.R., *J. Am. Chem. Soc.*, 1970, vol. 92, no. 8, p. 2365.
15. Dunken, H. and Fritzsche, H., *Z. Chem.*, 1962, vol. 2, no. 11, p. 345.
16. Besseau, F., Laurence, C., and Berthelot, M., *J. Chem. Soc., Perkin Trans. 2*, 1994, no. 3, p. 485.
17. Vokin, A.I., Oznobikhina, L.P., Shulunova, A.M., Fedorov, S.V., and Turchaninov, V.K., *Russ. J. Gen. Chem.*, 2005, vol. 75, no. 10, p. 1566.
18. Komarova, L.I., Lapina, N.N., Lokshin, B.V., Markova, G.D., and Vasnev, V.A., *Izv. Akad. Nauk, Ser. Khim.*, 1993, no. 4, p. 709.
19. Questel, J.-Y., Laurence, C., Lachkar, A., Helbert, M., and Berthelot, M., *J. Chem. Soc., Perkin Trans. 2*, 1992, no. 12, p. 2091.
20. Gramstad, T., *Spectrochim. Acta*, 1963, vol. 19, no. 5, p. 829.
21. Ghersetti, S. and Lusa, A., *Spectrochim. Acta*, 1965, vol. 21, no. 6, p. 1067.
22. Hadzi, D., Klofutar, C., and Oblak, S., *J. Chem. Soc. A*, 1968, no. 4, p. 905.
23. Filgueiras, C.A.L. and Rocha, O.G.F., *Tetrahedron*, 1982, vol. 38, no. 9, p. 1213.
24. Rassadin, B.V. and Iogansen, A.V., *Zh. Prikl. Spektrosk.*, 1969, vol. 10, no. 2, p. 290.
25. Aksnes, G. and Gramstad, T., *Acta Chem. Scand.*, 1960, vol. 14, nos. 7–8, p. 1485.
26. Gramstad, T. and Snaprud, S.I., *Acta Chem. Scand.*, 1962, vol. 16, no. 4, p. 999.
27. Gramstad, T., *Spectrochim. Acta*, 1963, vol. 19, no. 8, p. 1363.
28. Gramstad, T. and van Binst, G., *Spectrochim. Acta*, 1966, vol. 22, no. 10, p. 1681.
29. Rassadin, B.V. and Iogansen, A.V., *Zh. Prikl. Spektrosk.*, 1969, vol. 10, no. 3, p. 524.
30. Vdovenko, S.I., Zemlyanoi, V.N., and Kukhar', V.P., *Zh. Obshch. Khim.*, 1985, vol. 55, no. 10, p. 2210.
31. Iogansen, A.V., Rassadin, B.V., and Sorokina, N.P., *Zh. Prikl. Spektrosk.*, 1980, vol. 32, no. 6, p. 1089.
32. Matrosov, E.I., Kryuchkov, A.A., Nifant'ev, E.E., and Kabachnik, M.I., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, no. 4, p. 791.
33. Biscarini, P., Galloni, G., and Ghersetti, S., *Spectrochim. Acta*, 1964, vol. 20, no. 3, p. 436.
34. Chardin, A., Laurence, C., Berthelot, M., and Morris, D.G., *J. Chem. Soc., Perkin Trans. 2*, 1996, no. 6, p. 1047.
35. Becker, E.D., *Spectrochim. Acta*, 1961, vol. 17, no. 4, p. 436.
36. Rao, C.N.R., *J. Chem. Soc., Faraday Trans. 1*, 1975, no. 4, p. 980.
37. Rao, C.N.R., Dwivedi, P.C., Ratajczak, H., and Orville-Thomas, W.J., *J. Chem. Soc., Faraday Trans. 2*, 1975, no. 5, p. 955.
38. Kamlet, M.J., Abboud, J.-L., Abraham, M.H., and Taft, R.W., *J. Org. Chem.*, 1983, vol. 48, no. 17, p. 2877.
39. Abraham, M.H., Grellier, P.L., Abboud, J.-L.M., Doherty, R.M., and Taft, R.W., *Can. J. Chem.*, 1988, vol. 66, no. 11, p. 2673.
40. Bellamy, L.J. and Pace, R.J., *Spectrochim. Acta, Part A*, 1969, vol. 25, no. 2, p. 319.
41. Allerhand, A. and Schleyer, P.R., *J. Am. Chem. Soc.*, 1963, vol. 85, no. 4, p. 371.
42. Bellamy, L.J., Morgan, K.J., and Pace, R.J., *Spectrochim. Acta*, 1966, vol. 22, no. 3, p. 535.

43. Wayland, B.B. and Drago, R.S., *J. Am. Chem. Soc.*, 1964, vol. 86, no. 23, p. 5240.
44. Seguin, J.P., Nadjo, L., Uzan, R., and Doucet, J.P., *Spectrochim. Acta, Part A*, 1981, vol. 37, no. 3, p. 205.
45. Yoshida, Z. and Osawa, E., *J. Am. Chem. Soc.*, 1965, vol. 87, no. 7, p. 1467.
46. Seidel, H., Ritter, C., Fruwert, J., and Geiseler, G., *Spectrochim. Acta, Part A*, 1976, vol. 32, no. 4, p. 705.
47. Gramstad, T. and Sandstrom, J., *Spectrochim. Acta, Part A*, 1969, vol. 25, no. 1, p. 31.
48. Middaugh, R.L., Drago, R.S., and Neidzielski, R.J., *J. Am. Chem. Soc.*, 1964, vol. 86, no. 3, p. 388.
49. Powell, D.L. and West, R., *Spectrochim. Acta*, 1964, vol. 20, no. 6, p. 983.
50. Eyman, D.P. and Drago, R.S., *J. Am. Chem. Soc.*, 1966, vol. 88, no. 8, p. 1617.
51. Kamlet, M.J., Gal, J.-F., Maria, P.-C., and Taft, R.W., *J. Chem. Soc.*, *Perkin Trans. 2*, 1985, no. 10, p. 1583.
52. Baitinger, W.F., Schleyer, P.R., Murty, T.S.S.R., and Robinson, L., *Tetrahedron*, 1964, vol. 20, no. 7, p. 1635.
53. Kamlet, M.J., Solomonovici, A., and Taft, R.W., *J. Am. Chem. Soc.*, 1979, vol. 101, no. 14, p. 3734.
54. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.A., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Andres, J.L., Gonzalez, C., Head-Gordon, M., Replogle, E.S., and Pople, J.A., *GAUSSIAN-98*, Rev. A.6, Pittsburgh: Gaussian, 1998.