Interaction between the Carbonyl Group and a Sulphur Atom. Part 9.[1] The Relationship between Conformation and Ground- and Excited-state Interactions in Some α-Sulphur-substituted Cycloalkanones

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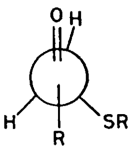
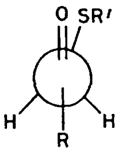
The conformations of some α-sulphur-substituted cycloalkanones are estimated approximately from the i.r. spectra. The decrease of the carbonyl stretching frequency in these compounds, by comparison with the corresponding unsubstituted ketones ($\Delta\nu_{CO}$), is reported and interpreted as due to hyperconjugative $\sigma C(2)-S-\pi_{CO}$ interaction on the basis of the dependence on the position of C(2)–S bond. Similarly, hyperconjugative interaction in the excited state is proposed to account for the bathochromic shift of the $n\rightarrow\pi^*$ band, at 300 nm, of the same compounds. The shorter wavelength u.v. absorption band, at 250 nm, is assigned to charge transfer from sulphur to the carbonyl group owing to its dependence on the position of the 3*p* orbital of sulphur relative to the carbonyl group.

OUR previous studies[2-5] have shown that some 2-alkylthio-ketones and 3-thiacycloalkanones exhibit ground- and excited-state interactions. It was suggested[6] that of four possible conformations (A)—(D), which differ in the relative positions of sulphur atom and carbonyl group, (A) and (C) seem to be the most plausible for such interactions.



(A)



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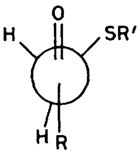

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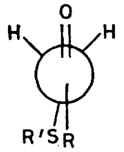


(D)

The aim of the present work was to investigate some cycloalkanones with an exocyclic sulphur atom bonded to the α-carbon, in order to examine how the change of rotation of the C(2)–S bond around C(1)–C(2) (angle ϕ) affects the spectroscopic properties of these compounds.

RESULTS AND DISCUSSION

Assignment of C(2)–S *Bond Conformations.*—The conformations of some sulphur-substituted cycloalkanones (1)—(5) were estimated approximately from the analyses of the i.r. spectra by comparison with the corresponding unsubstituted ketones (6)—(9) (Tables 1 and 2).

Table 1 shows that the 2-alkylthiocycloalkanones (1)—(3) exhibit two carbonyl bands, one at higher, another at lower frequency than those of the corresponding unsubstituted ketones (6)—(8). It seems reasonable, by analogy with the halogeno-ketones,[7,8] to attribute the higher frequency absorptions to the equatorial conformers, in which the field effect should operate and the lower ones to the axial conformers. This assignment was confirmed when the ratio of molar extinction coefficients $\varepsilon_{eq}/\varepsilon_{ax}$ increased on going from CCl_4 to $CHCl_3$, strongly indicating the absence of Fermi resonance. The approximate percentages of axial conformers in CCl_4 were estimated as 80% for (1) and 70% for (2a) and (3). These results are similar to those for the corresponding halogenocycloalkanones, for which the halogen atoms were reported to be predominantly axial. Therefore, by analogy with 2-halogenocyclopentanones,[8] 2-ethylthiocyclopentanone (1) may be considered to have a half-chair conformation with the projected angle ϕ between C(2)–S bond and σ_{CO} of *ca.* 77°.

However, it may be seen that the sulphur-substituted camphor (4) exhibits only one carbonyl band, indicating that only one conformer is present. This, again, is in accord with the halogeno-substituted camphor for which the C–X bond was suggested to be in an intermediate position between axial and equatorial, with the projected angle ϕ of *ca.* 55°.[8] The ^1H n.m.r. spectrum of the compound (4) indicated that the sulphur atom is *endo*.[9,10]

TABLE 1

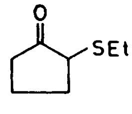
Carbonyl i.r. spectral data for some cycloalkanones

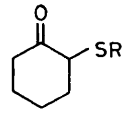
Compound	Solvent	ν_{CO}/ cm^{-1}	ε/ l mol^{-1} cm^{-1}	$\varepsilon_{eq}/\varepsilon_{ax}$
2-Ethylthiocyclopentanone (1)	CCl_4	1 733	560	0.21
		1 748	120	
	$CHCl_3$	1 727	368	0.37
		1 744	135	
2-Methylthiocyclohexanone (2a)	CCl_4	1 705	441	0.22 [c]
		1 708	517	
		1 722	106	
	$CHCl_3$	1 699	370	0.30 [c]
		1 707	296	
		1 723	99	
2-Methylthio-4-t-butylcyclohexanone (3)	CCl_4	1 709	439	0.38
		1 723	167	
	$CHCl_3$	1 705	367	0.50
		1 718	183	
2-Methylthiocamphor (4)	CCl_4	1 742	576	
	$CHCl_3$	1 738	630	
Cyclopentanone (6) [a]	CCl_4	1 746	0.74 [b]	
	$CHCl_3$	1 734	0.46 [b]	
Cyclohexanone (7)	CCl_4	1 718	920	
	$CHCl_3$	1 706	973	
4-t-Butylcyclohexanone (8)	CCl_4	1 721	1 013	
	$CHCl_3$	1 713	622	
Camphor (9)	CCl_4	1 747	997	
	$CHCl_3$	1 733	839	

[a] [2,2,5,5-$^2H_4$] Compound. [b] Absorbance values. [c] ε_{ax} is the mean value of two lower frequency bands.

Finally, the i.r. spectrum of 2-mercaptocyclopentanone

(5) was investigated in the ν_{SH} and ν_{CO} region and compared with those of cyclopentanethiol (10) and [$^2H_4$]-cyclopentanone (6) (Table 2).


(1)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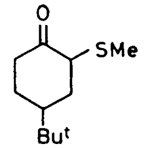
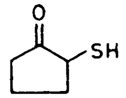

(3)

(a) R = Me; (b) R = Et


(4)


(5)

It may be seen that 2-mercaptocyclopentanone (5) exhibits, in CCl_4, two SH stretching bands, one of which is of the same frequency and the other of lower frequency than that of the corresponding thiol (10). This seems to indicate that 2-mercaptocyclopentanone exists as an equilibrium mixture of intramolecularly hydrogen bonded (–SH · · · O=C–) and free forms. In $CHCl_3$, the presence of a large band with a maximum shifted to lower frequency and increased ε, by comparison with the higher frequency band in CCl_4, indicates an increase in the proportion of the free form. In the ν_{CO} region two bands are also present, one slightly shifted to lower frequency, another to higher frequency, when compared with that of [$^2H_4$]cyclopentanone (6). The assignment of the former band to the unassociated form and the latter to the associated seems reasonable.[11,12] This is confirmed by the fact that the ratio $\varepsilon_{ass}/\varepsilon_{unass}$ for the ν_{CO} bands is practically the same as that for the corresponding ν_{SH} bands. Both ratios undergo a slight decrease on going from CCl_4 to $CHCl_3$, which indicates an increase of population of the unassociated form.

TABLE 2

I.r. data of 2-mereaptocyclopentanone and related compounds

Compound	Solvent	ν_{SH}/cm^{-1}	ε/ l mol^{-1} cm^{-1}	Ratio $\varepsilon_{ass} : \varepsilon_{unass}$	ν_{CO}/cm^{-1}	ε/ l mol^{-1} cm^{-1}	Ratio $\varepsilon_{ass} : \varepsilon_{unass}$
2-Mercaptocyclopentanone (5)	CCl_4	2 567 [a]	4.5	1.12	1 744 [b]	204	1.17
		2 576 [b]	4.0		1 750 [c]	240	
	$CHCl_3$	2 573	5.6		1 736 [b]	247	1.08
					1 740 [c]	267	
Cyclopentanethiol (10)	CCl_4	2 578	2.8				
	$CHCl_3$	2 577	2.0				
[2,2,5,5-$^2H_4$]Cyclopentanone (6)	CCl_4				1 746		
	$CHCl_3$				1 734		

[a] Associated form. [b] Unassociated form. [c] Maximum of a symmetrical band, resulting from two overlapping bands.

It may be observed that the ν_{CO} band, corresponding to the unassociated form, is only slightly shifted to lower frequency by comparison with that of [$^2H_4$]cyclopentanone, less than in the sulphur-substituted camphor (4) (Table 1). This indicates a conformer with the C(2)–S bond approaching the equatorial position. It would be desirable to carry out variable temperature studies to give additional support to our conformational interpretation.

Interactions occurring in the –S–CH$_2$–CO– *System through I.r., U.v., and Basicity Measurements.*—Inspection of Table 1 shows that the lower frequency bands in 2-alkylthiocycloalkanones (1)—(3), assigned to the axial conformers, are shifted to lower frequency, by comparison with the corresponding unsubstituted ketones (6)—(8). This has already been reported for the open-chain α-alkylthio-ketones [2,3] and for 3-thiacyclopentanone.[4] It may be observed that the decrease in $\nu_{CO}(\Delta\nu_{CO})$ has a maximum value in 2-ethylthiocyclopentanone (1) (12.6 cm^{-1}), in which the projected angle ϕ is *ca.* 77° and that it decreases, both with an increase and a decrease of this angle. Thus, $\Delta\nu_{CO}$ is 10 cm^{-1} for the 2-alkylthiocyclohexanones (2a) and (3), for which ϕ *ca.* 120°, and only 1.6 cm^{-1} for 3-thiacyclopentanone, [4] for which ϕ approaches 180°. On the other hand, for 2-methylthiocamphor (4), which has ϕ *ca.* 55°, $\Delta\nu_{CO}$ is 4.5 cm^{-1}, and is only 2 cm^{-1} in the nearly equatorial 2-mercaptocyclopentanone (5). These facts suggest that $\Delta\nu_{CO}$ for the axial conformers of 2-alkylthiocycloalkanones is not a vibrational effect, but is due to the decrease of the force constant of the carbonyl group as a result of an interaction occurring in the –S–CH$_2$–CO– system. It is noteworthy that no such effect has been described in the literature for other interacting systems.

The dependence of $\Delta\nu_{CO}$ on the position of the C(2)–S bond, a maximum in the quasi-axial position of 2-ethylthiocyclopentanone when this bond is aligned with the π_{CO} system, suggests that hyperconjugative interaction between σC(2)–S and π_{CO} is responsible for the decrease of the force constant of the carbonyl group.

Table 3 shows the u.v. spectra for the sulphur-substituted ketones (1)—(5), by comparison with the corresponding unsubstituted ketones (6)—(9), in n-hexane and methanol. As reported for the open-chain α-alkylthio-ketones [2] and 3-thiacycloalkanones [4] compounds (1)—(5) are characterized by a shorter wavelength band at *ca.* 250 nm and a longer wavelength one at *ca.* 300 nm. The latter, which undergoes a blue shift on going from n-hexane to methanol, is characteristic of an $n \longrightarrow \pi^*$ transition. A comparison of the $n \longrightarrow \pi^*$ bands in (1)—(5) with those for the corresponding unsubstituted ketones (6)—(9) shows that they are shifted to longer wavelengths and are more intense. This red shift is not in accord with the decrease of basicity of the carbonyl group, which occurs in the 2-alkylthiocycloalkanones (1)—(4), when compared with the corresponding unsubstituted ketones (6)—(9) (Table 4). It is noteworthy that the decrease in basicity has been also reported for a series of open-chain α-alkylthio-ketones[3,4] and, subsequently, confirmed by ionization potential data.[5] These facts seem to indicate that the bathochromic shift of the $n \longrightarrow \pi^*$ absorption is due to stabilization of the π^* level, which, most probably, results from hyperconjugative interaction between σ_{C-S}^* and antibonding π^* level.

TABLE 3

U.v. absorption spectra for some cycloalkanones

Compound	$\lambda_{max.}$(n-C_6H_{14})/ nm (ε)	$\lambda_{max.}$(CH_3OH)/ nm (ε)
(1)	310 (495)	308 (365)
	249 (787)	250 (455)
(2b)	309 (256)	306 (286)
	248 (321)	250 (282)
(3)	308 (280)	305 (320)
	248 (324)	249 (298)
(4)	315 (152)	310 (134)
	245 (203)	247 (195)
(5)	304 (104)	301 (135)
	237 (268)	237 (312) [a]
		313 (1 264) [b]
		255 (939) [b]
(6)	300 (18)	287 (18)
(7)	291 (15)	282 (15)
(8)	290 (16)	281 (18)
(8)	291 (25)	288 (33)

[a] Shoulder. [b] 10^{-3}M-KOH.

The shorter wavelength absorption has a bathochromic shift and hyperchromic effect when compared with the absorption in sulphides[13,14] [$\lambda_{max.}$ 229 nm (ε 139)]. It shows a slight but constant red shift on passing from n-hexane to methanol. It seems reasonable to deduce that the hypochromic effect, which is observed on increasing the polarity of solvent, is caused by a shift of the equilibrium towards the equatorial form.

TABLE 4

Equilibrium constants for association complexes between p-chlorophenol and some cycloalkanones

Compound	K_{ass}/l mol^{-1} [a]
(1)	8.4
(2b)	10.4
(4)	3.3
(6)	14.4
(7)	17.3
(9)	14.1

[a] From the $\Delta\nu_{OH}$ values of p-chlorophenol measured by n.m.r. spectroscopy and the corresponding ketone concentrations.

It may be observed that this shorter absorption band reaches a maximum value of 249 nm and highest intensity (ε 787) in the case of 2-ethylthiocyclopentanone (1). It undergoes a blue shift and becomes less intense with a decrease of the angle ϕ in the sulphur-substituted camphor (4), giving a minimum value of 237 nm in 2-mercaptocyclopentanone (5), which has the sulphur atom nearly equatorial. However, there is no regularity in the relationship between the wavelength and intensity of this band and the angle ϕ. Thus, no shift in the position of this band, but only a decrease in intensity (ε 320) is observed, on going to the 2-alkylthiocyclohexanones (2b) and (3) and a slight blue shift, but a larger decrease in intensity, on going to 3-thiacyclohexanone[4] [$\lambda_{max.}$ 247 nm (ε 295)] and 3-thiacyclopentanone[4] [$\lambda_{max.}$ 247 nm (ε 151)]. Recently, a long wavelength absorption of low intensity [$\lambda_{max.}$ 255 nm (ε 191)] was reported[15] for 7-thiabicyclo[2.2.1]heptan-2-one, which has a fixed conformation (A); this was assigned, due to the influence of solvent, to charge transfer from sulphur to the carbonyl group. These results seem to suggest that the shorter wavelength absorption does not depend only on the angle ϕ, but mainly on the position of the $3p$ orbital of sulphur relative to the carbonyl group. The modification, either of the position of the C(2)–S bond or of the size and conformation of the ring, may hinder the rotation of SR around the C(2)–S bond (described by θ[16]), preventing a suitable orientation of the $3p$ orbital.

Examination of molecular models shows that in the 2-ethylthiocyclopentanone the requirements for both interactions, hyperconjugative and sulphur lone-pair charge transfer, are fulfilled, as the C(2)–S bond is eclipsed by π_{CO} and the $3p$ orbital of sulphur is directed toward carbonyl group. On the other hand, in the nearly equatorial 2-mercaptocyclopentanone, neither the position of the C(2)–S bond, nor that of the $3p$ orbital of sulphur satisfy the requirements for the proposed interactions.

Support for electron transfer from divalent sulphur to the carbonyl group was obtained when the spectrum of 2-mercaptocyclopentanone (5) was measured in an alkaline solution (Table 3) and an intense band at 255 nm was observed. Two facts may explain the modification of the spectrum of 2-mercaptocyclopentanone in alkaline solution: the non-existence of an intramolecular hydrogen bonding permits the sulphur atom to become quasi-axial and the lack of an alkyl group on sulphur eliminates any restriction to the orientation of the $3p$ orbitals of sulphur towards the carbonyl group.

EXPERIMENTAL

Commercial Reagents.—All solvents for spectrometric measurements were spectrograde and were used without further purification. Commercial cyclopentanone, cyclohexanone, and p-chlorophenol were purified as described elsewhere.[17]

Products.—[2,2,5,5-$^2H_4$]Cyclopentanone,[18] 4-t-butylcyclohexanone,[19] and 2-ethylthiocyclohexanone[20] were prepared by literature procedures. The last was purified through its ethylene acetal. 2-Ethylthiocyclopentanone[21] and 2-ethylthio-4-t-butylcyclohexanone were prepared as described for the 2-ethylthiocyclohexanone. 2-Ethylthio-4-t-butylcyclohexanone was a *liquid*, b.p. 73.4—75.0° at 0.045—0.05 mmHg (Found: C, 67.2; H, 10.5. $C_{12}H_{22}OS$ requires C, 67.3; H, 10.3%); δ(CCl_4) 3.22 (1 H, m), 2.45 (2 H, q, J 7 Hz), 1.23 (3 H, t, J 7 Hz), 1.0—3.0 (7 H, m), and 0.98 (9 H, s). 2-Mercaptocyclopentanone was prepared by a literature method.[22] Its existence as a monomer was proved by its i.r. spectrum, $\nu_{max.}$ (film) 3 455 cm^{-1}, and by the addition of deuterium oxide which removed the coupling of the SH proton to the α-CH proton in the n.m.r. spectrum. 2-Methylthiocamphor was prepared by sulphenylation[23] with the ratio of ketone : base : disulphide of 1 : 2 : 2, in tetrahydrofuran solution with the addition of hexamethylphosphoramide. Purification by column chromatography (silica gel; anhydrous benzene), gave the pure *compound* in 40% yield as a liquid, b.p. 83—84° at 1 mmHg (Found: C, 66.6; H, 9.4. $C_{11}H_{18}OS$ requires C, 66.7; H, 9.1%); $\nu_{max.}$ (CCl_4) 1 746 (C=O) cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 1 739 (C=O) cm^{-1}; δ(CCl_4) 3.09 (1 H, d, *J* 5 Hz), 2.22 (3 H, s), 0.98 (3 H, s), 0.86 (3 H, s), 0.84 (3 H, s), and 1.16—2.40 (5 H, m).

U.v. Data.—U.v. spectra were recorded on a Beckman DK-2A spectrophotometer. Calibrated quartz cells of 1.00 cm pathway and spectrograde n-hexane and methanol were employed. For each substance, the spectra of three solutions of different concentration (10^{-4}—10^{-2}M) were recorded, and $\varepsilon_{max.}$ (l mol^{-1} cm^{-1}) was estimated by a linear regression of absorbance against concentration. All spectra were run at 25 ± 1°.

I.r. Measurements.—I.r. spectra were recorded on a Perkin-Elmer model 180 grating spectrometer at 30°. The spectral slit width was 3.0 cm^{-1} in the SH region and 2.0 cm^{-1} in the C=O region. The SH stretching frequencies were measured for 5×10^{-2}M solutions in carbon tetrachloride and chloroform. Further dilution did not affect the spectra remarkably. Quartz matched cells of 1 cm pathlength were used. The carbonyl frequencies were measured for 2.5—3.0×10^{-2}M solutions in carbon tetrachloride and chloroform, using a pair of 0.5 sodium chloride mm cells. Both C=O and SH stretching frequencies were accurate to ± 1 cm^{-1}.

N.m.r. Basicity Measurements.—The n.m.r. spectra and the association constants (K_{ass}) were determined as previously described.[4]

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