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Infrared spectroscopic studies of hydrogen bonding in substituted nitrophenols: substituent and solvent effects

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Abstract

A detailed infrared spectroscopic study of the substituted phenols 2-cyano-4,6-dinitrophenol and 4-cyano-2,6-dinitrophenol has been carried out (in several different solvents) in order to investigate the substituent and solvent effects on their intra- and inter-molecular hydrogen bonding properties. In benzene or dichloromethane it is found that both isomers form strong intramolecular hydrogen bonds with the 2-cyano (2CN) isomer having a stronger intramolecular interaction (in accordance with the higher pK_a). The 4-cyano (4CN) isomer shows two distinct NO_2 groups and exchange between the two possible hydrogen bonding sites is probably slow on the infrared time-scale. In protic solvents such as methanol the intramolecular hydrogen bonds are broken (more easily for the 4CN isomer) by intermolecular hydrogen bonding to the solvent. The differential "reactivity" towards methanol may be associated with steric congestion in the 4CN isomer leading to the forcing of at least one of the NO_2 groups out of the aromatic plane. The use of mixed solvents (benzene–methanol) has established that the two hydrogen bonded species are observed together and that a high concentration of methanol is required to drive the equilibrium towards the intermolecular hydrogen bonded species. In dimethyl sulphoxide the behaviour of the two isomers is even more interesting. The 4CN isomer is ionised to produce the corresponding phenolate. However the 2CN isomer remains neutral (but highly solvated). We attribute this difference to the requirement for the 4CN isomer to allow the 2- and 6-NO_2 groups to recover planarity with the aromatic ring. The energy compensation involved in this process is clearly sufficient to break a stronger intramolecular hydrogen bond.

Keywords: Infrared spectrometry; Hydrogen bonding; Nitrophenols

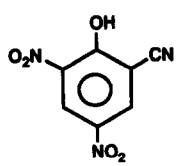
A considerable amount of work has been published [1–10] on the spectroscopic study of intramolecular hydrogen bonding in substituted phenols. Attempts have been made, for example, to relate spectral changes to the intramolecular electronic rearrangements [3,11–13] which occur due to the forming and breaking of such (strong) intramolecular interactions. Correlations with the available molecular orbital calculations [5] have also been attempted. Studies up until now have involved NMR and infrared (IR) frequency shifts. Very little work has been published on vibrational band shape and intensity changes caused by *intra* molecular hydrogen bonding. The most commonly studied compounds in the current context are (not surprisingly) the nitrophenols [1,3,7,9,10] and in most IR studies attention has been focussed on the NO_2 group vibrations. In this work we have attempted to shed greater light on the electronic and steric factors affecting intramolecular hydrogen bond formation by using compounds containing a nitrile chromophore. Although this obviously complicates the electronic effects on the benzene ring, it also affords another measure of the interactions occurring as a function of substituent position, solvent or concentration. We have also attempted to use the $\tilde{\nu}$(OH) and $\tilde{\nu}$(C=C) (ring) modes of the phenol (where appropriate in a deuterated solvent) to monitor the nature and extent of solvation as a

TABLE 1

Spectral characteristics of the main infrared bands of 2-cyano-4,6-dinitrophenol (2CN46DNP) and 4-cyano-2,6-dinitrophenol (4CN26DNP)

	2CN46DNP			4CN26DNP		
	$\tilde{\nu}$ [a]	$\Delta\tilde{\nu}_{1/2}$ [b]	A [d]	$\tilde{\nu}$ [a]	$\Delta\tilde{\nu}_{1/2}$ [b]	A [d]
$\tilde{\nu}_{as}(NO_2)$						
C_6H_6	1557 1536	16	9000	1547	14	18 000
CH_2Cl_2	1559 1540	15	7600	1549	14	20 300
CD_2Cl_2	1559 1540	15	7500	–	–	–
$CHCl_3$	–	–	–	1550	15	19 200
CH_3OH	1552 1537	27	5400	1552	21	14 000
CH_3OD	–	–	–	1550	20	16 600
DMSO	1546	15	7200	e	e	e
$\tilde{\nu}_s(NO_2)$						
C_6H_6	1334	13	24 800	1354 1316	30 14	9700
CH_2Cl_2	1346	14	24 000	1354 1316		9600
CD_2Cl_2	1346	14	23 000	–	–	–
$CHCl_3$	–	–	–	1354 1317	25	9700
CH_3OH	1348	15	16 300	1354 1315	24	8700
CH_3OD	–	–	–	1353	23	7600
DMSO	1358	e	e	1340	42	10 300
	2CNDNP			4CNDNP		
	$\tilde{\nu}$ [a]	$\Delta\tilde{\nu}_{1/2}$ [b]	A [c]	$\tilde{\nu}$ [a]	$\Delta\tilde{\nu}_{1/2}$ [b]	A [c]
$\tilde{\nu}(CN)$						
C_6H_6	2239	10	160	2238	11	180
CH_2Cl_2	2249	12	200	2240	12	180
CD_2Cl_2	2242	10	200	–	–	–
$CHCl_3$	–	–	–	2241	14.5	300
CH_3OH	2241	13	220	2238 [f] 2224	24	250
CH_3OD	–	–	–	2238 [f] 2224		
DMSO	2217	12	500	2213	12	550
$\tilde{\nu}(C=C)$						
C_6H_6	1617	18	10 700	1637	14	7000
CH_2Cl_2	1617	18	10 500	1640	13	7400
CD_2Cl_2	1617	18	10 500	–	–	–
$CHCl_3$	–	–	–	1639	14	8300
CH_3OH	1616	27	7200	1635	27	7900
CH_3OD	–	–	–	1634	24	8900
DMSO	1612	25	14 500	1635 1616	33	17 800

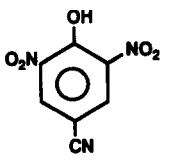
[a] $\tilde{\nu}$ in $cm^{-1} \pm 1$. [b] $\Delta\tilde{\nu}_{1/2}$ in $cm^{-1} \pm 1$. [c] A in $dm^3\ mol^{-1}\ cm^{-2} \pm 10$. [d] A in $dm^3\ mol^{-1}\ cm^{-2} \pm 100$. [e] Several unresolved bands in this region. [f] Two bands.



I $pK_a = 1.14$

2CN46DNP

2-CN-4,6-dinitrophenol



II $pK_a = 0.89$

4CN26DNP

4-CN-2,6-dinitrophenol

Scheme 1.

function of environment.The compounds of interest for this study are shown in Scheme 1. Our interest in these compounds arose from our related kinetics study [14] on the dealkylation of ring activated alkyl aryl ethers in DMSO to produce the corresponding phenolate. It was the differences in IR spectra caused by such ionisation in DMSO which led us to a more detailed study of the corresponding phenols. As far as we are aware, detailed IR spectra of these materials have not been published previously. Furthermore, they give an interesting and instructive insight into the subtleties of electron donating/withdrawing power of NO_2 and CN groups at different positions relative to the OH group. Comparison of spectra behaviour with and without hydrogen bonding was achieved by using the corresponding anisoles, 2-cyano-4,6-dinitroanisole (2CN46DNA) and 4-cyano-2,6-dinitroanisole (4CN26DNA).

EXPERIMENTAL

4-Cyano-2,6-dinitrophenol was prepared by the reaction of 4-cyanophenol with fuming nitric acid at room temperature for 24 h. On dilution with iced water, yellow crystals were formed which were dissolved in methanol, dried with $MgSO_4$ and recrystallised twice to give pale cream needles (m.p. = 134–136°C).

2-Cyano-4,6-dinitrophenol was prepared in three stages from 2-cyanochlorobenzene. Nitration with fuming nitric acid, was followed by reaction with NaOH to yield 2-cyano-4-nitrophenol. Further nitration gave the desired compound. It was recrystallised from methanol to give pale cream plates (m.p. = 180°C).

IR measurements were performed (with integrated mode 4) with a PE580B instrument. This gives a resolution between 4 and 1 cm^{-1} over the region examined. Spectra were recorded using freshly prepared solutions in cells of previously determined thickness (typically 6–25 μm) with calcium fluoride windows. The same cell was first used to record the spectrum of the respective solvent or mixture of solvents under identical conditions and spectral subtraction was then performed to remove the solvent spectrum. Data were transferred to an IBM PC for further analysis and are reported here in dimensionless absorbance units: $\log(I_0/I)$.

RESULTS AND DISCUSSION

The two isomeric cyano-dinitrophenols have been studied in a variety of solvents and mixed solvent systems in order to elucidate the species present under different environmental conditions. Table 1 summarises the band parameters found for a range of solvents. The $\tilde{\nu}$(OH) band parameters are not tabulated here but alluded to below. In non-polar aprotic solvents it is well-known [1,6–8] that *o*-nitrophenols form strong intramolecular hydrogen bonds. The spectra of both compounds in dichloromethane are shown in Fig. 1 in the $\tilde{\nu}$(OH) region. The only $\tilde{\nu}$(OH) band observed is that in the 3100–3200 cm^{-1} region showing (a) that only intramolecular hydrogen bonds are present, (b) that there are only negligible "free" phenol OH groups (the equilibrium constant for the complexation is large). (Sharper $\tilde{\nu}$(CH) bands are, of course, found in the 3100 cm^{-1} region). The 4CN26DNP isomer shows a greater hydrogen bonding shift than the 2CN46DNP implying that the "acidity" of the former compound is greater (as is indicated by the pK_a values shown in Scheme 1). The 4CN26DNP $\tilde{\nu}$(OH) band is also broader ($\Delta\tilde{\nu}_{1/2}$ = 195 cm^{-1} as compared with $\Delta\tilde{\nu}_{1/2}$ = 125 cm^{-1} for the 2CN46DNP band). The origin of this extra width is unclear. It should be noted, how-

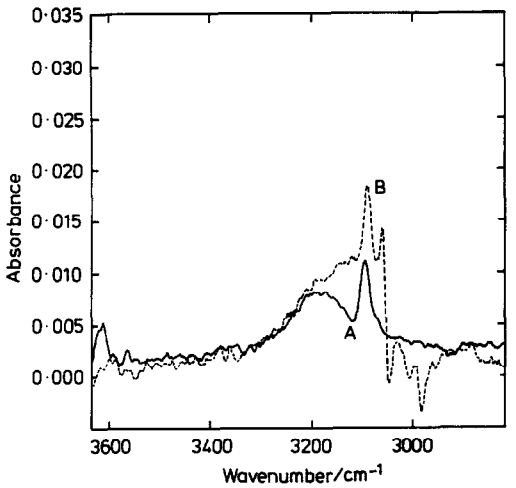
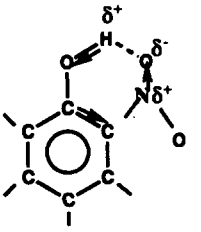


Fig. 1. Comparison of $\tilde{\nu}$(OH) bands of (A) 2CN46DNP and (B) 4CN26DNP in dichloromethane.

ever, that for the 4CN26DNP an intra-molecular hydrogen bond is possible in principle to *either* of the *ortho*-nitro groups. Since the interaction is very strong it seems unlikely that exchange occurs between the two NO_2 groups on the IR time scale but a contribution from exchange broadening [15,16] cannot be completely ruled out. This would be the equivalent of a delocalised hydrogen bond [11].

There is some evidence [11,13] that steric factors contribute to the apparently very large hydrogen bond strength in these two cyanodinitrophenols. This is because of the bulkiness of the two *ortho*-nitro groups which may hinder free rotation about the C–O bond and therefore enhance interaction of the OH group with *one* of the *o*-NO_2 groups, the other *o*-NO_2 group being twisted out of the aromatic ring plane [8]. Nevertheless, electronic factors must also be important, especially in the origin of the difference, between the two isomers. *o*-NO_2 and *p*-NO_2 groups are both expected to increase the π-electron conjugation between the OH-group and the ring, thereby raising the rotational barrier about the C–OH bond. However, *o*-NO_2 groups are expected to be more effective in doing so. This may account for the enhanced acidity of the 4CN26DNP isomer since the OH group is rigidly held in the *cis*-con-



Scheme 2.

formation. The effect of an *o*-NO_2 substituent is to redistribute the π-electron charge on the OH oxygen atom as shown in Scheme 2. This leads to an increase in both the π-donor power of the OH group and the π-acceptor ability of the NO_2 group. Another electron with drawing group in *ortho*- or *para*-positions may well reinforce this redistribution to enhance the OH electron donation ability to the ring (and hence stabilise the intramolecular hydrogen bond). It is certainly true that the $\tilde{\nu}$(OH) shifts for 2,4-dinitrophenols and 2,6-dinitrophenol DNP are less [11] than those for the cyanonitrophenols studied here. The *ortho*- or *para*-CN group therefore seems to increase the acidity. However, the $\tilde{\nu}$(OH) band width is greater for the nitrophenols, so the nitrile group clearly has a particular electronic effect on the intramolecular interaction.

In non-polar solvents the $\tilde{\nu}$(CN) band is remarkably insensitive to substituent position or, indeed (Table 2) to the presence or absence of intramolecular hydrogen bonding. Comparison of the spectra of phenol and anisole (Fig. 2) show that they are almost identical (and nearly Gaussian in shape). The band frequency seems to de-

TABLE 2

$\tilde{\nu}$(CN) band positions as a function of the number of nitrogroup substituents

Compound	$\tilde{\nu}$(CN)(cm^{-1})
2-CN-4,6DNP	2239
2-CN-4,6DNA	2240
4-CN-2,6DNP	2238
4-CN-2,6DNA	2240
2-CN-4-nitrophenol	2233
2-CN-4-nitroanisole	2234
4-CN-phenol	2225

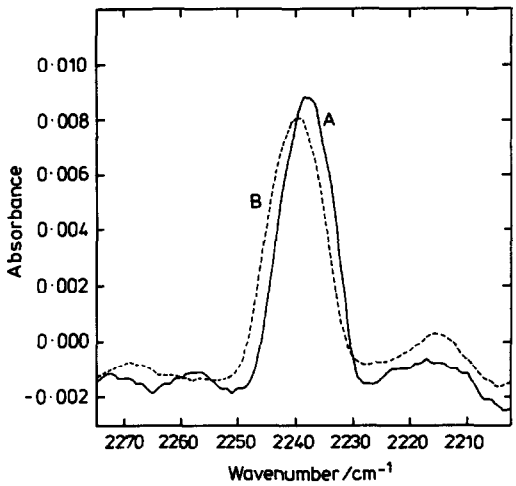
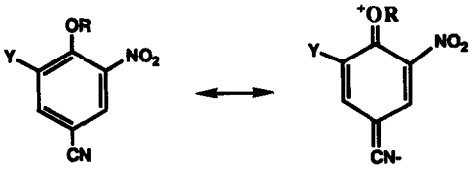


Fig. 2. Comparison of $\tilde{\nu}$(CN) bands of (A) 4CN26DNP and (B) 4CN26DNA in benzene.

pend on the number of nitro group substituents increasing as the number of substituents increases as shown in Table 2. The intensity of this band (which *is* sensitive to hydrogen bond formation [17]) also remains constant for cyanonitrophenols but increases by a factor of 10–15 for *p*-CN-phenol. Such effects are associated with the degree of conjugation of the nitrile group with the aromatic ring. The interaction of a π-donor such as OH or OCH_3 with a π-acceptor such as NO_2 results in a reduction in the amount of σ and π charge transfer from the ring to the CN group. So, for example, the contribution of resonance form (2) (Scheme 3) would be minimal for $Y = NO_2$ but would be important for *p*-cyanophenol where there is no competition with other acceptor groups.. The net increase in negative charge on the CN group will lead [17,18] to (a) a frequency shift to the red, because electron



(1) (2)

Scheme 3.

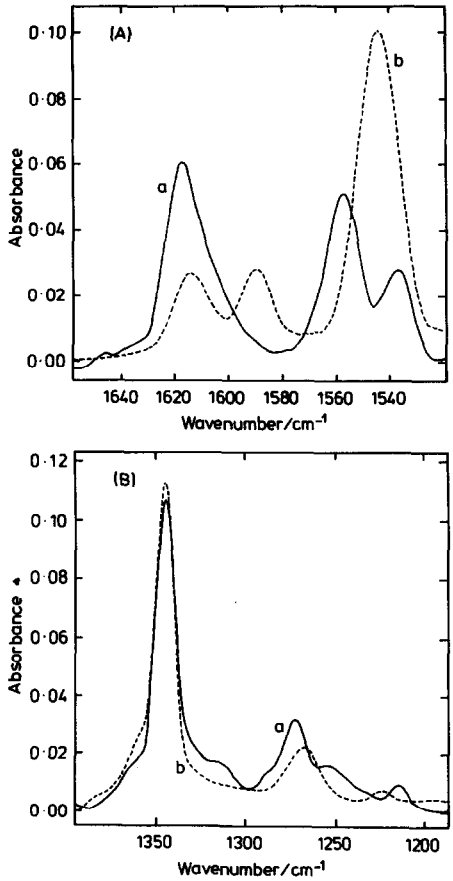


Fig. 3. Comparison of $\tilde{\nu}(NO_2)$ bands of (a) 2CN46DNP with those of (b) 2CN46DNA in benzene, (A) the $\tilde{\nu}_a(NO_2)$ region, (B) the $\tilde{\nu}_s(NO_2)$ region.

density goes into antibonding orbitals, (b) an increase in intensity due to dynamic intramolecular charge transfer [13,19]. The behaviour of our spectra in this region shows clearly that hydrogen bonding has little or no influence on the CN bond electronic structure and that (for the 2CN46DNP isomer) the CN group is not involved in hydrogen bonding. Intramolecular hydrogen bonding thus affects only the region of the molecule associated with the OH and *o*-NO_2 groups (Scheme 2).

The nitro group $\tilde{\nu}(NO_2)$ region is probably the most interesting spectroscopically. Figures 3–5 show the antisymmetric and symmetric stretching bands, $\tilde{\nu}_a(NO_2)$ and $\tilde{\nu}_s(NO_2)$, of the two com-

pounds under investigation along with the corresponding bands of trinitrophenol (TNP) for comparison. The spectra of the corresponding anisoles are also shown for reference. The data are summarised in Table 3. For the 2CN46DNP isomer the two nitro groups are formally different and two sets of bands would be expected. For the phenol in benzene one set should correspond to an intramolecularly hydrogen bonded NO_2 group. A survey of the (old) literature [12,20,21] seems to show (Table 4) that hydrogen bonding causes a small red shift ($\approx 7\ cm^{-1}$) of $\tilde{\nu}_s(NO_2)$ band and a large blue shift (≈ 20–$30\ cm^{-1}$) of the $\tilde{\nu}_{as}(NO_2)$ band. Such shifts may be understood in terms of differing degrees of resonance on hydrogen bonding and the change in planarity of the NO_2 group with the ring. Thus, the vibrational bands of the *p*-NO_2 and *o*-NO_2 groups may be assigned (Fig. 3) quite straightforwardly (Table 3). Although the anisole does not show two separate sets of $\tilde{\nu}(NO_2)$ bands, the phenol does. In the case of the 4CN26DNP isomer, only one $\tilde{\nu}_{as}(NO_2)$ band is observed (Fig. 4A) with some narrowing on going to the phenol (Table 3). However, the $\tilde{\nu}_s(NO_2)$ band shows dramatic splitting on going from anisole to phenol and band width of the $\tilde{\nu}_s(NO_2)$ band increases by 50%. It seems likely that this band broadening is due to hydrogen bonding (and maybe connected with the fact that there are two possible "sites"). However, the trinitro analogues

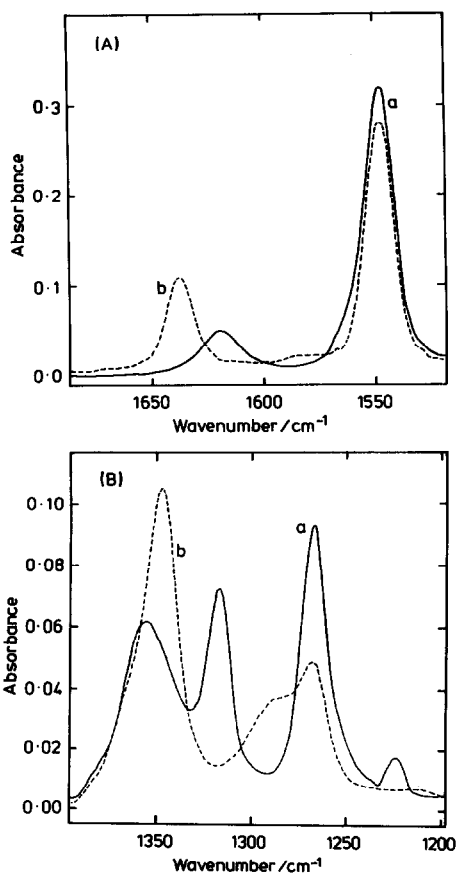


Fig. 4. Comparison of $\tilde{\nu}(NO_2)$ bands of (a) 4CN26DNP with those of (b) 4CN26DNA in benzene, (A) the $\tilde{\nu}_a(NO_2)$ region, (B) the $\tilde{\nu}_s(NO_2)$ region.

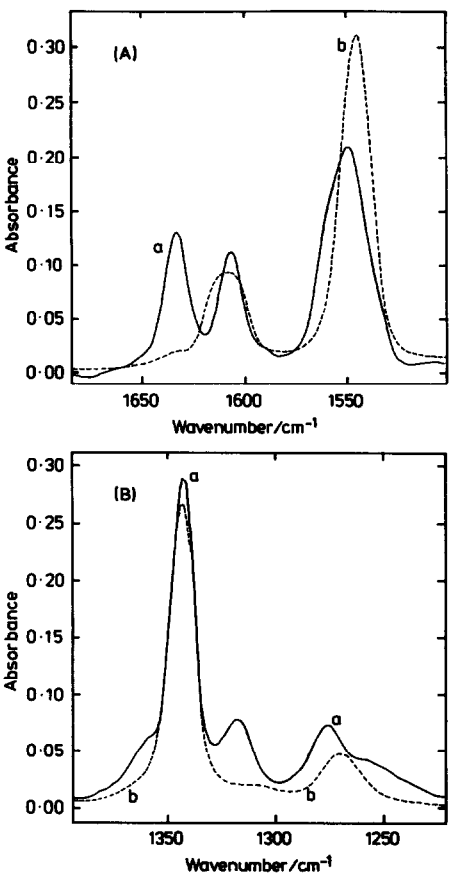
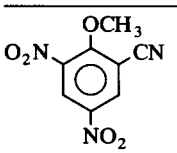
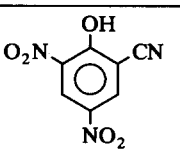
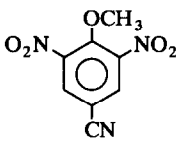
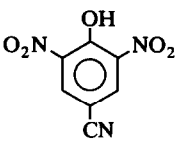
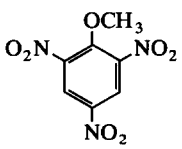
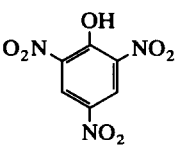


Fig. 5. Comparison of $\tilde{\nu}(NO_2)$ bands of (a) TNP with those of (b) TNA in benzene, (A) the $\tilde{\nu}_a(NO_2)$ region, (B) the $\tilde{\nu}_s(NO_2)$ region.

TABLE 3

Summary of $\tilde{\nu}(NO_2)$ band spectral data for the cyanonitrophenols and anisoles studied here (the full half-widths are shown in brackets)

Compound	$\tilde{\nu}_{as}$	$\tilde{\nu}_s$	A_a/A_s ratio	Compound	$\tilde{\nu}_{as}$	$\tilde{\nu}_s$	A_a/A_s ratio
 2CN46DNA	1546 (19)	1345 (13) (1360) sh?	0.7	 2CN46DNP	1560 (*o*) (13) 1536 (*p*)	1323 (sh) (13) 1344	0.36
 4CN26DNA	1548 (16)	1347 (20)	3.0	 4CN26DNP	1550 (14)	1320 (14) 1354 (30)	1.86
 TNA	1550 (18)	1348 (14)	1.1	 TNP	1552 (24) (0) (+ two shoulders)	(1360 sh) 1325 (15) 1344 (14)	0.48

(Table 3 and Fig. 5) do not appear to show this effect. Although the TNP shows two $\tilde{\nu}_s(NO_2)$ bands they are both about ≈ 15 cm^{-1} wide. Except for the extreme broadening in the 4-CN compound, the phenols show a remarkably consistent frequency pattern with inequivalent NO_2 groups in all cases. However, the intensity pattern is quite different. It appears that if there is no *p*-NO_2 group the intensity ratio A_{ass}/A_{sym} for these $\tilde{\nu}(NO_2)$ bands increases dramatically. This is due to a massive intensity increase of the $\tilde{\nu}_a(NO_2)$ band when the *p*-NO_2 group is removed, presumably due to drastic electronic changes caused by loss of coupling between *ortho*- and *para*-NO_2 groups.

TABLE 4

Summary of the steric, electronic and hydrogen bonding processes on the $\tilde{\nu}_{as}(NO_2)$ and $\tilde{\nu}_s(NO_2)$ bands of substituted nitrophenols (numbers give references)

Type of effect	$\tilde{\nu}_{as}(NO_2)$		$\tilde{\nu}_s(NO_2)$	
	Freq.	Int.	Freq.	Int.
Steric [a]	21.20 ↑	↑ 8	↑ 8	–
Conjugation	↓ 21	–	↓ 6	↑ 6
Hydrogen bonding	↑ 8	↑ 8	↓ 8	↑ 8

[a] NO_2 rotates out of the ring plane [8,21].

In polar solvents these compounds are expected to behave in a somewhat different way. In hydrogen bonding solvents (Table 1) such as methanol the possibility of replacing intramolecular hydrogen bonds by their intermolecular counterparts (to the solvent) is obvious. However, there are likely to be more subtle effects such as the (intermolecular) interactions between solvent and the NO_2 and/or CN groups. Unfortunately, we have not been able to examine the $\tilde{\nu}$(OH) region in detail for phenols in methanol (or other protic solvents) because of rapid exchange with

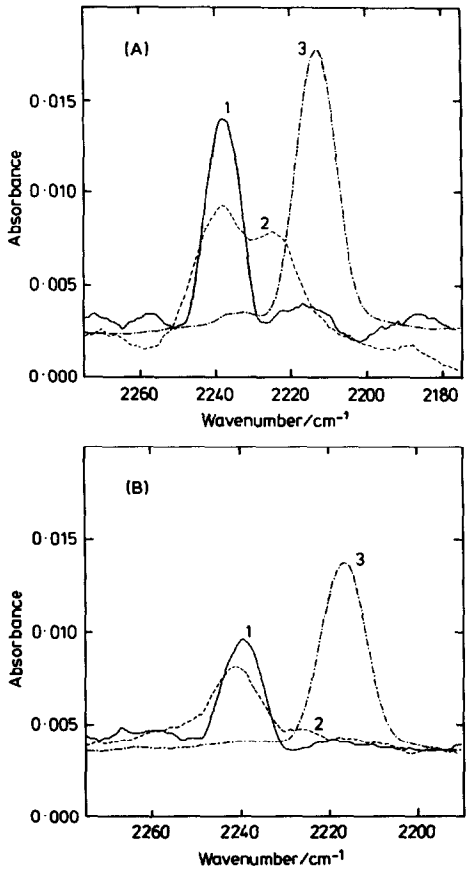
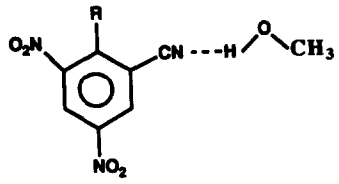


Fig. 6. Comparison of the $\tilde{\nu}$(CN) band of (A) 4CN26DNP and, (B) 2CN46DNP, in several solvents. (1) Benzene, (2) methanol, (3) dimethyl sulphoxide.

the deuterated solvents. However, the $\tilde{\nu}$(CN) and $\tilde{\nu}(NO_2)$ modes have been examined in detail in a variety of media (Table 1). We concentrate attention here on the spectra in methanol (MeOH) and dimethyl sulphoxide (DMSO).

The $\tilde{\nu}$(CN) band shows considerable variation in different solvents. Figure 6 shows that two bands (at 2238 and 2224 cm^{-1}) are clearly seen in methanol. One of these is at a position very close to that in benzene. The other is shifted to the red by about 16 cm^{-1}. However, the total intensity seems to be little changed (but is redistributed among two sites?). The same pattern is followed by both isomers in methanol although the "new" site has a much lower intensity for the 2CN46DNP isomer. This site might, at first sight, to be thought



Scheme 4.

due to a hydrogen bonded complex of the type shown in Scheme 4. However, there is much evidence [17] that such interaction causes a change in $\tilde{\nu}$(CN) to *higher* frequency so a "blue" rather than a "red" shift would be expected. This shift is connected with a change in polarity of the CN bond caused by electron donation from the nitrogen lone pair. Another possibility is that the second band is due to ionisation in polar solvents since the cyanonitrophenoxides [21] also have a $\tilde{\nu}$(CN) band near 2224 cm^{-1}. However, other parts of the spectrum show that this is not the case. For example, Fig. 7 shows that on going to a methanolic solvent the intermolecular hydrogen-bonded $\tilde{\nu}$(OH) band near 3450 cm^{-1} tends to dominate the spectrum. The equilibrium shown in Scheme 5 therefore gives rise to the two $\tilde{\nu}$(CN) bands due to "complexed" and "free" CN groups on the IR time scale. Hydrogen bonds with the NO_2 groups are also expected of course (see

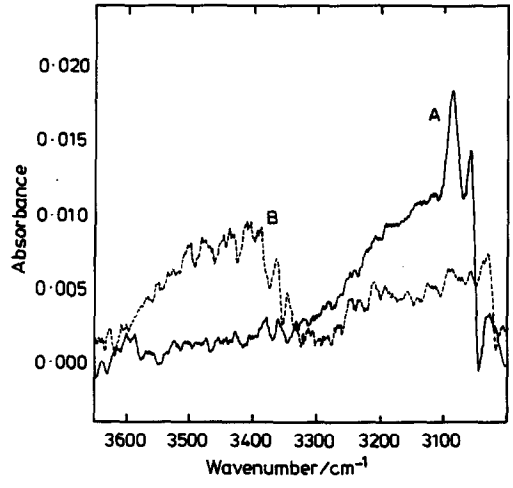
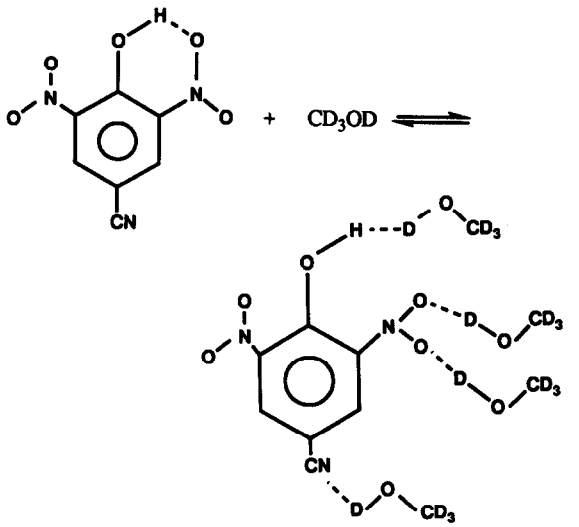
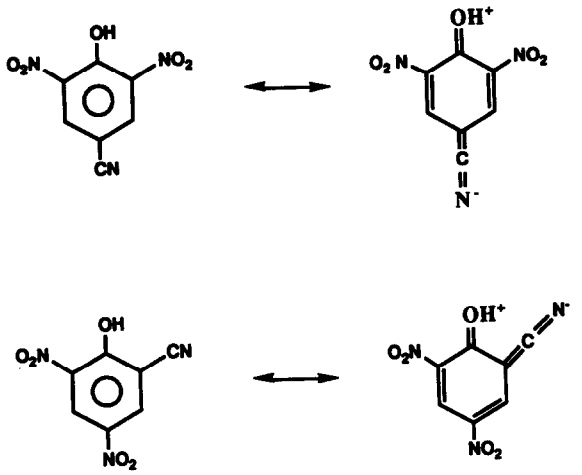


Fig. 7. Comparison of the $\tilde{\nu}$(OH) bands of 4CN26DNP in (A) benzene and (B) methanol-d_4.



Scheme 5.



Scheme 6.

below). Furthermore, the aromatic ring modes (except for some broadening in methanol) are not very sensitive (Table 1) to changing from benzene to methanol. We have attempted to quantify this equilibrium for the 4CN26DNP isomer by using a mixed benzene–methanol solvent. Figure 8 shows that, as the mole fraction of methanol in the mixture is raised, the $\tilde{\nu}$(CN) band at ≈ 2224 cm^{-1} increases in intensity. Quantification is obviously difficult but it is equally clear that quite a large excess of methanol is needed to shift the equilibrium significantly to the right hand side. This maybe due to bridging of the OH and NO_2 groups by one methanol molecule. From Fig. 6 it also appears that the breaking of the intramolecular hydrogen bond appears to be easier for the 4CN isomer. This process leads to a decrease in the CN bond order, and must be associated with adjustments in the degree of resonance of the CN group with the ring (although changes of electronic structure within the ring and the C-O group appear to be minimal). These may arise if the methanol, in breaking the intramolecular hydrogen bond, forces one or both NO_2 groups out of the aromatic ring plane. This would reduce NO_2 group π-acceptor ability and cause the CN group to accept more electron density. In resonance terms this may be represented as shown in Scheme 6 and be *less* probable in the case of the 2CN46DNP because there is less steric congestion near the OH group. Such effects ought to be also seen in the spectra of the NO_2 group. Examination of Table 1 and Figs. 9 and 10 shows that the pattern of $\tilde{\nu}(NO_2)$ bands is mostly similar in methanol to what it is in benzene. However, there are some significant differences. For the 4CN26DNP isomer, dissolution in methanol results in the loss of the $\tilde{\nu}_s(NO_2)$ band at 1316

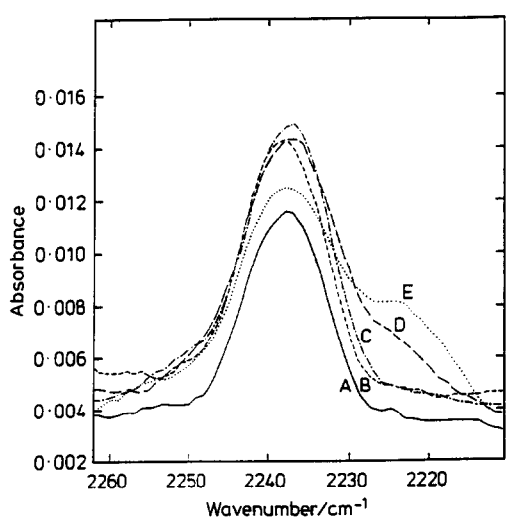


Fig. 8. Variation of $\tilde{\nu}$(CN) band of 4CN26DNP in mixtures of benzene and methanol. The methanol mole fractions are (A) 0.04, (B) 0.09, (C) 0.16, (D) 0.50, (E) 0.69.

cm^{-1} previously assigned (Table 3) to the intramolecularly hydrogen bonded NO_2 group (Fig. 9). Figure 11 shows that the two bands show the expected relative intensity change in a benzene–methanol mixture and this confirms the conclusion drawn from the $\tilde{\nu}$(CN) band analysis. Figure 12 shows that the equilibrium is relatively little affected until the mole fraction of methanol reaches ≈ 0.4. This phenomenon is related to the replacement of benzene by methanol in the first solvation shell. The same feature may occur for the 2CN46DNP isomer (Fig. 9) but the 1323 cm^{-1} band is of low intensity and this makes it difficult to be certain. The $\tilde{\nu}_a(NO_2)$ region is less

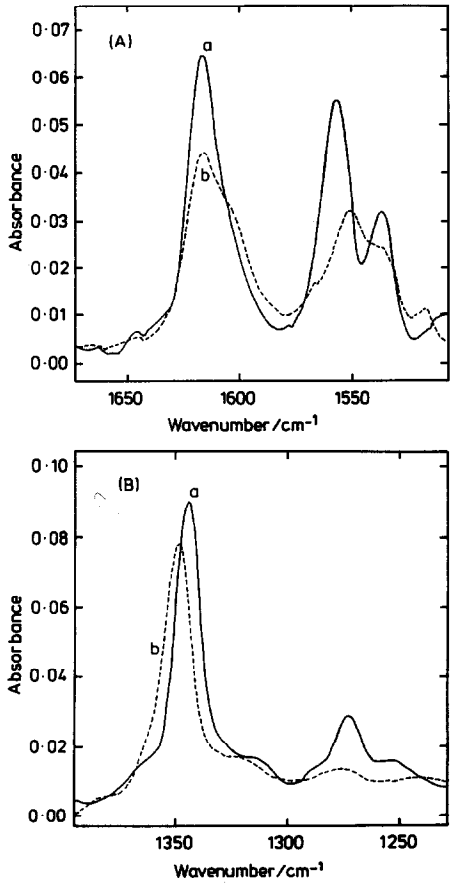


Fig. 9. Comparison of the $\tilde{\nu}_a(NO_2)$, $\tilde{\nu}_s(NO_2)$ and ring $\tilde{\nu}$(C = C) bands of 2CN46DNP in (a) benzene, (b) methanol. (A) Ring breathing and $\tilde{\nu}_{as}$ (NO_2) bands, (B) $\tilde{\nu}_s(NO_2)$ and $\tilde{\nu}$(C–O) bands.

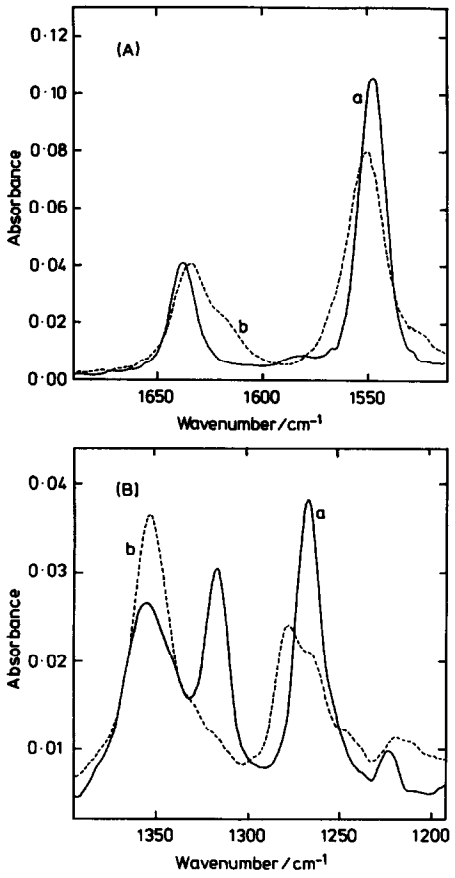


Fig. 10. Comparison of the $\tilde{\nu}_a(NO_2)$, $\tilde{\nu}_s(NO_2)$ and ring $\tilde{\nu}$(C = C) bands of 4CN26DNP in (a) benzene and (b) methanol. (A) Ring breathing and $\tilde{\nu}_{as}(NO_2)$ bands, (B) $\tilde{\nu}_s(NO_2)$ and $\tilde{\nu}$(C–O) bands.

definitive but the 2CN46DNP isomer does show a dramatic intensity decrease of the 1546 cm^{-1} (o-NO_2) band in methanol. This may also be associated with breaking of the intramolecular hydrogen bond. Interestingly both isomers show two bands in the 1620–1650 cm^{-1} region in methanol (Figs. 9 and 10) due to an additional ring breathing mode environment.

The behaviour of these molecules in an aprotic, but polar, solvent such as DMSO is even more interesting. In DMSO, the $\tilde{\nu}$(OH) region for the 2CN26DNP isomer shows only one broad, asymmetric band at ≈ 3380 cm^{-1}. This band (Fig. 13) is due to a strong hydrogen bond formed

between the phenol and the solvent. This behaviour is very similar to that of *p*-cyanophenol and the interpretation is confirmed by the NMR spectra which show the appropriate down field shifts due to intermolecular hydrogen bonding (as compared with the non-polar solvents). The NMR spectrum of 2CN46DNP in benzene shows spin coupled bands, $J = 3$ Hz, at δ 7.53 and 8.06 due to the ring hydrogens at H_3 and H_5 with a band at δ 10.7 due to the hydroxyl proton. In DMSO the ring proton bonds are shifted downfield to δ 11.9. The differential shifts with charge in solvent for protons H_3 (δ 0.89), and H_5 (0.59) shows that the DMSO solvation is influenced by the 2CN group, the proton H_3 showing a larger solvent shift than the H_5 proton. The resulting interaction of DMSO at the CN group should be seen as a shift of the $\tilde{\nu}$(CN) band. Figure 6 shows that this shift is to about 2220 cm^{-1}. The behaviour of the 4CN26DNP derivative in DMSO is, however, totally different. Figure 14 shows the ^1H NMR spectra of this isomer in both benzene-d_6 and DMSO-d_6. Although a broad hydrogen bonded OH signal (δ 10.8) is observed in C_6D_6 no such signal appears in DMSO-d_6 solution. Instead we get a singlet at δ 8.26 and a line at δ 7.0 whose shape is dependent on concentration. The latter is due to species [23] such as $[(CD_3)_2SO{-}H{-}OS(CD_3)_2]^+$ showing that ionisation has occurred. The IR spectra of the $\tilde{\nu}$(CN) band also support this assignment. Figure 15 and Table 5 show the data for a mixed solvent of benzene with DMSO. As the proportion of DMSO in the mixture is increased both $\tilde{\nu}$(CN) bands shift to lower frequency band B shifting faster until in pure DMSO it reaches ≈ 2213 cm^{-1}. This is

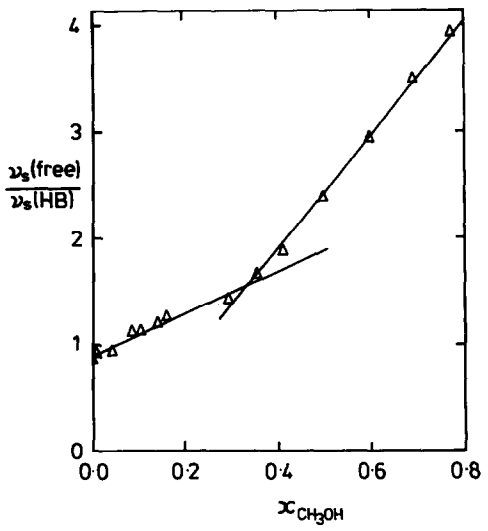


Fig. 12. Variation in the $\tilde{\nu}_s$(free)/$\tilde{\nu}_s$(HB) band height ratio (R), for the $\tilde{\nu}_s(NO_2)$ band of 4CN26DNP in benzene–methanol mixtures.

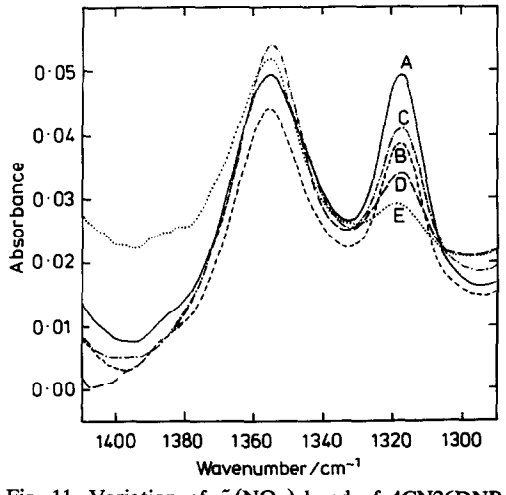


Fig. 11. Variation of $\tilde{\nu}_s(NO_2)$ band of 4CN26DNP in benzene–methanol mixtures. The mole fractions of methanol are the same as those given for Fig. 8.

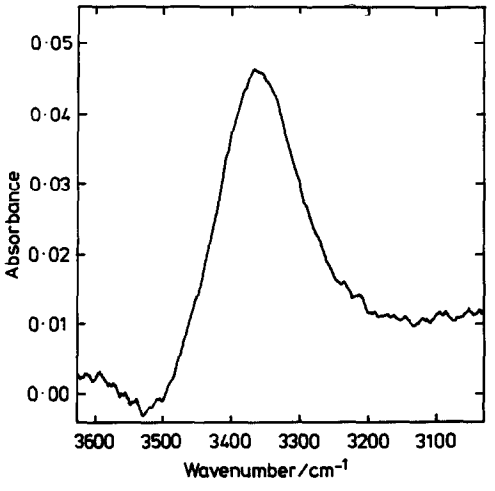


Fig. 13. The broad $\tilde{\nu}$(OH) band for 2CN46DNP in DMSO.

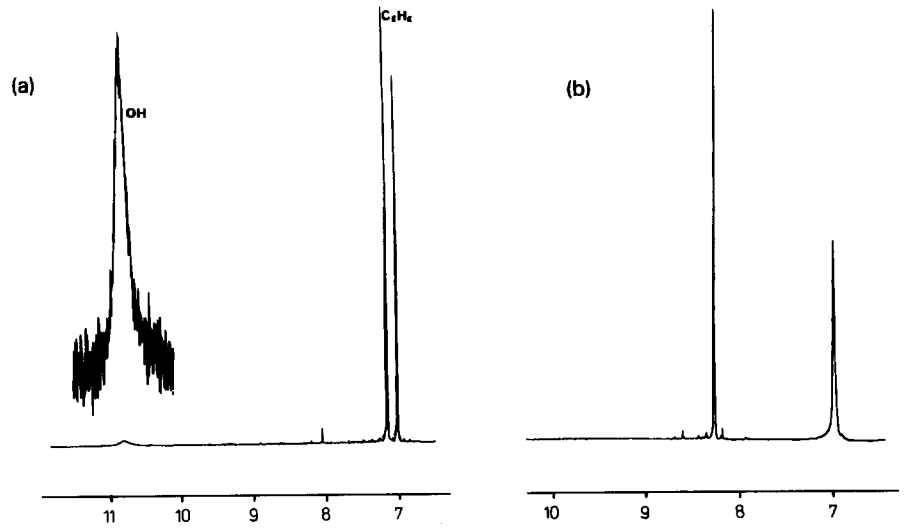


Fig. 14. The ^1H NMR spectra of 4CN26DNP in (a) C_6D_6, (b) DMSO-d_6.

identical with the $\tilde{\nu}$(CN) band position in 4CNDNPh$^-$Na$^+$ [22] and confirms that ionisation occurs in DMSO. The $\tilde{\nu}$(CN) band and $\tilde{\nu}_s(NO_2)$ band shifts (Table 5) with increasing solvent polarity again reflecting the sort of solvation illustrated in Scheme 7. It appears that the proportion of DMSO molecules in the mixture needs to be high (> 0.5 mf) before specific solvation effects are observed. This seems to be especially true for the NO_2 groups. The situation is, of course, complicated by the competing effects of solvation and ionisation, there being two solvated species at intermediate DMSO concentrations.

This difference in behaviour between the two cyanonitrophenols is an interesting one. Clearly the 4CN analogue forms the stronger intramolecular hydrogen bond. However, this is the hydrogen bond which is most easily broken by methanol solvation and it is the 4CN isomer which is ionised in DMSO. This result is almost certainly associated with steric interactions at the two *ortho*

TABLE 5

Infrared bands of 4CN26DNP in solvent mixtures of benzene and DMSO

Mixture (mf DMSO)	$\tilde{\nu}$(CN)		$\tilde{\nu}$ (ring)	$\tilde{\nu}_{as}(NO_2)$	$\tilde{\nu}_{s1}(NO_2)$ [a]	$\tilde{\nu}_{s2}(NO_2)$ [b]	$\tilde{\nu}$(CO)
	A	*B*					
0	2239	–	1637	1547.0	1354.5	1316.0	1267.1
0.01	2234.3	2219.0	1630	1547.3	1354.7	1306.8	1268.7
0.06	2234.3	2219.0	1630	1547.3	1354.7	1315.2	1267.0
0.11	2233.4	2216.8	1631	1547.0	1354.7	1311.8	1262.9
0.22	2233.4	2214.0	1633	1547.0	1354.7	1313.2	1258.7
0.43	2232.8	2212.8	1636/1618	1547.5	1354.4		1256.7
1.0	2233.0	2213.0	1635/1615		1340		1257.0

[a] $\tilde{\nu}_{s1}(NO_2)$: symmetric stretching vibration of the "free" *o*-NO_2 group. [b] $\tilde{\nu}_{s2}(NO_2)$: symmetric stretching of the hydrogen bonded *o*-NO_2 group.

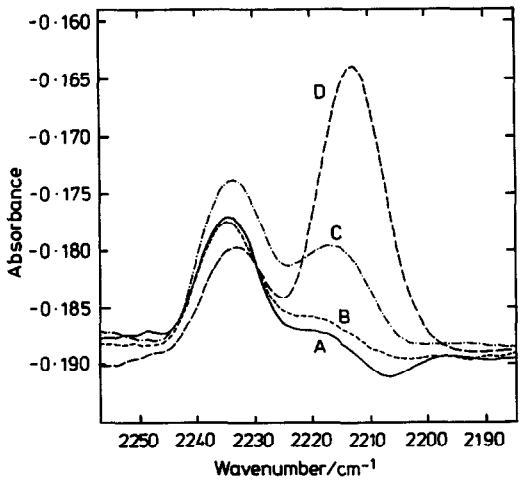
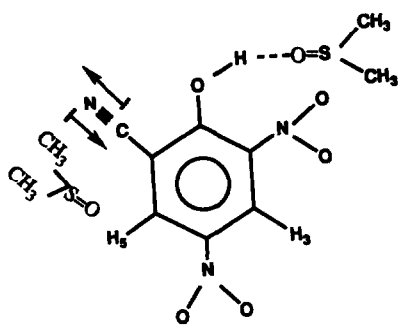


Fig. 15. Infrared spectra of the $\tilde{\nu}$(CN) band of 4CN26DNP in different benzene–DMSO mixtures. The mole fractions of DMSO are (A) 0.01, (B) 0.06, (C) 0.22, (D) 0.42.

positions relative to the OH group. Both the breaking of the intramolecular hydrogen bond and the ionisation lead to solvated species which may allow the two *ortho*-nitro groups to recover planarity with the aromatic ring. This may provide the necessary energy compensation for the breaking of a stronger intramolecular interaction.

Conclusions

In non-polar solvents (benzene or dichloromethane) both isomeric phenols form strong intramolecular hydrogen bands and in the order expected from their pK_a values (Scheme 1). There is good evidence in the case of the 4CN isomer that the two nitro groups are distinct and



Scheme 7.

therefore that there is no "delocalisation" of the hydrogen bonded interaction on the IR time scale. In protic solvents, such as methanol, the intramolecular hydrogen bonds are broken (more easily for the 4CN isomer) despite the intermolecular hydrogen bond being "weaker" (as measured from the $\tilde{\nu}$(OH) band shift). This maybe due to relief of steric interactions which allow the *o*-NO_2 group(s) to recover planarity with the aromatic ring. But it is also probably related to distribution of "solvation" interactions in protic solvents. In aprotic, but polar, solvents (such as DMSO) the 4CN isomer is progressively ionised producing the corresponding phenolate (and a protonated solvent molecule). However, the 2CN isomer remains in the neutral but highly solvated form, presumably due to the (relative) lack of energy requirements caused by steric congestion at the *ortho* positions.

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