Complex Formation and Proton Transfer in the Polarizable Hydrogen Bonds of Two *N,N'*-Dioxides + Substituted Phenol Systems as a Function of the pK_a of the Phenols. An FTIR Study

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Complex formation, and proton transfer processes in the polarizable hydrogen bonds formed, have been studied with 1,8-bis(dimethylaminomethyl)naphthalene *N,N'*-dioxide (**1**) + R-phenol and with 1,2-bis(dimethylaminomethyl)benzene *N,N'*-dioxide (**2**) + R-phenol systems in acetonitrile solutions as a function of the pK_a of the substituted phenols. In the first family of systems the complex formation is not complete but increases with decreasing pK_a of the phenols, whereas in the second one it is always complete.

In both complexes an $OH \cdots ON \rightleftharpoons O^- \cdots H^+ON$ equilibrium is observed. With decreasing pK_a of the phenols the left hand well of the double minimum proton potential is first raised. After formation of a strong shorter hydrogen bond with almost no barrier within the proton potential, which is on average largely symmetrical, the right hand well is lowered and finally the proton is localized at the *N*-oxide group. The proton polarizability of the hydrogen bond first increases and then decreases again. With compound **2**, besides the heteroconjugated hydrogen bonds increasingly shorter homoconjugated intramolecular $NO \cdots H^+ \cdots ON$ hydrogen bonds are formed with decreasing pK_a of the phenols. In the systems with more acidic phenols only this species is present.

The IR spectra of carboxylic acid + trimethylamine *N*-oxide (TMAO) systems in acetonitrile solutions have already demonstrated that a broad flat single minimum proton potential in $COO^- \cdots H^+ \cdots ON$ hydrogen bonds changes with decreasing pK_a of the acid to a double minimum proton potential in $COOH \cdots ON \rightleftharpoons COO^- \cdots H^+ON$ bonds. The equilibrium shifts with decreasing pK_a in favour of the polar structure.[1]

R-Phenol + trimethylamine *N*-oxide (TMAO) systems in dichloromethane solutions have been studied, whereby the pK_a of the phenols was changed over a very large range.[2] With decreasing pK_a of the phenols the proton potential changed from a single minimum at the phenol to a double minimum, then to a broad, flat, single minimum (in the most symmetrical case) then again to a double minimum and finally to a single minimum at the acceptor (TMAO).

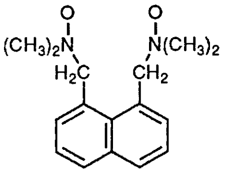
Furthermore, structurally symmetrical intramolecular homoconjugated $NO^+H \cdots ON \rightleftharpoons NO \cdots H^+ON$ and $N^+H \cdots N \rightleftharpoons N \cdots H^+N$ bonds were investigated.[3–6] The *N*-oxide systems show continua mainly in the region 1700–800 cm^{-1}, indicating the proton polarizability of these hydrogen bonds due to shifts of the proton in a broad flat single minimum potential. In contrast to these results the amine systems exhibit IR continua over the whole region with a band-like structure in the region 3000–1800 cm^{-1}, indicating the proton polarizability of these hydrogen bonds due to proton motion within a double minimum potential.[3]

Recently Sobczyk *et al.*[7] studied phenol + diamine systems in acetonitrile solutions using IR spectroscopy. They postulated the formation of very short $N \cdots H^+ \cdots N$ bonds caused by steric factors. Additionally, their formation depends on the pK_a of the respective phenols. The other hydrogen bonds present in these systems are phenol–phenolate hydrogen bonds.

In this paper we study 1,8-bis(dimethylaminomethyl)-naphthalene *N,N'*-dioxide (compound **1**) + R-phenols and 1,2-bis(dimethylaminomethyl) benzene *N,N'*-dioxide (compound **2**) + R-phenol systems in acetonitrile solutions as a function of the pK_a of the phenols using FTIR spectroscopy.

Experimental

The preparation of 1,8-bis(dimethylaminomethyl)naphthalene is described in ref. 8. Compounds **1** and **2** were synthesized following a procedure described in ref. 9.



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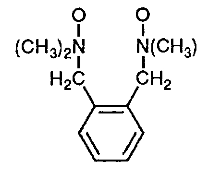

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The pK_a values of compounds **1** and **2** were measured in acetonitrile following the procedure given in ref. 10. The glass electrode was calibrated in picric acid–tetraethylammonium picrate buffers as described in ref. 11. The reproducibility of the procedure was checked with various bases of known pK_a values in acetonitrile. The concentrations of picric acid and both *N,N'*-dioxides were varied in the region (1–5) × 10^{-4} mol dm^{-3}.

All phenols were purchased from Merck (FRG) and Fluka (Switzerland) and were purified by sublimation.

The complexes were prepared by mixing equimolar amounts of the corresponding phenols and compound **1** or **2** in acetonitrile. The concentration of the solutions prepared for the measurements was 0.1 mol dm^{-3}. All preparations and transfers of solutions were carried out in a carefully dried glove box under a nitrogen atmosphere.

The IR spectra were taken with a FTIR spectrophotometer, Bruker IFS 113 v, using a cell with Si windows (layer thickness 0.26 mm), detector DTGS, and 250 scans were collected (resolution 2 cm^{-1}).

Results and Discussion

The *N,N'*-dioxides **1** and **2** were used.

The pK_a value of compound **1** in acetonitrile is 9.29. No

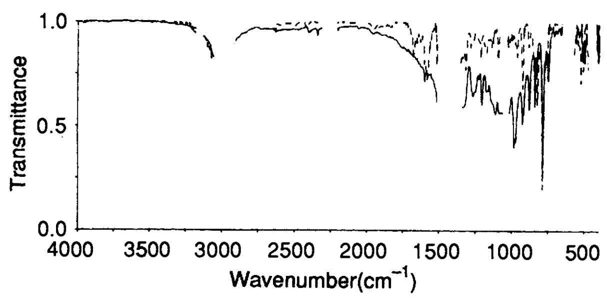


Fig. 1 FTIR spectra of saturated acetonitrile solution of (– – – –) compound **1**, and (——) of its 2:1 complex with $HAuCl_4$

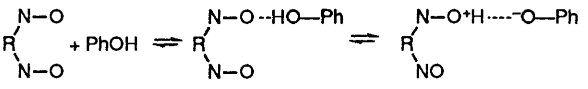
second pK_a value was found with this compound, indicating that no intramolecular hydrogen bond can be formed between the two NO groups owing to steric factors. With compound **2** two pK_a values were obtained: pK_1 = 12.70 and pK_2 = 10.40. The fact that two pK_a values were obtained indicates that within this molecule an intramolecular hydrogen bond may be formed between the two NO groups. The first pK_a value is higher since the proton must be removed from the intramolecular hydrogen bond.

Complexes of Compound **1**.—With $HAuCl_4$ in acetonitrile compound **1** forms only 2:1 complexes. This is shown by elemental analysis and especially by NMR spectroscopy. The result is obtained from the ratio of the integrated intensities of the signal of the hydrogen-bonded proton and the sum of signals of the aromatic CH_2 and CH_3 protons. It amounts to 1:(12 + 8 + 24). Thus, a homoconjugated intermolecular structurally symmetrical NO·H$^+$·ON hydrogen bond is formed. This result is in agreement with the observation that compound **1** has only one pK_a value.

The FTIR spectrum of an acetonitrile solution of this 2:1 complex is shown in Fig. 1. The hydrogen-bonded proton causes only a broad band at *ca.* 1000 cm^{-1} with a wing toward larger wave numbers. Thus, the proton potential in the NO·H$^+$·ON bonds is narrow and hence, the proton polarizability due to proton shifts within this hydrogen bond is small.[12]

In Table 1 all systems studied are summarized. First we consider the complexes formed by compound **1** with phenols (ratio 1:1) as a function of the pK_a of the phenols. Fig. 2 shows selected examples of the FTIR spectra of acetonitrile solutions.

The following equilibria are observed with the complexes formed by compound **1**.



I II III

Using the phenol band at *ca.* 3350 cm^{-1} the percentage of the complex formation, I $\rightleftharpoons$ [II + III], equilibrium, was calculated and is given in Table 1. The complex formation improves with decreasing pK_a of the phenols. The ν(OH) band of the phenols is shifted toward lower wavenumbers compared to its position in CH_2Cl_2 (*ca.* 3600 cm^{-1}) since the OH groups are bound to the acetonitrile molecules.

To illustrate the changes in the shape of the proton potentials as a function of the equilibrium between structures II and III in Fig. 3 the changes of the proton potential (with energy levels) are shown for a longer and a shorter hydrogen bond. Of course, in all systems, especially in those with large proton polarizability, broad distributions of such potentials are present as demonstrated by the IR continua.

The 4-fluorophenol + compound **1** system [Fig. 2(*a*)] shows two bands with maxima at *ca.* 2500 and 1800 cm^{-1}. No continuum is found. In this case the transition at 2500 cm^{-1} is the proton transition and that at 1800 cm^{-1} a transition which is intensified by the first one due to Fermi resonance. This spectral feature is characteristic of an OH · · · ON bond, *i.e.* a strong hydrogen bond with a single minimum at the phenol [Fig. 3(i)(*a*)]. This hydrogen bond shows almost no proton polarizability. In the series of the R-phenol + compound **1**

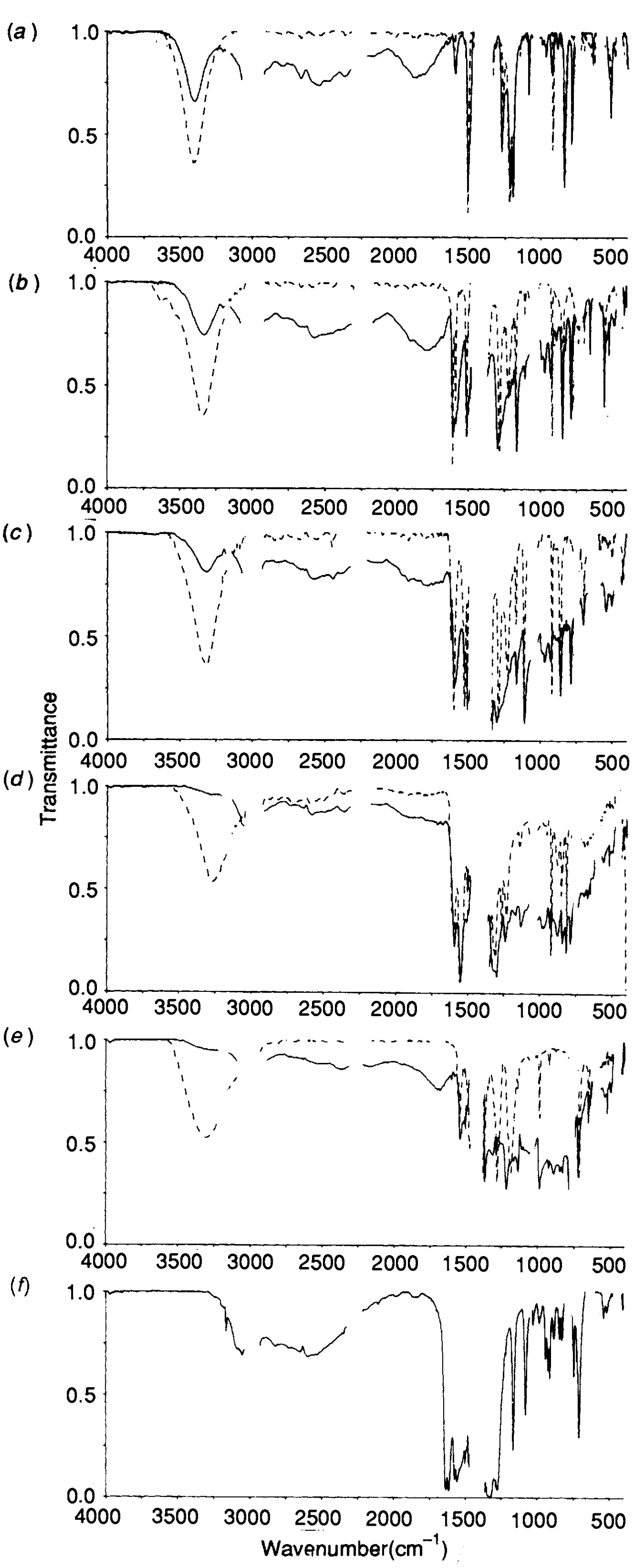


Fig. 2 FTIR spectra of 0.1 mol dm^{-3} acetonitrile solutions of: (– – – –) R-phenols, and (——) of their 1:1 mixtures with compound **1** (*a*) R = 4-F, (*b*) R = 4-CN, (*c*) R = 4-NO_2, (*d*) R = 3,4-di-NO_2, (*e*) R = 2,3,4,5,6-penta-Cl, and (*f*) R = 2,4,6-tri-NO_2

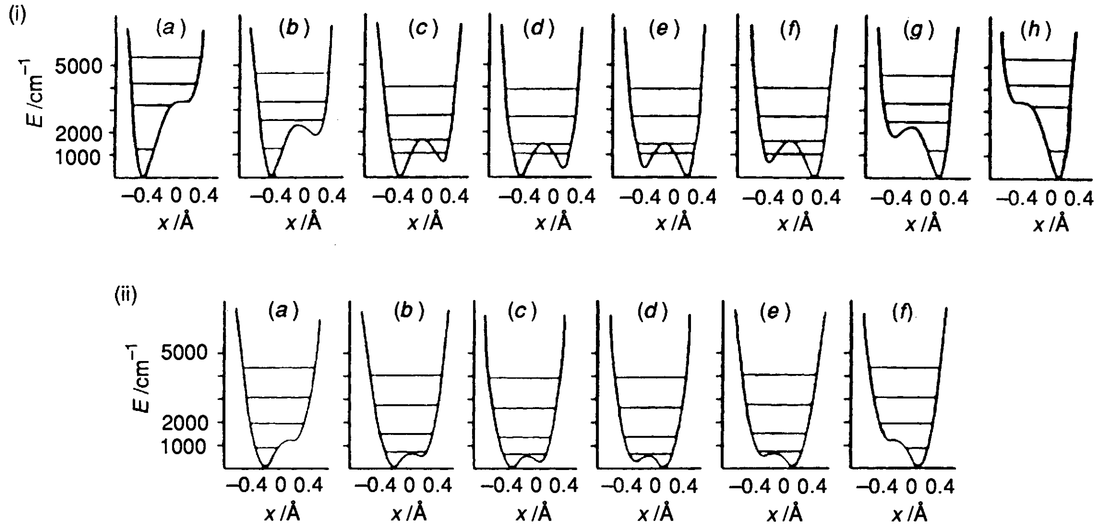


Fig. 3 Model proton potentials with the energy levels: (i) in the case of a longer hydrogen bond; (ii) in the case of a shorter hydrogen bond

Table 1 Percentage of complex formation of compounds **1** and **2** with various phenols in acetonitrile (0.1 mol dm^{-3})

Phenol	pK_a[a]	**1**	**2**
4-Methoxyphenol	10.21	58	100
4-Methylphenol	10.17	60	100
4-Fluorophenol	9.81	67	100
4-Chlorophenol	9.42	70	100
4-Bromophenol	9.37	71	100
4-Methoxycarbonylphenol	8.50	78	100
4-Cyanophenol	7.95	80	100
4-Nitrophenol	7.16	85	100
3,4-Dinitrophenol	5.42	98	100
Pentachlorophenol	5.26	99	100
2,4-Dinitrophenol	4.07	100	100
2,6-Dichloro-4-nitrophenol	3.70	100	100
2,4,6-Trinitrophenol	0.33	100	100

[a] Ref. 13.

systems the distribution of the proton transitions shifts with decreasing pK_a of the R-phenols toward lower wavenumbers, *i.e.* the proton potentials shift in favour of a distribution of potentials of the type in Fig. 3(i)(*b*) and then to the type in Fig. 3(i)(*c*).

In the proton transfer equilibrium, **II** $\rightleftharpoons$ **III**, structure **III** gains more and more weight. As shown for the 4-cyanophenol + compound **1** system in Fig. 2(*b*), this results in an intensity increase of the band at 1800 cm^{-1} and a continuum which extends from 1600 cm^{-1} toward lower wavenumbers indicating that the hydrogen bond now shows proton polarizability. With the 4-nitrophenol + compound **1** system [Fig. 2(*c*)] the intensity of the continuum below 1600 cm^{-1} is much more intense and extends to lower wavenumbers, demonstrating that a distribution of potentials of the types in Fig. 3(i)(*c*) and (*d*) predominates. The hydrogen bonds show high proton polarizability and the equilibrium is even more shifted in favour of structure **III**.

The 3,4-dinitrophenol + compound **1** system [Fig. 2(*d*)] no longer shows bands in the region 2800–1600 cm^{-1}. An intense continuum is observed in the region 1600 cm^{-1} to *ca.* 500 cm^{-1}. This spectral feature indicates that the hydrogen bond is shorter. A distribution of proton potentials as shown in Fig. 3(ii)(*b*)–(*e*) is present. The system is, on average, almost symmetrical.

The pentachlorophenol + compound **1** system [Fig. 2(*e*)] shows a strong continuum in the region below 1600 cm^{-1} which vanishes at *ca.* 500 cm^{-1}. However, in the region 2800–1600 cm^{-1} the continuum is again observed. The latter result demonstrates the increasing double minimum character of the proton potential whereby the deeper well is now at the ON group. A distribution of types of potentials Fig. 3(i)(*e*)–(*f*) and 3(ii)(*d*) is now present and the polar structure O^{-} • • •HON (**III**) now has greater weight.

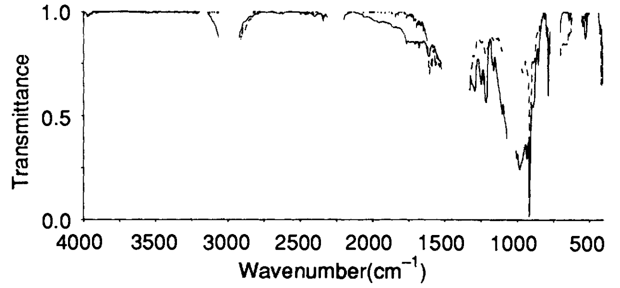


Fig. 4 FTIR spectra of saturated acetonitrile solutions of: (– – – –) compound **2** and (——) of 0.1 mol dm^{-3} solution of its 1:1 aurate salt

With increasingly acidic systems the equilibrium, **II** $\rightleftharpoons$ **III**, is more and more shifted to the right-hand side. Finally, in the case of the complex with the most acidic phenol, *i.e.* the picric acid + compound **1** system [Fig. 2(*f*)], a continuous absorption is no longer observed. Instead, a very broad band is found in the region 3200–2000 cm^{-1} with a maximum at *ca.* 2600 cm^{-1}. This result indicates that the proton has transferred, *i.e.* the equilibrium is shifted in favour of structure **III**. A potential similar to the type shown in Fig. 3(i)(*h*) is now present in the hydrogen bond. It no longer shows proton polarizability.

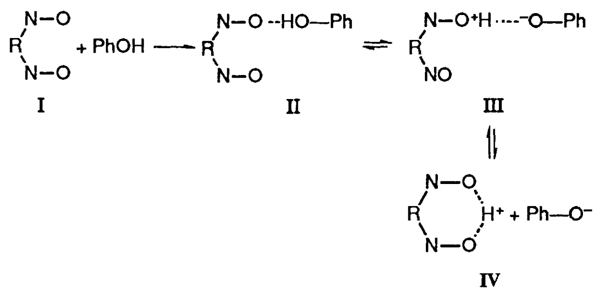
In summary we can state that with this family of systems the change of the proton potential with the pK_a of the R-phenols is very similar to the results obtained with the R-phenol + TMAO family of systems.[2]

Complexes of Compound 2.—In the following, the complexes formed by compound **2** with phenols are considered as a function of the pK_a value of the phenols.

Fig. 4 shows the FTIR spectrum of an acetonitrile solution of the 1:1 complex of compound **2** and $HAuCl_4$. As with compound **1** this result was obtained from NMR data. A band is found at *ca.* 1000 cm^{-1}. Within this band, especially in the high wavenumber region, several strong Evans holes are present. Furthermore, this broad band shows a wing toward higher wavenumbers. This spectral feature is characteristic of a structurally symmetrical, very strong NO•H^{+}•ON bond with a relatively narrow proton potential well. Such bonds show only very weak proton polarizability since the amplitude of the proton fluctuation is relatively small.[12]

We consider the complexes formed by compound **2** with phenols as a function of the $\mathrm{p}K_a$ of the phenols. Fig. 5 shows the FTIR spectra of selected examples of acetonitrile solutions of a 1:1 mixture of the phenols and compound **2**.

The following equilibria may be present in these systems.



With all systems complete complex formation is found (Table 1), since no ν(OH) stretching vibration indicating species **I** is observed in the region 3500–3300 cm^{-1} (Fig. 5).

The 4-methoxyphenol + compound **2** system [Fig. 5(*a*)] shows two bands with maxima at *ca.* 2600 and *ca.* 1800 cm^{-1}. From the latter band a weak continuum extends down to 800 cm^{-1}. With increasing acidity of the phenols [Figs. 5(*b*) and Fig. 5(*c*)] the intensity of the two bands in the region 3000–1800 cm^{-1} decreases and the intensity of the continuum increases extending more and more toward lower wavenumbers. Thus, with these systems the same behaviour is observed regarding the equilibrium and the proton potential in the (**II**) $\mathrm{OH}\cdots\mathrm{ON} \rightleftharpoons \mathrm{O}^-\cdots\mathrm{H}^+\mathrm{ON}$ (**III**) hydrogen bonds as with the systems of compound **1**, except that in analogous systems the equilibria are shifted slightly more in favour of the polar structure **III** due to the higher $\mathrm{p}K_a$ values of the *N*-oxide.

The 4-nitrophenol + compound **2** system is shown in Fig. 5(*d*). In this spectrum the IR continuum in the region 3000–1800 cm^{-1} is still observed. The intensity of this continuum increases strongly; however, in the region below 1800 cm^{-1} it shows a maximum at *ca.* 1000 cm^{-1}. Below 1000 cm^{-1} it decreases but is still found with weak intensity at 500 cm^{-1}. The fact that the continuum is found also at higher wavenumbers shows that the hydrogen bond is longer than in the corresponding system formed by compound **1**. Hence, a distribution of proton potentials in between those shown in Fig. 3(i)(*d*) and (*e*) and Fig. 3(ii)(*c*) is present. The particularly high intensity of the continuum found at *ca.* 1000 cm^{-1} has, however, another reason: with decreasing $\mathrm{p}K_a$ value of the phenols more and more intramolecular homoconjugated $\mathrm{NO{\cdot}H^+{\cdot}ON}$ hydrogen bonds are formed, which cause a broad band only in the region around 1000 cm^{-1}, similar to the band observed in the case of the $\mathrm{HAuCl_4}$ salt of compound **2** (Fig. 4). The resulting phenolate forms no homoconjugated phenol–phenolate bonds, since no broad band is found in the region 3000–2500 cm^{-1}, which is characteristic for these intramolecular bonds (0–2 transition).[11] Thus, besides the heteroconjugated phenol + compound **2** hydrogen bonds, such homoconjugated $\mathrm{NO{\cdot}H^+{\cdot}ON}$ bonds are observed in this system and contribute to the intense continuum around 1000 cm^{-1}. An equilibrium with species **IV** is present.

These homoconjugated complexes, *i.e.* species **IV**, may already be present in the 4-cyanophenol + compound **2** system [Fig. 5(*c*)] in lower concentration. With decreasing $\mathrm{p}K_a$ of the phenol, the concentration of these homoconjugated hydrogen bonds increases. In the case of the 3,4-dinitrophenol + compound **2** system [Fig. 5(*e*)] almost only homoconjugated $\mathrm{NO{\cdot}H^+{\cdot}ON}$ hydrogen bonds, *i.e.* only species **IV** is found. The same is true for all systems with more acidic phenols. This is demonstrated by the comparison of the spectra [Fig. 5(*e*) and 5(*f*)] with that of the 1:1 complex of compound **2** and $\mathrm{HAuCl_4}$ (Fig. 4). In all these cases a broad band is observed at *ca.* 1000 cm^{-1} indicating these hydrogen bonds in species **IV**.

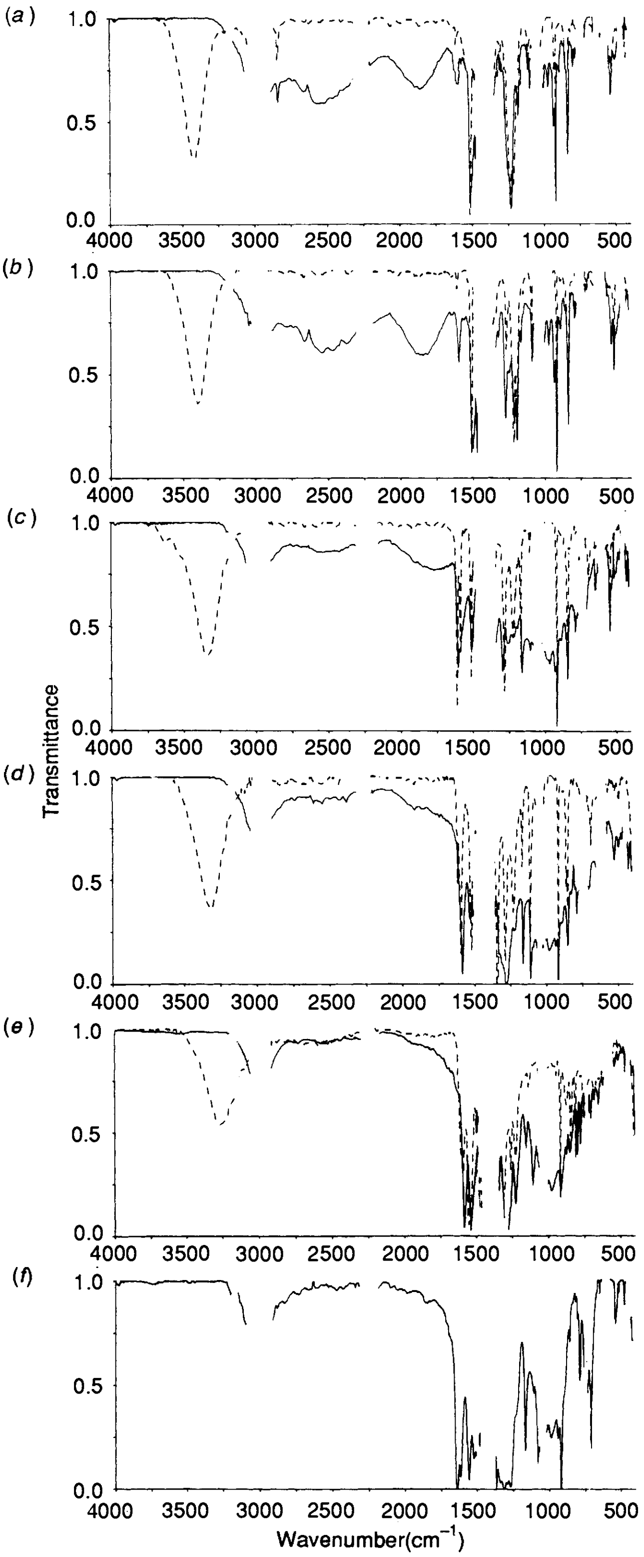


Fig. 5 FTIR spectra of 0.1 mol dm^{-3} acetonitrile solutions of (– – – –) R-phenols and (——) of their 1:1 mixtures with compound **2**. (*a*) R = 4-$\mathrm{OCH_3}$, (*b*) R = 4-F, (*c*) R = 4-CN, (*d*) 4-$\mathrm{NO_2}$, (*e*) 3,4-di-$\mathrm{NO_2}$, (*f*) 2,4,6-tri-$\mathrm{NO_2}$.

Conclusions

With $\mathrm{HAuCl_4}$ compound **1** forms an intermolecular 2:1

complex owing to steric factors, whereas compound **2** forms a 1:1 complex with an intramolecular hydrogen bond. These structurally symmetrical homoconjugated $NO{\cdot}H^{+}{\cdot}ON$ bonds are very short, having a relatively narrow proton potential and, hence, they show only small proton polarizability.

The complex formation of compound **1** ($pK_a = 9.29$) with the phenols is not complete in acetonitrile but increases with decreasing pK_a value of the phenols. With compound **2** ($pK_1 = 12.70$ and pK_2 10.40) the complex formation is always complete.

Comparing the complexes formed by compound **1** with those of compound **2** the $OH \cdots ON \rightleftharpoons O^{-} \cdots H^{+}ON$ equilibria of the corresponding systems are shifted slightly to the right owing to the higher pK_a value of compound **2**.

In both cases the left hand well in the double minimum proton potential is initially raised with decreasing pK_a of the phenol, the proton polarizability increases and the hydrogen bonds become shorter. In the case of the complexes formed by compound **1** in the most symmetrical case the barrier nearly vanishes. With further decreasing pK_a of the phenol a double minimum with a deeper well at the ON group is observed and finally only the polar proton limiting structure $O^{-} \cdots H^{+}ON$ is found, *i.e.* the proton is localized at the ON group. The large proton polarizability of the phenol–*N*-oxide hydrogen bond has almost vanished.

In the case of compound **2** with decreasing pK_a of the phenol a new equilibrium is found. Besides the heteroconjugated complexes, homoconjugated intramolecular $NO{\cdot}H^{+}{\cdot}ON$ bonds are formed. The proton potential well within the hydrogen bonds of these complexes is relatively narrow. Hence, these hydrogen bonds show much smaller proton polarizabilities than bonds with double minimum proton potentials. Besides these complexes free phenolate ions are present. In the case of the most acidic phenol only the intramolecular $NO{\cdot}H^{+}{\cdot}ON$ hydrogen bonds are found. This different complex formation is caused by the higher pK_a values of compound **2**.

The comparison of the studied *N*,*N*′-dioxides + R-phenol systems with the respective di-N-base systems[7] shows that with the latter systems heteroconjugated intermolecular complexes are never formed.

Acknowledgements

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