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The ORD, CD and UV Spectra of Sulphides Derived from Carvone

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The ord and cd spectra of aromatic and aliphatic sulphides derived from carvone are compared with the spectra of dicarvone sulphide and related compounds. The spectra are discussed in relation to the structure of the molecules, as evidenced by the nmr spectrum, and correlated with the electronic transitions involved.

(Keywords: Carvone sulphides; CD; NMR; ORD)

ORD-, CD- und UV-Spektren von Sulfiden des Carvons

Die CD- und ORD-Spektren aromatischer und aliphatischer Sulfide von Carvon werden mit Spektren von Dicarvonsulfid und verwandten Verbindungen verglichen. Die Spektren werden in bezug auf Molekülstrukturen, die durch NMR-Spektren bewiesen wurden, diskutiert und mit den betreffenden Elektronenübergängen in Wechselbeziehung gebracht.

Introduction

This series of compounds comprises the sulphides formed from carvone by the addition of *R*SH across the endocyclic double bond, together with the same structures where additionally the exocyclic double bond has been hydrogenated or had the elements of methanol added to it. This work originates from the study of compounds related to dicarvone sulphide[1].

The preparation of these sulphides by the addition of thiols across the endocyclic double bond of (—)-(*R*)-carvone may theoretically result in four isomers when the sulphur is attached to C 3. In fact, there

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appear to be only two isomers formed in any quantity. Thus the addition, in the cold, of thiophenol to (—)-carvone in the presence of sodium acetate gave compound **4 A** (Fig. 1), m. p. 76-78°, $[\alpha]_D^{20}$—12°, whereas under reflux in the presence of triethylamine, compound **4 B** (Fig. 1), m. p. 68-69°, $[\alpha]_D^{20}$—9.5°, was obtained. The presence of the sulphide group at the 2 position is unlikely in view of the high yield of dicarvone sulphide which is obtained by the action of H_2S on carvone. Whilst the addition of thiols to double bonds, and to endocyclic double bonds in particular, has been the subject of much study, it seems clear that in a complex molecule it is not possible to determine likely isomers by theretical predictions on the basis of existing groups. The concept of the "reactive face" of a double bond has been employed[2] but, since this depends on quite distant groups as well as on the neighbouring groups, predictions with a high probability of success are not possible; thus it is necessary to determine the structures unambiguously from experimental evidence.

Results and Discussion

Conclusive evidence for the structure of these compounds is provided by the 220 MHz spectrum of the phenyl sulphide (Tables 1 a, 1 b). The analysis of the nmr spectrum of compound **4 A** shows that C 3-H is equatorial because none of its coupling constants is large enough to give axial-axial coupling[3]; with C 4-H the resonance is well down-field from C 5-H because of its proximity to sulphur. The coupling constants of C 5-H show that it is axially disposed and the down-field shift of the methyl group at C 2 in deuteriopyridine shows that it is equatorial[4]. The fine structure of the spectrum may be interpreted as due to interaction between hydrogens at C 4 and C 6 which have a coupling constant of about 2 Hz. The coupling of C 2-H to C 3-H shows a value of about 5 Hz, which is large enough for axial-equatorial coupling but too small for axial-axial coupling[3]. Partial twist forms were not considered in the absence of overcrowding and bonding forces likely to interfere with the usual preference for the chair form[5].

By contrast, C 3-H in compound **4 B** (Table 1 b) is axial in view of its coupling constants (J-H_{32a} 12 Hz, J-H_{34a} 12 Hz), so that the sulphide group is equatorial and the downfield shift in deuteriopyridine shows that the methyl group at C 2 is also equatorial[4], thus the difference between compounds **4 A** and **4 B** is in the stereochemistry at C 3 only.

The stereochemistry of compounds **5 A** and **6 A** can be assumed to follow similar lines to that of compound **4 A**, in that the form prepared at room temperature has C 3-H equatorial, whilst in that prepared at the higher temperature C 3-H is axial.

Table 1a. *Chemical shifts and coupling constants of protons in (S)-2-methyl-(S)-5-isopropenyl-(R)-3-thiophenylcyclohexanone* (**4A**); *220 MHz in* $CDCl_3$

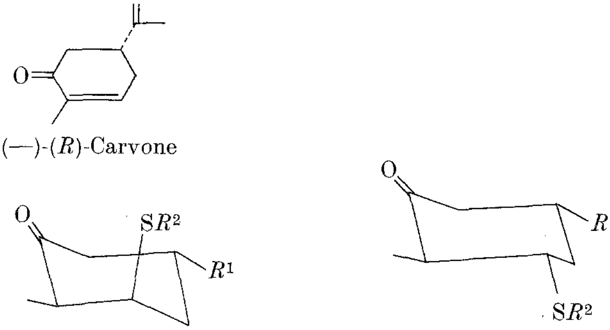
Proton	ppm	J/Hz
CH_3 at C 2	1.20	$J_{CH_3\text{-}H}$ 7.0
CH_3 in isopropenyl	1.66	
H_2	2.84	J_{23} 5
H_3	3.88	J_{34a} 3.5, J_{34e} 3.5
H_{4a}	1.94	J_{4a4e} 15
H_{4e}	2.14	
H_5	3.09	J_{4a5} 11.5, J_{56a} 15 J_{4e5} 3.5, J_{56e} 3.5
H_{6e}	2.52	
H_{6a}	2.32	J_{6a6e} 13

Table 1b. *Relative chemical shifts of protons in deuteriochloroform and deuteriopyridine at 100 MHz*

Compound	$CDCl_3$ ppm			J/Hz	C_5D_5N ppm		J/Hz	$\Delta CDCl_3$—C_5D_5N	Assignment
4A	(3 H)	1.20	d	6.5	1.30	d	6.5	—0.10	CH_3 at C 2
4B	(3 H)	1.33	d	6.0	1.43	d	6.5	—0.10	CH_3 at C 2
	(3 H)	1.68	s		1.57	s		+ 0.11	CH_3 in isopropenyl
	(5 H)	2.1-2.5	m		2.2-2.6	m		—	
	(1 H)	2.91	td		3.14	td		—0.25	H 3
				12			12		H_3H_{2a}
				12			12		H_3H_{4a}
				3.5	3.5				H_3H_{4e}
	(2 H)	4.72	m		4.69	m		+ 0.03	CH_2
	(3 H)	7.32	m		7.26	m		+ 0.06	*m* and *p*H in phenyl
	(2 H)	7.40	m		7.56	m		—0.16	*o*H in phenyl

In steric terms alkyl and phenyl groups cannot be regarded as equivalent nor can they be regarded as equivalent in terms of exchange forces, so that it is necessary to have experimental evidence to determine the stereochemistry at C 3 for compounds **7** to **12**. Fortunately, the evidence from the circular dichroism is very clear cut — all the compounds in this series produced at room temperature have a positive band at around 290 nm and another positive band at around 240 nm, whereas those produced at the higher temperature have a negative band at the longer wavelength. It is therefore not necessary to have a detailed analysis by high-resolution nmr for the stereochemistry of compounds **5** to **12** (Fig. 1) to be determined. It is noteworthy that **1** and **2** have the same type of cd spectrum as the low temperature form; as has already been suggested, these compounds have the sulphide group in the axial position[1]. It would seem to be reasonable to suppose that the C 2 methyl group is similarly disposed in all these compounds, i.e. in the equatorial position. The compounds are therefore determined as shown in Scheme 1.

Scheme 1



	A series	**B** series
	R^1	R^2
4 A (B)	isopropenyl	phenyl
5 A	isopropyl	phenyl
6 A	methoxy isopropyl	phenyl
7 A (B)	isopropenyl	ethyl
8 A (B)	isopropyl	ethyl
9 A (B)	methoxy isopropyl	ethyl
10 A	isopropenyl	*t*-butyl
11 A	isopropyl	*t*-butyl
12 A	methoxy isopropyl	*t*-butyl

4 A: (*S*)-2-methyl-(*S*)-5-isopropenyl-(*R*)-3-thiophenylcyclohexanone.
4 B: (*S*)-2-methyl-(*S*)-5-isopropenyl-(*S*)-3-thiophenylcyclohexanone.

UV, ORD, and CD Spectra

The cd spectrum of compounds **1** and **2** consists of two positive peaks at 247 and 290 nm, and a negative peak at 217 nm. The same cd peaks would appear to be shown by **3** at 243 and 288 nm, but the 217 nm peak was not reached. In **4 A** there would appear to be a bathochromic effect, giving 267 and 295 nm for the positive peaks and 248 nm for the negative peak. From the uv absorption 267 nm would appear to be the benzenoid peak. At 227 nm a further positive peak appears; this contrasts with the negative peak at 217 nm in **2**. In compound **5 A** there is a similar spectrum to that of **4 A** with peaks at 261 and 297 nm, but the negative peak was not observed in the cd whilst in **6 A** only the peak at 295 nm was observed. The failure to observe the other cd peaks is clearly not due to their absence since they show clearly in the ord, but is due to the relative values of uv and cd absorption in the benzenoid region. The corresponding ethyl derivatives, compounds **7 A**, **8 A** and **9 A**, show three cd peaks quite clearly. The amplitude of the band at 290 nm is greatest in **7 A** and weakest in **8 A** and **9 A**, all the peaks being positive, whereas the band at 220 nm is weakest in **7 A**, and strongest in **9 A**, **8 A** being intermediate. The middle band at 245–250 nm has roughly the same strength in all three ethyl compounds. In the corresponding tertiary butyl dihydro compound, **10 A**, the 220 and 290 nm bands are of the same order of magnitude, the latter being about the maximum for the alkyl carvone sulphides. In the tetrahydro compound, **11**, the 220 nm band is much enhanced in intensity, whereas the 290 nm band is rather reduced. In the methoxytetrahydro compound, **12**, the position is almost identical with that in the tetrahydro compound. The three bands in these compounds are all of the same sign, and their origin in the different compounds is, presumably, similar. The 240 nm band, which is relatively invariant in the alkyl cycloalkyl sulphides, would appear to relate to sulphur, in particular to the promotion of lone pair electrons from the 3 P orbitals on sulphur to a non-bonding orbital b_1-b_2^* (*Rosenfield J. S.* and *Moscovitz A.*[6,7]). In the phenyl cycloalkyl sulphides, on the other hand, this band, if present, would appear to be bathochromically shifted and masked by phenyl absorption at around 260 nm. The 220 nm band appears to involve the promotion of lone pair electrons on sulphur to an antibonding orbital[6]. The spectra of **8 A** and **9 A** show a peak at 205 nm which could involve the bathochromic displacement of the n-σ* transition of the carbonyl group, whilst the 215 nm band involves promotion of the lone pair electrons on sulphur, as above.

The 290 nm band is clearly that due to the n-π* transition of the carbonyl group.

CD and ORD Spectra in Relation to Molecular Structure

The cd and ord spectra of compounds **4** to **12** form a rather nice family, or, perhaps, three families.

The shapes of the curves obtained from the compounds formed at room temperature are rather similar, and differ from the shapes of those

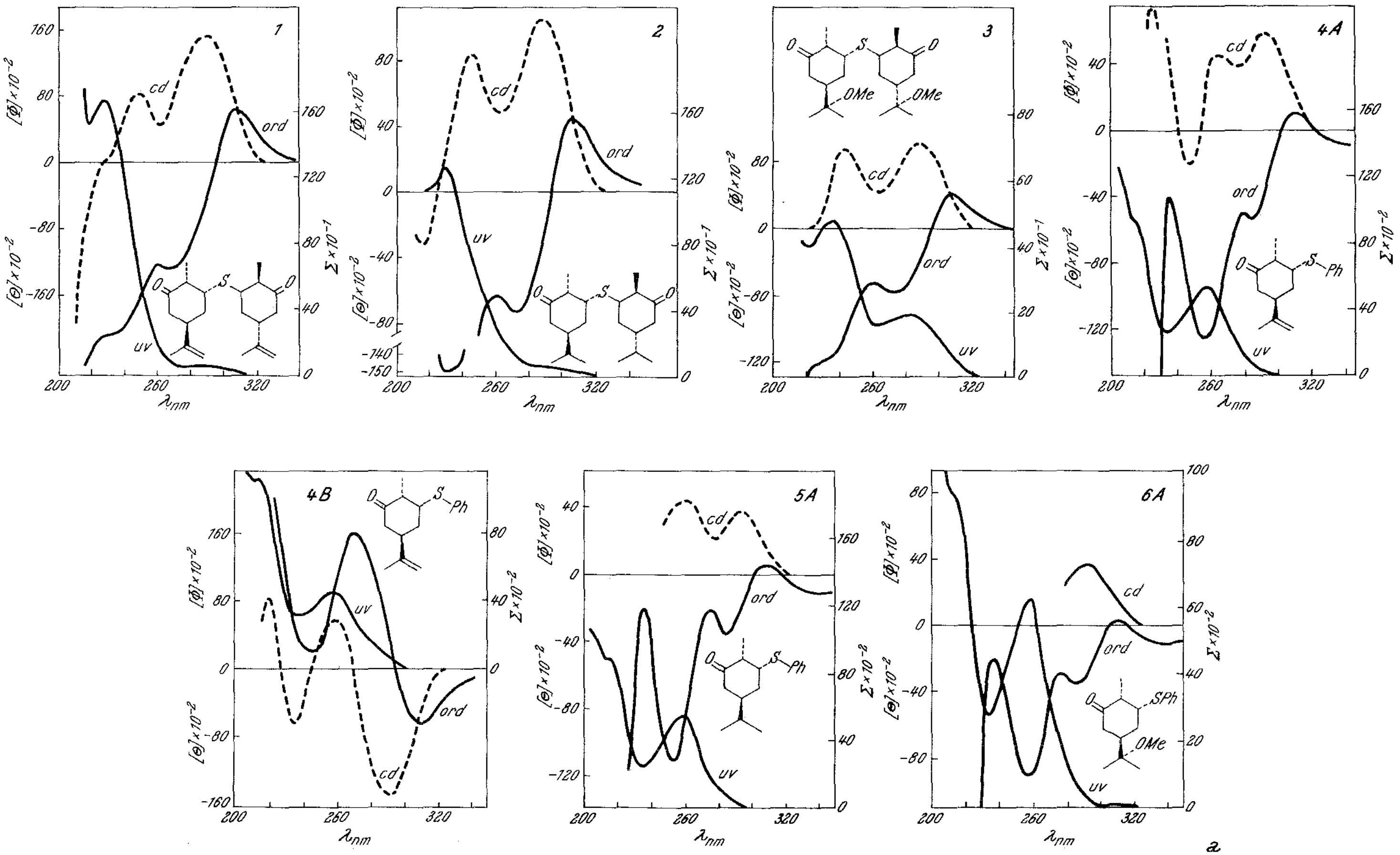


Fig. 1a–c. Uv, cd, and ord spectra of sulphides derived from (−)-(R)-carvone, in methanol

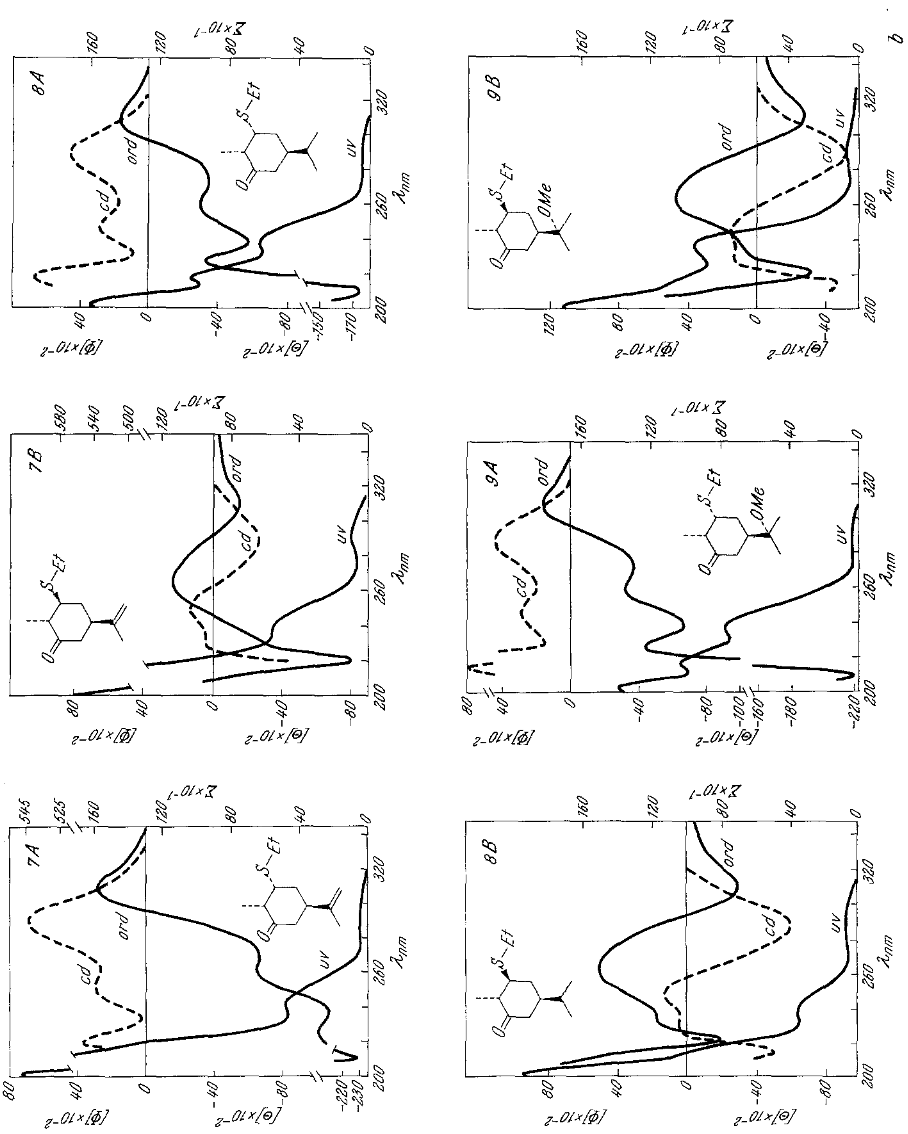

7A
7B
8A
8B
9A
9B
b
cd
ord
uv
S—Et
OMe
O
λnm
[Φ]×10⁻²
[Θ]×10⁻²
ε×10⁻¹
200
260
320

Fig. 1b

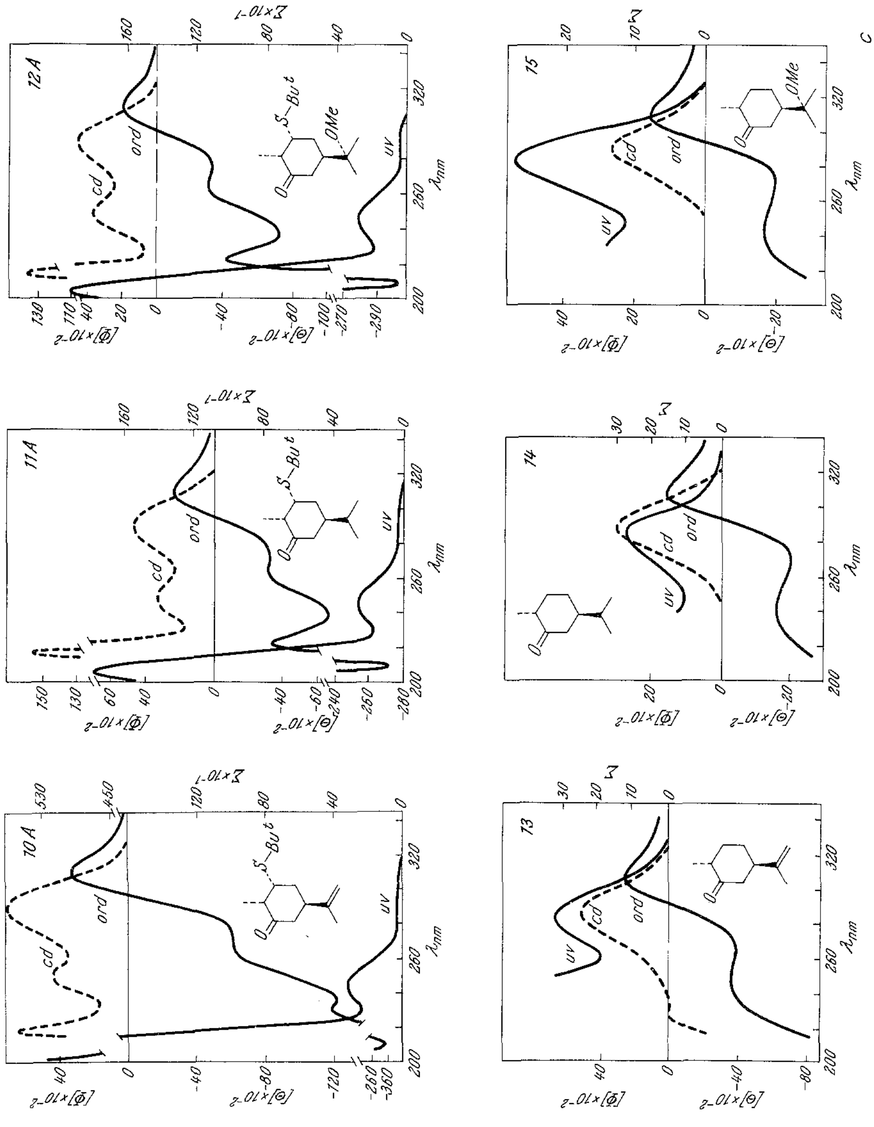


Fig. 1c

formed at the higher temperatures in respect of the sign of the band at about 290 nm. If it is assumed that this band derives from n-π^* transitions of the carbonyl group then it is clear that the unsaturated group on C-7 interacts with the carbonyl group of the same or an adjacent molecule to increase the positive intensity of the cd band as is the case in the parent compound. With this assumption the results fall into place because it explains both the auxochromic effect on the positive cd in the **A** series (**7 A**, **8 A**, **9 A**) and the reducing effect on the negative cd in the **B** series at the same wavelengths. This argument can be taken a stage further. The positive band at this wavelength is seen in the parent compounds **13**, **14**, **15**, but the intensity is higher and the wavelength rather longer in the **A** series sulphides than in the parent compounds.

The band at around 240-250 nm is naturally absent in the parent compounds since it derives from the sulphide chromophore, (although there is a "tail" of the carbonyl absorption down to 250 or even as low as 240 nm with the unsaturated side chain).

In dicarvone sulphide and its derivatives the sulphide absorption is at 242-248 nm; in the phenyl carvone sulphide, **4 A** and **4 B**, this absorption comes at around 266 nm, which suggests mixing of sulphide and phenyl chromophore with some assistance from the unsaturated side-chain. The absorption of the S-*Et* and S-Bu^t compounds is at a longer wavelength (250-252 nm for the **A** series) than in the dicarvone compounds. Again, the unsaturated side-chain would appear to have a slight bathochromic effect (vide **8** and **9**). This is also seen in the dicarvone series (**1**, **2**, **3**).

In the **B** series there is an extra absorption in the observed cd at 229-235 nm. In the alkyl cycloalkyl sulphides but not in the phenyl cycloalkyl sulphide this is positive in the cases where figures are available.

The other absorption takes place at roughly the same wavelength as in the **A** series. The extra band which appears in the spectrum of the ethyl carvone sulphides, which have an equatorial sulphide group (i.e. the **B** series), may arise either from the interaction of the sulphide group with the keto chromophore through the achievement of co-planarity, or from a splitting of the sulphide absorption due to conformational preference. Whereas the cd at 220 nm is positive, the ord is markedly negative, which implies that the "control" of the rotation from the vacuum uv is fundamentally negative.

The cd spectra of the axially-disposed sulphides of the **A** series are clearly quite distinct from the equatorial **B** series in that in the compounds derived from (—)carvone, the 290 nm band is negative in

Table 2 a. *Extinction coefficients, molecular ellipticities and molecular rotations of the listed sulphides in methanol at 20 °C*

Compound No.	Uv λ_{max}/nm	ε	Cd λ_{max}/nm	[θ]	Ord λ_{max}/nm	[Φ]
1	292	60	288	+ 15 500	314^{a}	+ 5 000
	227	1680	247	+ 8 400	307	+ 6 600
	227	1680	227^{b}	0	270	— 12 800
2	286^{a}	60	289	+ 10 770	316^{a}	+ 3 800
					307	+ 4 600
	230	1300	247	+ 8 400	273	— 7 500
			216	— 3 400	230	— 15 300
3	282	190	288	+ 10 540	309	+ 4 600
	234	480	243	+ 9 800	273	— 7 600
					234^{a}	— 15 500
4 A	—		294	+ 5 900	312	+ 11 000
	258	5400	265	+ 4 500	286	— 5 400
	217	9400	227	+ 15 400	255	— 12 700
4 B			291	— 15 400	311	— 6 800
	260	4500	260	+ 5 500	273	+ 16 400
			235	— 6 700		
			221	+ 8 500		
5 A	—				337	— 1 100
	—				309	+ 600
	—		295	+ 3 800	285	— 3 500
	258	5700	260	+ 4 500	253	— 11 200
	216	9100				
6 A	—		—		339	— 1 100
	308	100	294	+ 3 700	311	+ 300
	259	6500			286	— 3 600
	214^{a}	9700			257	— 9 100
7 A	293^{a}	40	290	+ 7 000	309	+ 2 700
			252	+ 3 000	269	— 6 700
	242	490	221	+ 3 700	237	— 2 200
	(201)	(547)			210	— 23 000
7 B	290	90	290	— 2 600	310	— 1 400
	239^{a}	5650	250	+ 1 459	266	+ 2 400
			231	+ 500	220	— 8 000
8 A	290^{a}	40	291	+ 4 600	310	+ 1 500
	238	650	248	+ 2 800	274	— 3 700
	220	1060	220	+ 6 600	239	— 6 000
	(203)	(1660)			210	— 17 400
8 B	290	75	288	— 6 000	311	— 3 000
	240	345	249	+ 1 300	263	+ 5 100
			230	+ 400	233^{a}	+ 1 700
			216	— 5 250	222	— 2 000

Table 2a (continued)

Compound	Uv		Cd		Ord	
No.	λ_{max}/nm	ε.	λ_{max}/nm	[θ]	λ_{max}/nm	[Φ]
9A	288[a]	40	290	+ 4410	310	+ 1600
	237	800	248	+ 2750	273	— 3750
	218	1060	216	+ 7900	240	— 6750
	(203)	(1430)			209	— 21600
9B	292	70	289	— 5200	309	— 2800
	237	970	247	+ 1500	265	+ 4650
			229	+ 1300	239[b]	+ 900
			215	— 4700	223	— 3100
10A	289	30	290	+ 7200	311	+ 3300
	244	335	253	+ 4300	275[a]	— 6100
			218	+ 6450	237	— 12200
					210	— 36000
11A	290	30	290	+ 4740	308	+ 2400
	245	280	248	+ 3400	273	— 3240
	(205)	(1800)	217	+ 15700	239	— 6600
12A	291	40	291	+ 4620	311	+ 2000
	245	290	249	+ 3650	287	— 3300
	(205)	(1960)	215	+ 13600	238	— 6150
					208	— 30100

[a] Shoulder.
[b] Inflexion.

Table 2b. *Extinction coefficients, molecular ellipticities and amplitudes for n–π* carbonyl transition of listed sulphides in cyclohexane at 20 °C*

Compound	Uv		Cd		Ord	
No.	λ_{max}/nm	ε	λ_{max}/nm	[θ]	Extrema/nm	Amplitude
4A	—		304	5610	288, 320	63
5A	—		303	3280	292, 319	30
6A	—		301	3280	293, 320	34
7A	296	25	296	7030	273, 321	86
8A	296	26	298	3220	278, 320	48
9A			296	3400	276, 320	48
10A	296	32	296	7230	274, 322	104
11A	298	21	298	4160	275, 321	62
12A	295	20	296	4290	275, 321	62

the **B** series, whilst the band at 260 nm is positive, and that at 220 nm is positive in **4 B** but negative in **7 B**, **8 B** and **9 B**, so that this must be the effect of the phenyl group on the sulphur chromophore. In the **A** series, the band at 225 nm is positive in all the cases where it was observed, and the band at about 250 nm is positive in all cases except for **4 A**, where the influence of the phenyl group appears to cause an inversion of the sign and the new band introduced at about 265 nm. Thus, the peaks due to sulphur at 250 nm in **4 A** and 235 nm in **4 B** are both negative, whereas in the other compounds, where information is available, they are positive.

In structure **4** only the n-π* transition of the carbonyl group changes sign on going from **4 A** to **4 B**. In structure **7** not only the n-π* band but also that at 200 nm changes sign on going from **7 A** to **7 B**. This change of sign is repeated in **8 A** and **8 B**, and **9 A** and **9 B** and, since the π-π* transition of the olefin is absent in **8** and **9**, the 220 nm transition must be associated with the sulphur or carbonyl group, rather than with the olefinic side-chain. Since the behaviour of this band at 220 nm is rather similar to that of the band at 250 nm it is clearly influenced by the phenyl group; it is reasonable to suppose that the transition concerned relates to sulphur.

The results also show that the S-phenyl group in the equatorial position interacts with the carbonyl group to give substantially increased carbonyl phenyl cd absorption, compared with the axial phenyl sulphide. In general, absorption of the **A** series is similar to that of the parent compounds, except that there is an extra band at about 250 nm. Since the intensities of the uv absorption spectra are rather similar for both the **A** and **B** series, it follows that the main effect of the axial equatorial difference is in the symmetry rather than in the promotion from one level to another. It is, however, worth nothing that at 280 nm εmax for **4 B** is almost twice as high as in **4 A**. This is not the case at 260 nm. This enhancement of the uv absorption at 290 nm also shows in **7 A** and **7 B**, and **8 A** and **8 B**. The situation is reversed at 240 nm, where εmax for **8 A** is almost double that for **8 B**. **9 A** and **9 B** behave similarly.

If these results are examined in terms of the octant rule, which has been applied to ketones[8], there is seen to be conformity with the rule. In **4 A**, C-3-H is equatorial and C 2-*Me* is also equatorial, so that C 3-S-*Ph*, which is axially disposed, lies in the right back octant giving a negative contribution, but the S-*Ph* group will also overlap into the front octant, giving a positive contribution. In **4 B**, where the C 3-S-*Ph* group is equatorial, it will lie wholly in the negative rear octant and thus give a wholly negative contribution. The experimental results show a strong negative contribution for **4 B**, whereas **4 A** gives a weak positive contribution.

The side chain in either case is in the rear left octant which should give rise to a positive contribution. It would be reasonable for the unsaturated group to give a more positive contribution which is in accord with the experimental results.

Experimental

(S)-2-Methyl-(S)-5-isopropenyl-(R)-3-phenylthiocyclohexanone (**4 A**)

To (—)-carvone (2.9 g) and sodium acetate (3.0 g) in methanol (10 ml) under nitrogen cooled in an ice bath, was added thiophenol (2 ml; 1.15 molar equivalent) dropwise with stirring. The precipitated product was stirred with water to remove sodium acetate and then recrystallised from aqueous methanol. Yield 3.3 g, 65.0%, white needles mp. 76-78°, $[\alpha]_D^{20}$ —121° ($CHCl_3$; $c = 0.7$, $l = 1$).

$C_{16}H_{20}OS$*. IR: 3 100, 1 705, 1 650, 1 590, 900, 750, 695. The compound yielded a 2,4-dinitrophenylhydrazone, mp. 149-150°.

(S)-2-methyl-(S)-5-isopropyl-(R)-3-phenylthiocyclohexanone (**5**)

5 was obtained by a similar process: to (—)-carvotanacetone (2-methyl-5-isopropylhexa-2-ene-1-one) (3.5 g) and sodium acetate (0.5 g) in methanol (10 ml) under nitrogen, was added thiophenol (4 ml), to give after 0.5 h 3.9 g of product; 65% white needles, mp. 94.5°, $[\alpha]_D^{20}$ —115° ($CHCl_3$; $c = 2$, $l = 1$).

$C_{16}H_{22}O_2S$*. IR: 1 705, 1 575, 1 380, 1 360, 750, 692. The compound yielded a 2,4-dinitrophenylhydrazone mp. 133-135 °.

(S)-2-Methyl-(S)-5-methoxyisopropyl-(R)-3-phenylthiocyclohexanone (**6**)

6 was similarly obtained by reaction of (—)-8-methoxycarvotanacetone (0.6 g) and sodium acetate (0.2 g) in methanol (1 ml) with thiophenol (0.7 ml) after 8 h. Yield 0.27 g, 28% white flakes, mp. 46-47 °C, $[\alpha]_D^{20}$ —110° ($CHCl_3$; $c = 0.6$, $l = 1$). $C_{17}H_{24}O_2S$*. IR: 2 820, 1 700, 1 575, 1 380, 1 360, 1 075, 750, 692.

(S)-2-methyl-(S)-5-isopropenyl-(R)-3-ethylthiocyclohexanone (**7 A**)

To (—)-carvone (10 g) stirred with sodium acetate (2.5 g) in methanol stirred in an ice bath for 20 min, was added dropwise with stirring ethanethiol (4.8 g, 1 mol equivalent). After stirring in the ice bath for a further 5 h the mixture was poured into water (150 ml) and extracted with chloroform (2 × 50 ml). The chloroform extracts were repeatedly washed with water, the solution (dried $MgSO_4$) had the solvent removed under reduced pressure, the fraction bp. 109-110°/0.3 mm was collected from a 6″ *Vigreux* column. Yield 9.5 g, 67%, mp 33-35°, $[\alpha]_D^{20}$ —61° ($CHCl_3$; $c = 2.3$, $l = 1$).

$C_{12}H_{20}OS$*. IR: 3 100, 1 710, 1 645, 890. The compound gave a 2,4-dinitrophenylhydrazone derivative, mp. 140-142°..

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* Micro-analytical data in excellent agreement (C, H, S).

(S)-2-methyl-(S)-5-isopropyl-(R)-3-ethylthiocyclohexanone (**8 A**)

8 A was similarly prepared from (—)carvotanacetone (5.6 g) dissolved in sodium acetate (1.3 g) in methanol, using ethanethiol (4 ml) to yield 4.25 g, 54%, bp. 119–120°/1.2 mm, $n_D{}^{23}$ 1.5014, $[\alpha]_D^{20}$ —60.4° ($CHCl_3$; $c = 4$, $l = 1$).

$C_{12}H_{22}OS$*. IR: 1710, 1350, 1360. The compound gives a 2,4-dinitrophenylhydrazone, mp. 147–149°.

(S)-2-methyl-(S)-5-methoxyisopropyl-(R)-3-ethylthiocyclohexanone (**9 A**)

9 A was likewise prepared from (—)-8-methoxycarvotanacetone (5.5 g) and sodium acetate (2 g) in methanol in reaction with ethanethiol (4 g) giving 3.2 g of product; 46%, bp. 137–139°/0.5 mm, $n_D{}^{17}$ 1.5022, $[\alpha]_D^{20}$ —59.5° ($CHCl_3$; $c = 4$, $l = 1$). $C_{13}H_{24}O_2S$*.

(S)-2-methyl-(S)-5-isopropenyl-(R)-3-t-butylthiocyclohexanone (**10**)

To (—)-carvone (8.0 g) stirred for 15 min with sodium acetate (2.5 g) in methanol (10 ml), was added dropwise *t*-butylmercaptan (6 g). The stirring was continued for 6 h at ambient temperature. After working up as above the unreacted ketone was separated by distillation under reduced pressure under nitrogen and the residue crystallised from aqueous methanol, 3.4 g, 46%, mp. 68.5–69.5, $[\alpha]_D^{20}$ —24° ($CHCl_3$; $c = 1$, $l = 1$).

$C_{14}H_{24}OS$*. IR: 3100, 1710, 1645, 900. The compound yielded a 2,4-dinitrophenylhydrazone, mp. 152–153°.

(S)-2-Methyl-(S)-5-isopropyl-(R)-3-t-butylthiocyclohexanone (**11**)

11 was prepared in a similar manner to the above: (—)-carvotanacetone (5.6 g) in a suspension of sodium acetate in methanol, with *t*-butyl thiol (3.0 g) gave 2.0 g (26%) of product, mp. 53.5–54.5°, $[\alpha]_D^{20}$ —31° ($CHCl_3$; $c = 2$, $l = 1$).

$C_{14}H_{26}OS$*. IR: 1710, 1380, 1360. The compound yielded a 2,4-dinitrophenylhydrazone, mp. 134–136°.

(S)-2-Methyl-(S)-5-methoxyisopropyl-(R)-3-t-butylthiocyclohexanone (**12**)

(—)-8-Methoxycarvanoacetone (5.2 g) dissolved in a solution of sodium acetate (2.0 g) in methanol (10 ml) reacted with *t*-butylmercaptan (3 g), to yield a product, 2.7 g 24%, mp. 70–71°, $[\alpha]_D^{20}$ —31° ($CHCl_3$; $c = 4$, $l = 1$).

$C_{15}H_{28}O_2S$*. IR: 2830, 1715, 1380, 1360, 1060.

(S)-2-methyl-(S)-5-isopropenyl-(S)-3-phenylthiocyclohexanone (**4 B**)

To thiophenol (50 ml) and triethylamine (10 ml) refluxing under nitrogen, was added (—)carvone (15.1 g) dropwise over 1 h. The mixture was refluxed under nitrogen for a further 18 h. Unreacted thiophenol and triethylamine were distilled off at 30–60°/0.5 mm in a current of nitrogen. The crude product, 24.7 g, was then distilled at 134–161°/0.7–0.8 mm, $[\alpha]_D^{20}$—8.9° ($CHCl_3$; $c = 4$, $l = 1$). The distillate solidified almost immediately and was recrystallised to constant mp. and rotation from aqueous methanol. The product was homogeneous as judged by GLC on silica and nmr spectra. It had mp. 68–69°, $[\alpha]_D^{20}$—9.5° ($CHCl_3$; $c = 4$, $l = 1$).

$C_{16}H_{20}OS$*. IR: 3090, 1710, 1245, 1575, 905, 750, 692.

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* Micro-analytical data in excellent agreement (C, H, S).

(S)-2-methyl-(S)-5-isopropenyl-(S)-3-ethylthiocyclohexanone (**7 B**)

To (—)carvone (20 g), ethanethiol (17 g) was added potassium hydroxide (4.5 g) in ethanol (10 ml). The mixture was heated on the steam bath for 5-6 h. The reaction mixture was then poured into water, the aqueous layer was extracted with ether and the ethereal solution was washed free from potassium hydroxide, dried Na_2SO_4, and the solvent removed by evaporation under reduced pressure. The liquid residue was then distilled using a 6″ *Vigreux* column to give a product bp. 132-134°/5 mm, n_D^{17} 1.5130, $[\alpha]_D^{20}$ —5.4° ($CHCl_3$; $c = 2$, $l = 1$).

$C_{12}H_{20}OS$*. IR: 3 095, 1 710, 1 645, 892. The 2,4-dinitrophenylhydrazone had mp. 135-138°.

(S)-2-methyl-(S)-5-isopropyl-(S)-3-ethylthiocyclohexanone (**8 B**)

To (—)carvotanacetone (2-methyl-5-isopropylhexan-2-one) (7.1 g) in 4 ml ethanethiol was added potassium hydroxide in 5 ml ethanol. The mixture was heated for 6 h to yield 4.6 g product, 46%, bp. 114-116°/1 mm, n_D^{21} 1.4980, $[\alpha]_D^{20}$ —14.5° ($CHCl_3$; $c = 2$, $l = 1$). $C_{12}H_{22}OS$*. IR: 1 710, 1385, 1 365. The 2,4-dinitrophenylhydrazone had mp. 125-127°.

(S)-2-methyl-(S)-5-methoxyisopropyl-(S)-3-ethylthiocyclohexanone (**9 B**)

In a similar manner, 2-methyl-5-methoxyisopropylcyclohexa-2-enone (4.2 g), ethanethiol (2 ml), and potassium hydroxide (1 g), in 5 ml ethanol, yielded 3.3 g (58%) of a product, bp. 129-131°/0.5 mm, n_D^{21} 1.4996, $[\alpha]_D^{20}$ —20.1° ($CHCl_3$, $c = 2.5$, $l = 1$). $C_{13}H_{24}O_2S$*. IR: 2 820, 1 710, 1 380, 1 360, 1 075.

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* Micro-analytical data in excellent agreement (C, H, S).