Interaction Between the Carbonyl Group and a Sulphur Atom. Part VI.[1] Some 3-Thiacycloalkanones †

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The u.v. and carbonyl i.r. absorptions for some 3-thiacycloalkanones, and the equilibrium constants for association complexes which they form with *p*-chlorophenol as measured by n.m.r. spectroscopy, suggest excited and ground-state interactions between sulphur and the carbonyl group. The data indicate that these interactions are different from those of the transannular type, described previously for 5-thiacyclo-octanone, and now shown to occur also in cyclohex-3-enone, but similar to those in the corresponding open-chain keto-sulphides.

OUR past investigations[1-5] on the u.v. absorption, i.r. carbonyl frequencies, and hydrogen bonding abilities of some α-alkylthio-ketones and carboxylic acid derivatives have shown that the ground and excited state interactions between the carbonyl group and the sulphur atom take place. It has been reported[3] that the Δν values for phenol associated with the α-alkylthio-ketones, measured by i.r. and n.m.r. spectroscopy are slightly smaller than those for phenol associated with the unsubstituted ketones. This result could be considered significant and interpreted in terms of a decrease in basicity of the carbonyl group if the possibility of steric hindrance to the approximation of the proton donor owing to introduction of a bulky ethylthio-group is excluded. Due to this fact it was of interest to extend our studies to the cyclic keto-sulphides, in which a more favourable steric condition for hydrogen bonding was reported.[6]

Although a great deal of attention has centred on 5-thiacyclo-octanone,[7] for which studies of the influence of solvent on the u.v. and i.r. absorption bands and dipolar moment data indicated the existence of ground and excited state transannular charge transfer from sulphur to the carbonyl group, not much interest has been displayed in the kind of interaction responsible for an unusual u.v. absorption in some 3-thiacycloalkanones.[8]

It seems that hydrogen bond measurements could contribute to a better understanding of the interaction in 5-thiacyclo-octanone and also to investigate whether the interaction in the 3-thiacycloalkanones is of a transannular type or similar to that occurring in the open-chain keto-sulphides.

This paper deals with some studies of solvent effects on u.v. absorption, carbonyl group frequencies, and the ability for hydrogen bonding in a number of cyclic keto-sulphides and related compounds, such as sulphur-substituted open-chain ketones, the corresponding unsubstituted ketones, a cyclic oxygen analogue, and an unsaturated non-conjugated cyclic ketone.

RESULTS AND DISCUSSION

Table 1 shows the u.v. absorption bands reported by previous authors for 5-thiacyclo-octanone (1),[7] *trans*-cyclodec-5-enone (2),[9] some 3-thiacycloalkanones (3)—(5),[8] and 4-thiahexan-2-one (6).[10]

It can be seen that 5-thiacyclo-octanone (1) and *trans*-cyclodec-5-enone (2) in cyclohexane, show a normal $n \longrightarrow \pi^*$ band and an intense band at 226 and 188 nm respectively. It has been reported[7,9] that the latter bands are shifted, in ethanol, to longer wavelength and suggested that they are due to electron transfer from sulphur or double bond to the carbonyl group. The u.v. spectra for 3-thiacyclo-pentanone (3), -hexanone (4), -heptanone (5), and 4-thiahexan-2-one (6), measured in ethanol,[8,10] also show two bands, one at *ca.* 300 nm ($\log \varepsilon$ *ca.* 2.3) which is a perturbed $n \longrightarrow \pi^*$ transition and another at *ca.* 250 nm ($\log \varepsilon$ *ca.* 2.5). Table 1 also shows our measurements in n-hexane and 95% ethanol for compounds (3)—(6). They indicate that the maxima at 250 nm do not show any dependence on solvent polarity. We cannot offer, at the moment, an explanation for this invariance, but we may suggest that it is indicative of the non-occurrence of a charge transfer interaction.

It was of interest to find out whether the replacement of sulphur by a double bond in the cyclohexane ring would lead to a similar interaction or to that of the charge transfer type reported for *trans*-cyclodec-5-enone (2). For this purpose the u.v. spectra for cyclohex-3-enone (7) in some solvents of different polarities were measured. Table 1 shows that in n-hexane a band at *ca.* 275 ($\log \varepsilon$ 1.4) and a shoulder at 219 nm appear, the former being practically a non-perturbed $n \longrightarrow \pi^*$ transition. However, in ethanol (95%) the latter turns out to be a maxima at 219 ($\log \varepsilon$ 2.56), which is shifted to 226 nm ($\log \varepsilon$ 2.89) in ethanol (50%). This result suggests charge transfer from the $\pi_{C=C}$ orbital to the π carbonyl system, similar to that occurring in 5-thiacyclo-octanone (1) and *trans*-cyclodec-5-enone (2), but of a different type from the interaction in the 3-thiacycloalkanones (3)—(5) and a 4-thiahexan-2-one (6).

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TABLE 1

U.v. spectra for some ketones

No.	Compounds	Lit. values [nm (log ε)]		Our values [nm (log ε)]	
		C_6H_{12}	abs. EtOH	n-C_6H_{14}	95% EtOH
(1)	5-Thiacyclo-octanone [7]	226 (3.38)	238 (3.41)		
		288 (1.25)			
(2)	*trans*-Cyclodec-5-enone	188 (3.94)	214.5 (3.94) [a]		
		279 (1.25)			
(3)	3-Thiacyclopentanone		252 (2.37) [8]	247 (2.18)	248 (2.19)
			298 (2.08)	300 (1.82)	298 (1.88)
(4)	3-Thiacyclohexanone		250 (2.37) [8]	247 (2.47)	247 (2.47)
			307 (2.34)	305 (2.22)	305 (2.38)
(5)	3-Thiacycloheptanone		249 (2.54) [8]		
			298 (2.34)		
(6)	4-Thiahexan-2-one		243 (2.56) [10]	243 (2.66)	244 (2.52)
			299 (2.41)	301 (2.35)	297 (2.36)
(7)	Cyclohex-3-enone			219sh (2.59)	219 (2.56)
				270.5 (1.35)	272 (1.38)
				277 (1.39)	277.5 (1.38)
					226 (2.89) [b]
					270 (1.44) [b]
					275 (1.44) [b]

[a] 2,2,3,3-Tetrafluoropropanol; [b] 50% v/v EtOH–H_2O.

The relative basicity measurements by i.r. and n.m.r. spectroscopy through association with *p*-chlorophenol were designed in order to achieve some understanding of the contribution of the interaction in the 3-thiacycloalkanones' ground-state. These measurements were performed with ternary systems, ketone–proton donor–CCl_4, in which the molar concentration of the proton donor was kept constant and as low as possible to prevent self-association and the molar ratios n_{OH}/n_{CO} were varied over a range such that a large excess of ketone was used in order to guarantee 1 : 1 association. When the changes in the frequencies of hydroxy-group (in cm^{-1}) or of proton signal (in Hz) due to association ($\Delta\nu$) were plotted against the corresponding values of molar ratios (n_{OH}/n_{CO}) linear correlations were obtained. Figures 1 and 2 show the results obtained by i.r. and n.m.r. measurements respectively, using *p*-chlorophenol as proton donor for the thiacycloalkanones (1) and (3)—(5), corresponding unsubstituted ketones (8)—(11), 3-oxacyclopentanone (12), and cyclohex-3-enone (7). The straight lines were extrapolated to $n_{OH}/n_{CO} = 0$ to give the $\Delta\nu^{\circ}_{OH}$ values. Inspection of these Figures indicates that, for each associating pair the $\Delta\nu_{OH}$ values increase linearly as the concentrations of the ketones

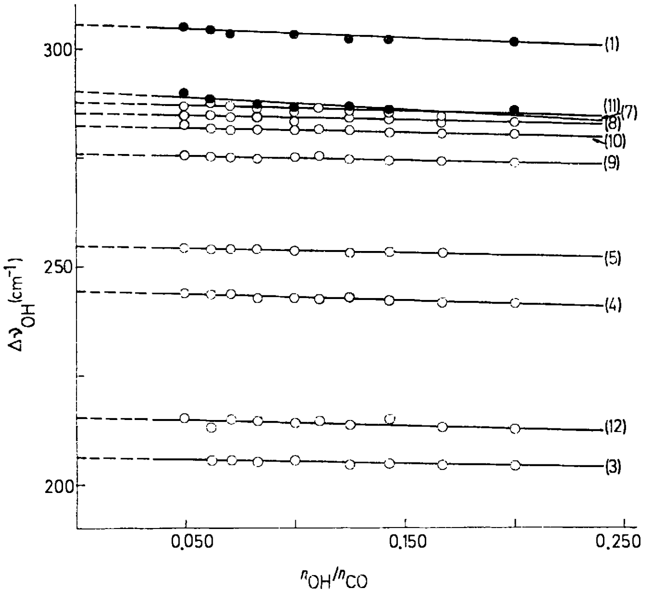


FIGURE 1 Correlations between $\Delta\nu_{OH}$ for *p*-chlorophenol by i.r. spectroscopy and n_{OH}/n_{CH}

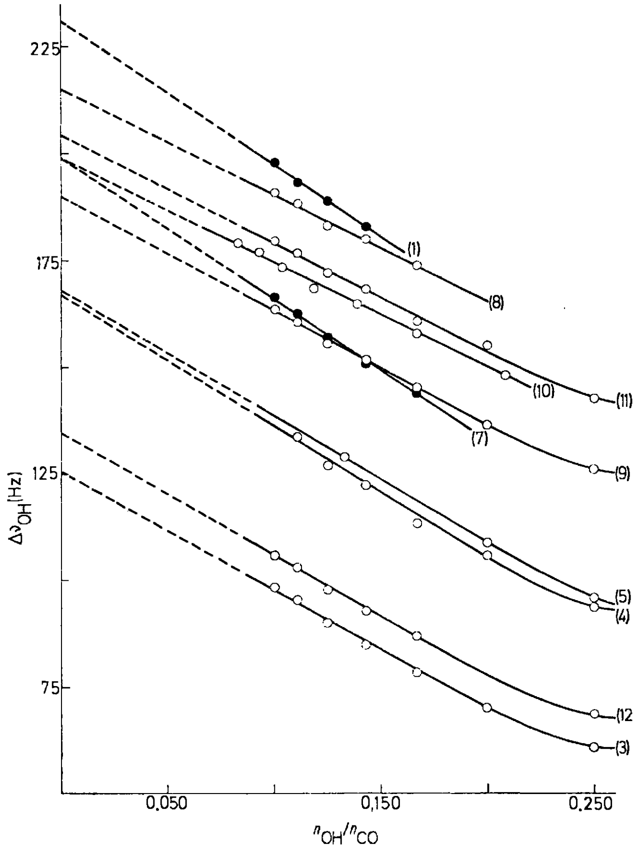
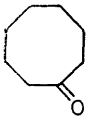


FIGURE 2 Correlations between $\Delta\nu_{OH}$ for *p*-chlorophenol by n.m.r. spectroscopy and n_{OH}/n_{CO}

increase over the range involved. Limiting values are obviously reached at higher concentrations as the mixture approaches a solution of proton donor in liquid ketone.

A similar dependence of the magnitudes of the frequencies upon the concentrations of proton acceptor was recorded by previous authors for the i.r. spectra of other hydrogen-bonded systems and has been attributed to the solvent effect.[11,12]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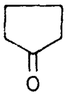
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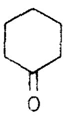
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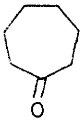
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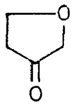
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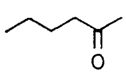
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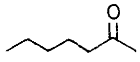
(14)

It may be observed in Figures 1 and 2 that the lines for 5-thiacyclo-octanone (1) and cyclohex-3-enone (7) undergo a rapid ascent with increase of the ketone concentration. The much stronger sensitivity of the $\Delta\nu_{OH}$ values to solvent effect in the case of 5-thiacyclo-octanone, by comparison with other ketones, is in accord with the proposed existence of a mixture of a non-interacted and a more polar interacted conformation,[7] as the population of the latter may increase with an increase of polarity of the environment. The fact that the $\Delta\nu_{OH}$ values for cyclohex-3-enone undergoes a similar abnormal solvent effect suggests that the charge transfer from the $\pi_{C=C}$ orbital to the π carbonyl system, which was shown to occur in the excited state of this compound, may be also a ground state interaction. Thus, at low ketone concentrations when a non-interacted conformation should predominate the decrease of $\Delta\nu_{OH}$ in comparison with cyclohexanone (10) would be due to the inductive effect of the double bond, but this could be offset to some extent by a charge transfer in the opposite direction with increase of the population of an interacted conformation due to an increase of solvent polarity.

The $\Delta\nu^{\circ}_{OH}$ values obtained from i.r. and n.m.r. measurements are shown in Table 2, in which the data for 4-thiahexan-2-one (6) and the unsubstituted open-chain ketones (13) and (14) by the n.m.r. method are also included.

From the $\Delta\nu_{OH}$ values measured by n.m.r. spectroscopy and the corresponding ketone concentrations the equilibrium constants (K) for 1 : 1 association complexes were derived by a graphic method developed by Mathur *et al.*[13] The values of K for the series of ketones studied are also included in Table 2. According to these values three main groups of ketones may be differentiated. It may be seen that higher K values are exhibited by the cyclic unsubstituted ketones (8)—(11), in the range 14.4—19.9, lower values by the open chain unsubstituted ketones (13) and (14) of *ca.* 11.2, and the lowest by the 3-thiacycloalkanones (3)—(5), 3-oxacyclopentanone (12), and open-chain keto-sulphide (6) in the range 4.5—8.2.

The order of the decrease of K in the unsubstituted cyclic ketones, which follows the order of decrease of ring size, is in accord with previous reports.[6,14] It may be seen that the same trend is maintained in the 3-thiacycloalkanones. The small values of K for the latter compounds, in comparison with the corresponding unsubstituted cyclic ketones, show a large decrease of basicity due to the introduction of the sulphur atom into the ring. The difference in the K values between the unsubstituted and the corresponding sulphur containing compounds is *ca.* 10 in the cyclic series. Although in the open-chain series the K value for the sulphur-containing compound is in the same range as those for the 3-thiacycloalkanones, the difference with the corresponding unsubstituted ketones is only *ca.* 3.

TABLE 2

I.r. and n.m.r. data ($\Delta\nu^{\circ}_{OH}$) [a] and the equilibrium constants (K) for association complexes between *p*-chlorophenol and some ketones

Compound no.	I.r. $\Delta\nu^{\circ}_{OH}$(cm^{-1})	$\Delta\nu^{\circ}_{OH}$(Hz)	K_{ass} (l mol^{-1})
(1)	305	231	17.7
(3)	206	126	4.57
(4)	244	167	7.34
(5)	255	166	
(6)		161	8.25
(7)	290	200	12.1
(8)	285	215	19.9
(9)	276	190	14.4
(10)	282	199	17.3
(11)	288	203	17.4
(12)	215	135	6.70
(13)		188	11.2
(14)		192	11.4

[a] Obtained by extrapolation of linear correlations (see Figures 1 and 2) to $n_{OH}/n_{CH} = 0$.

TABLE 3

Ketone carbonyl i.r. spectral data (cm^{-1})

Compound no.	n-C_6H_{14}	CCl_4
(3)	1 744	
(4)	1 721	
(5)	1 704	
(6)		1 709
(8)		1 705
(9)	1 754	
(10)	1 720	
(11)	1 704	
(12)	1 764	
(13)		1 719

It was of interest to find out whether modifications of the bonding abilities of the carbonyl group in these compounds would be followed by appropriate changes of the force constant. For this purpose the carbonyl frequencies were measured. They are shown in Table 3.

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It may be observed that the order of the carbonyl frequencies in the cyclic unsubstituted ketones is eight- and seven-membered ring (8) and (11) < six-membered ring (10) < five-membered ring (9). On the other hand a decrease of the *K* values is observed going from the larger ring ketones to cyclopentanone. Therefore, the increase of the carbonyl frequencies seems to indicate the increase of the force constant of the carbonyl group. This probably may be due to the hybridisation changes at the carbonyl carbon atom.[15]

The frequency value for 3-oxacyclopentanone (12) is also normal, as an increase in comparison with cyclopentanone (9) is observed. This, supported by the decrease of the *K* value (Table 2) may be attributed to the inductive effect of the oxygen atom.

The carbonyl frequencies for 5-thiacyclo-octanone (1) in various solvents have been reported previously[7] and are shown in Table 4. The band at 1 713 cm^{-1} and a shoulder at lower frequency, in CCl_4 solution, which undergo a shift to lower frequencies in more polar solvents, were attributed[7] to a non-interacted and an interacted conformation, respectively. Similar results were obtained now, for cyclohex-3-enone (7) (Table 4). The i.r. spectrum of this compound, in n-hexane, shows a carbonyl band at 1 727 cm^{-1}, and a shoulder at lower frequency which is difficult to localise. The increase of the frequency by 7 cm^{-1} from that of cyclohexanone is probably due to the inductive effect of the double bond. However, it may be observed that going over to more polar solvents the band and the shoulder are shifted to lower frequencies, the latter becoming intensified and easier to localise.

It is noteworthy that the solvent effect on the carbonyl absorption in cyclohex-3-enone gives support to the existence of a mixture of non-interacted and interacted transannular conformations which we proposed in order to explain the effect of ketone concentration on the proton accepting ability.

As reported previously[5] (Table 3) the carbonyl frequency for 4-thiahexan-2-one (6) is lower than that for the unsubstituted ketone. A decrease of carbonyl frequency is observed also for 3-thiacyclopentanone (3) and no significant alterations for 3-thiacyclo-hexanone (4) and -heptanone (5) by comparison with the corresponding unsubstituted ketones (9)—(11). These results are not in accord with the large decrease of basicities observed for these compounds, which normally, if due to the common inductive or field effect, or in the case of cyclic ketones, to the strain caused by introduction of sulphur into the ring, should be accompanied by a large increase in the carbonyl frequencies.

It should be mentioned that the same anomalous relationship between basicities and carbonyl frequencies has been reported for the thiolesters and thiolactones and was tentatively interpreted[15,16] as due to a charge transfer from the carbonyl group to the vacant 3*d* orbital of the sulphur atom. Thus, the introduction of the sulphur atom, either directly or α to the carbonyl group, seems to have a similar effect.

TABLE 4

Carbonyl stretching frequencies (cm^{-1}) in various solvents

Compound no.	n-C_6H_{14}	CCl_4	CH_3CN	CH_2Cl_2	$CHCl_3$
(1)	1 713[a]	1 704	1 701	1 698	1 695
	1 696sh	1 690sh	1 691	1 689	1 686
(7)	1 727	1 721	1 716	1 715	1 713
		1 712sh	1 706sh	1 705sh	1 704sh

[a] Cyclohexane.

Our results suggest that excited and ground state interactions occur in the 3-thiacycloalkanones. They seem to be of different type from the transannular one but similar to those in the corresponding open-chain keto-sulphides. Although the basicity measurements for the thiacycloalkanones seem to suggest the occurrence of interactions of donation and back donation between sulphur and the carbonyl group with conformational dependence, it is far from clear which orbitals contribute most and whether it is a through-space or through-bond interaction.[17]

EXPERIMENTAL

Reagents.—All solvents for the spectrometric measurements were spectrograde and were used without any further purification. Commercial pentan-2-one, heptan-2-one, cyclopentanone, cyclohexanone, and *p*-chlorophenol were purified as described elsewhere.[18] Cyclo-heptanone and -octanone,[19] 3-thiacyclopentanone and 3-oxacyclopentanone,[20] 3-thiacyclo-hexanone and -heptanone,[21] 5-thiacyclo-octanone,[7] cyclohex-3-enone[22] and 4-thiahexan-2-one[4] were prepared by literature procedures. All compounds were analysed by g.l.c. to assess their purity.

Spectrometric Measurements.—The u.v. spectra were recorded on a Beckman DK-2A spectrometer using calibrated 1.00 cm quartz cells. All measurements were made at room temperature (26 ± 1°). Carbonyl frequencies were measured for 0.01M solutions in carbon tetrachloride on a Perkin-Elmer model 180 grating spectrometer using a pair of potassium bromide 2 mm cells. The basicity measurements were performed on a Perkin-Elmer model 457-A grating spectrometer, using a pair of potassium bromide cells with variable path. Dilution studies of *p*-chlorophenol in carbon tetrachloride were made over a concentration range 0.045—0.002M. The stretching frequency (ν_0) of *p*-chlorophenol in carbon tetrachloride extrapolated to infinite dilution was 3 615 cm^{-1}. The frequencies (ν') of OH in the proton donor-ketone complexes in carbon tetrachloride were determined maintaining the concentration of *p*-chlorophenol (0.01M) constant and

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varying the molar ratios *p*-chlorophenol : ketone (n_{OH}/n_{CO}) between 0.05 and 0.20. For each solution five spectra were recorded and the mean values calculated. The $\nu_0 - \nu'$ values ($\Delta\nu$) were plotted against n_{OH}/n_{CO} and the straight lines extrapolated to $n_{OH}/n_{CO} = 0$ to give the $\Delta\nu^{\circ}_{OH}$ (cm^{-1}) values (Table 2). Carbonyl and hydrogen-bonded band frequencies are accurate to ± 1 (model 180) and ± 4 cm^{-1} (model 457-A), respectively. All i.r. measurements were made at room temperature (23 ± 1°). 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 carbon tetrachloride were performed using a concentration range 0.003—0.8M and the chemical shift (ν_0) of the OH group in *p*-chlorophenol extrapolated to infinite dilution was 180 Hz. The chemical shifts (ν') of OH in the proton donor–ketone complexes in carbon tetrachloride were determined maintaining the concentration of *p*-chlorophenol (0.03M) constant and varying the molar ratios *p*-chlorophenol : ketone (n_{OH}/n_{CO}) between 0.10 and 0.25. For each solution five spectra were recorded and the mean values calculated. The $\nu' - \nu_0$ values ($\Delta\nu$) were plotted against n_{OH}/n_{CO} and the straight lines extrapolated to $n_{OH}/n_{CO} = 0$ to give the $\Delta\nu^{0}_{OH}$ (Hz) values (Table 2). The association constants (K_{ass}) were calculated by the method of Mathur *et al.*[13] by plotting $1/\Delta\nu$ against $1/c$ where c is the concentration of ketone. The precision of all measurements are ± 2 Hz. All n.m.r. measurements were made at 35°.

The plots for both i.r. and n.m.r. data were treated by appropriate least-square regression analysis with the aid of a Hewlett–Packard calculator 9100A to obtain the best straight lines which fit the results.

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