Comparison between the Cyano-group Hydrogen Bonding Abilities, Infrared Frequencies, and Intensities in Some α-Alkylthio-nitriles

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The formation of the complexes between phenol or *p*-chlorophenol and a large number of the unsubstituted and α-alkylthio-nitriles are studied by i.r. and n.m.r. spectroscopy and the equilibrium constants are correlated with the frequency shifts of proton donors. The vibrational frequencies and intensities of the C≡N bond are also measured and compared with the equilibrium constants. The existence of an interaction between the cyano-group and the α-sulphur atom is suggested.

IN a preliminary communication[1] it was reported that the introduction of an α-ethylthio-group to some aliphatic nitriles leads to a slight decrease of the basicity and that this is accompanied by a decrease of cyano-group frequencies. This anomalous relationship, as well as some modifications of the u.v. spectra in the α-alkylthio-nitriles, by comparison with those of some dialkyl sulphides, were interpreted in terms of ground and excited state interactions between the cyano-group and the sulphur atom. The relative basicities were determined by two methods: n.m.r. measurements of the CH shifts for phenylacetylene–nitrile systems and the extent of the unusual increase of the CN stretching frequencies in the presence of phenol.

This paper details the evidence for the point made in the communication and provides data from measurements of the cyano-group hydrogen bonding ability using phenol and *p*-chlorophenol as proton donors and of the C≡N bond stretching frequencies and polarities of a larger number of nitriles. The equilibrium constants for the association complexes between *p*-chlorophenol and nitriles are of interest since they are not available in the literature.

RESULTS AND DISCUSSION

The frequency shifts of hydroxylic group of phenol and *p*-chlorophenol ($\Delta\nu_{OH}$) measured by i.r. and n.m.r. spectroscopy, the equilibrium constants for association complexes (K_{as}), the cyano-group stretching frequencies (ν_{CN}), and intensities (A) for a series of unsubstituted nitriles (1)—(9), and α-(10)—(15), β-(16) and (17), γ-(18), and δ-alkylthio-nitriles (19), and for oxygen (20) and selenium (21) analogues are shown in the Table.

The values of the three $\Delta\nu_{OH}$ measurements correlate linearly, as well as each of them with the log K_{as} values, as exemplified by the plots of $\Delta\nu_{OH}$ of phenol by i.r. against $\Delta\nu_{OH}$ of *p*-chlorophenol by n.m.r. (r 0.985) (Figure 1) and of $\Delta\nu_{OH}$ of phenol by i.r. against log K_{as} (r 0.981) (Figure 2).

The inspection of the K_{as} values shows that they increase in both series, the unsubstituted and the α-alkylthio-nitriles, with increasing number of methylene groups and by branching at the α-carbon atom. Thus, the K_{as} values for compounds (9) and (15) are higher than those for (7) and (11), respectively.

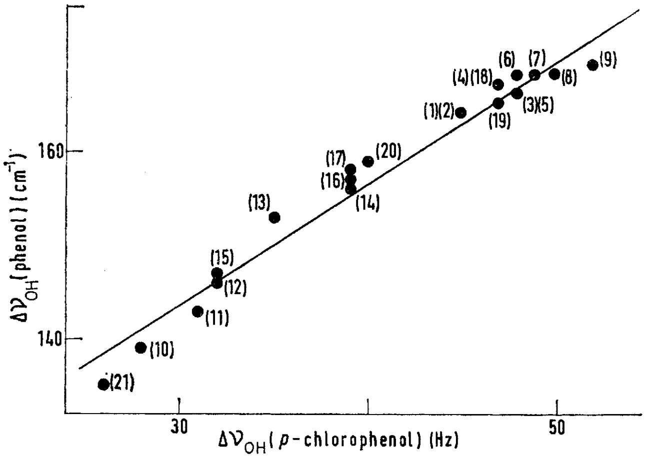

FIGURE 1 Correlation between $\Delta\nu_{OH}$ for phenol by i.r. spectroscopy and $\Delta\nu_{OH}$ for *p*-chlorophenol by n.m.r. spectroscopy. The key to the numbering is in the Table

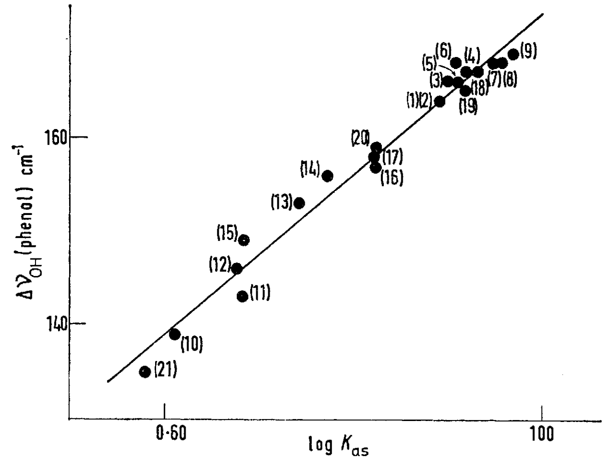

FIGURE 2 Correlation between $\Delta\nu_{OH}$ for phenol by i.r. spectroscopy and log K_{as}. The key to the numbering is in the Table

The fact that the K_{as} values are affected by the α-methyl groups and by the size of the carbon-chain indicates that the estimation of the relative hydrogen bonding ability of an α-alkylthio-nitrile should be made by comparison with an unsubstituted nitrile of the same framework with a methylene group instead of a sulphur atom bonded to the α-carbon. On this basis it may be seen that there is a decrease of the cyano-group basicities in the α-alkylthio-nitriles by comparison with the corresponding unsubstituted nitriles and that the decrease of

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the K_{as} values is practically invariant (*ca.* 3.5) for three pairs of α-alkylthio- and unsubstituted nitriles here studied: (3) and (11); (8) and (14); (9) and (15).

The effect of methylene and α-methyl groups influences slightly the cyano-group stretching frequencies. Thus, the ν_{CN} values for (9) and (15) are lower than those for (3) and (11), respectively.

Comparison of the α-alkylthio-nitriles (11), (14), and (15) with the corresponding unsubstituted nitriles (3), (8), and (9) indicates that a slight decrease of the ν_{CN} values (4—9 cm^{-1}) takes place by substitution of the methylene group bonded to the α-carbon by a sulphur atom. This frequency shift can hardly be attributed to the mass change due to substitution of the methylene group by sulphur as in this case masses greater than 12 are involved.[2] Therefore, it may be interpreted as due to a decrease of the force constant of the cyano-group.

Data [a] on the hydrogen bonding of phenol and *p*-chlorophenol with nitriles RCN, cyano-bond frequencies, and intensities

		$\Delta\nu_{OH}$ [b]					
		Phenol	*p*-Chlorophenol		K_{as} [c]/	ν_{CN} [b]/	$10^{-2}A$ [d]/
No.	R	(cm^{-1})	(cm^{-1})	(Hz)	l mol^{-1}	cm^{-1}	l mol^{-1} cm^{-2}
(1)	Et	164	177	45	7.8	2 250	5.3
(2)	$CH_3[CH_2]_2$	164	178	45	7.8	2 250	5.9
(3)	$CH_3[CH_2]_3$	166	178	48	7.9	2 249	
(4)	$CH_3[CH_2]_4$	167	179	47	8.3	2 246	6.6
(5)	$CH_3[CH_2]_5$	166	178	48	8.1	2 247	
(6)	$CH_3[CH_2]_6$	168	179	48	8.1	2 247	6.6
(7)	Pr^i	168	179	49	8.8	2 247	5.9
(8)	$CH_3[CH_2]_2C(CH_3)$	168	180	50	9.0	2 242	7.6
(9)	$CH_3[CH_2]_2C[CH_2]_2$	169	183	52	9.3	2 239	8.5
(10)	CH_3SCH_2	139	152	28	4.1	2 244	4.2
(11)	$EtSCH_2$	146	159	32	4.7	2 245	5.3
(12)	$(CH_3)_3CSCH_2$	149	161	32	4.8	2 248	
(13)	$CH_3SCH(CH_3)$	143	155	31	4.8	2 238	
(14)	$EtSCH(CH_3)$	153	168	35	5.5	2 237	6.2
(15)	$EtSC[CH_3]_2$	156	170	39	5.9	2 230	7.5
(16)	$EtS[CH_2]_2$	157	173	39	6.6	2 249	
(17)	$EtSCH(CH_3)CH_2$	158	173	38	6.3	2 249	
(18)	$EtS[CH_2]_3$	167	179	47	8.5	2 248	
(19)	$EtS[CH_2]_4$	165	179	47	8.3	2 248	
(20)	$EtOCH(CH_3)$	135	148	26	3.8		
(21)	$EtSeCH_2$	159	172	40	6.6	2 242	8.5

[a] Solvent CCl_4. [b] By extrapolation to zero concentration of nitrile. [c] From n.m.r. measurements. [d] Integrated absorption intensities.

The decrease of the cyano-group stretching frequencies in the α-alkylthio-nitriles is not in accord with the decrease in basicity shown by the same compounds. This anomalous relationship seems to indicate that the decrease in basicity can hardly be due to the inductive effect of sulphur, as this, normally, should lead to an increase of the cyano-bond frequencies. Evidence that the inductive effect of sulphur is not responsible for the decrease of the cyano-group basicity was provided[3] when the K_{as} values for a large number of nitrile–*p*-chlorophenol complexes were correlated with the σ* Taft values for the corresponding substituents. A linear correlationship was obtained for all nitriles, except α-alkylthio-nitriles.

It seems reasonable to suggest that the decrease in hydrogen bonding ability in the α-alkylthio-nitriles, accompanied by the decrease of the cyano-group stretching frequencies is due to an interaction between the cyano-group and sulphur.

The Table also shows the K_{as} data for some alkylthio-nitriles with sulphur further removed from the cyano-group. The comparison of the K_{as} values for the β-alkylthio-nitriles (16) and (17) with those for the corresponding unsubstituted nitriles (4) and (8) indicates a slight decrease of the hydrogen bonding ability in the former compounds. This result is not in accord with our previous measurements of the CH phenylacetylene shift,[1] which indicated an increase of basicity for one of these compounds (16) by comparison with the unsubstituted nitriles. We cannot at present offer any plausible explanation for this difference. It is noteworthy that the γ- and δ-alkylthio-nitriles (18) and (19) do not show any alteration in basicity and cyano-group frequency by comparison with the corresponding unsubstituted nitriles (5) and (6).

The data of the cyano-group stretching band intensities (*A*) (see Table) confirm the previous observation[4] that the intensity of the cyano-group vibration band rises to a steady value as the chain-length increases. It may also be seen that the value for isobutyronitrile (7) is too low, practically the same as that for the corresponding straight chain nitrile (2). However, the *A* values for the long-chain nitriles (4) and (6) increase markedly as one or two methyl groups are introduced in the α-position to give (8) and (9).

The low *A* values for the short-chain nitriles were attributed to self-association.[5-8] It seems likely that

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self-association is also responsible for the low A value of isobutyronitrile (7), in which it should be stronger due to the increased polarity of the cyano-group. As for the compounds (8) and (9) self-association may become difficult due to the increase of the chain-length.

The low A values for the short-chain nitriles constitute the main cause for the lack of a linear relationship between the K_{as} and A values for the unsubstituted and α-alkylthio-nitriles. The K_{as} values do not show any influence of self-association, which is probably suppressed in the presence of strong proton donors, such as phenol and *p*-chlorophenol. The lack of correspondence between the basicities and polarities of the cyano-group seems to be an exception to a general rule, considering that for other classes of compounds linear relationships were reported to exist[9] between the hydrogen bonding ability and i.r. intensity of the proton accepting group.

It is noteworthy that the A data agree with those of K_{as}, showing a decrease for the α-alkylthio-nitriles (11), (13), and (14) compared with the corresponding unsubstituted nitriles (4), (8), and (9). This suggests that the interaction between the cyano-group and sulphur decreases the polarization of the C≡N bond.

The Table also shows the K_{as} data for the oxygen analogue (20) and the K_{as}, ν_{CN}, and A data for the selenium analogue (21). The low K_{as} value for α-ethoxypropiononitrile (20) may be easily explained by the inductive effect of the oxygen atom. The inspection of the data for α-ethylselenoacetonitrile (21) indicates that the K_{as} value, though lower than that for the unsubstituted nitrile (3), is higher than for α-ethylthio-acetonitrile (11) and that ν_{CN} is lower and A higher than those for (3) and (11).

The K_{as} and high A values for the α-ethylseleno-nitrile (21) suggest that the interaction between the cyano-group and selenium is practically suppressed. The stronger association complex and increased polarization of the cyano-group may be due to the electron-repelling effect of selenium, which is less electronegative than carbon. Therefore, contrary to expectation, considering the size of the sulphur and selenium *p* orbitals, the interaction is much stronger in the α-alkylthio-nitriles.

Although it is obvious that an interaction between the cyano-group and sulphur is responsible for the size of the basicity and cyano-group stretching frequency, it is far from clear whether it is a through-space or through-bond interaction,[10] and which orbitals contribute most to it.

EXPERIMENTAL

Reagents.—All solvents in the spectrometric measurements were spectrograde reagents and were used without any further purification. Commercial propiononitrile, isobutyronitrile, phenol, and *p*-chlorophenol were purified as described elsewhere.[11] Butyronitrile,[12] valeronitrile,[13] capronitrile,[13] heptanenitrile,[13] octanenitrile,[13] 2-methylpentanenitrile,[14] 2,2′-dimethylpentanenitrile,[15] methylthioacetonitrile,[16] α-methylthiopropiononitrile,[17] ethylthioacetonitrile,[18] α-ethylthioisobutyronitrile,[19] β-ethylthiopropiononitrile,[20] γ-ethylthiobutyronitrile,[21] and α-ethoxypropiononitrile[22] were prepared by literature procedures. t-Butylthioacetonitrile, b.p. 68° at 9.5 mmHg, α-ethylthiopropiononitrile, b.p. 73° at 13 mmHg, β-ethylthiobutyronitrile, b.p. 98° at 11 mmHg, and δ-ethylthiovaleronitrile, b.p. 103° at 1.5 mmHg were prepared by known methods[19,20,23] and gave correct analyses. Ethylselenoacetonitrile, b.p. 84° at 2 mmHg, was prepared by the reaction of chloroacetonitrile with ethylselenomagnesium bromide, by the procedure described for ethylselenoacetone[24] and gave correct analysis.

The cyano-bond frequencies and i.r. basicity measurements were performed on a Perkin-Elmer model 457-A grating spectrometer using a sodium chloride cell. All measurements were made at room temperature (23 ± 1°).

C≡N Bond Frequencies.—C≡N Bond frequencies were measured for carbon tetrachloride solutions over a concentration range 0.60–0.06M. The ν_{CN} values were obtained by extrapolation to infinite dilution. The C≡N bond frequencies are accurate to ± 2 cm^{-1}.

I.r. Basicity Measurements.—Dilution studies of phenol and *p*-chlorophenol in carbon tetrachloride were made over a concentration range 0.045—0.002M. The stretching frequencies (ν_0) of phenol and *p*-chlorophenol extrapolated to infinite dilution were 3 616 and 3 615 cm^{-1}, respectively. The frequencies (ν') of OH of phenol and *p*-chlorophenol were determined by maintaining the concentration of phenol (0.030M) or *p*-chlorophenol (0.028M) constant and varying the molar concentrations of nitrile between 0.03 and 0.30M. For each solution five spectra were recorded and the mean value calculated. The $\nu_0 - \nu'$ values ($\Delta\nu$) were plotted against the molar concentrations of nitrile and the straight lines extrapolated to zero concentration of nitrile to give $\Delta\nu_{OH}$ (cm^{-1}) values[25] (Table). The i.r. data were submitted to statistical analysis to afford the mean values and standard error. The precision of the i.r. measurements is ± 4 cm^{-1}.

N.m.r. Basicity Measurements.—N.m.r. spectra were recorded at 60 MHz on a Varian T-60 spectrometer. The chemical shifts were determined relative to cyclohexane as internal standard. Dilution studies of *p*-chlorophenol in

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carbon tetrachloride were performed using a concentration range 0.045—0.002M and the chemical shift (ν_0) of the hydroxy-group in *p*-chlorophenol extrapolated to infinite dilution was 178 Hz. The chemical shifts (ν') of OH in the proton donor–nitrile complexes in carbon tetrachloride were determined maintaining the concentration of *p*-chlorophenol (0.028M) constant and varying the molar concentrations of nitrile between 0.08 and 0.28M. For each solution five spectra were recorded and the mean value calculated. The $\nu' - \nu_0$ values ($\Delta\nu$) were plotted against the molar concentrations of nitrile and the straight lines extrapolated to zero concentration of nitrile to give $\Delta\nu_{OH}$ (Hz) values (Table). The association constants (K_{as}) were calculated by the method of Mathur *et al.*,[26] by plotting $1/\Delta\nu$ against $1/c$ where c is the molar concentration of nitrile. All n.m.r. measurements were made at 35°. The n.m.r. data were submitted to statistical analysis to afford the mean values and standard error. The precision of the n.m.r. measurements is ±2 Hz.

C≡N *Bond Intensity Measurements*.—Spectra were recorded on a Perkin-Elmer model 180 grating spectrometer. In all measurements the spectral slit width, 1.75 cm^{-1}, and the temperature, 25°, were maintained constant. The C≡N group band intensities were measured for carbon tetrachloride solutions, in five low concentrations for each nitrile (between 0.025 and 0.065M). The integrated absorption intensities were calculated by the method of direct integration [27] for all concentrations and the mean value (A) taken. The precision of the A values is ±5%.

All plots for i.r. and n.m.r. measurements data were treated by appropriate least-square regression analysis to obtain the best straight lines which fit the results. The analysis of the data was accomplished with the aid of a Hewlett–Packard 9820 A.

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