Solid- and Solution-state Carbon-13 Nuclear Magnetic Resonance Studies of a Series of Sulphur-containing Heterocycles

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Thiin-4-one (**3a**) and 3-methoxycarbonylthiin-4-one (**7a**) together with their dihydro- and tetrahydro-analogues and a number of the corresponding sulphoxides and sulphones have been studied using solution- and solid-state ^{13}C n.m.r. These investigations highlight the usefulness of solid-state ^{13}C n.m.r. spectroscopy for the study of keto–enol tautomerism in β-keto esters and provide new information concerning the aromaticity of thiin-4-ones.

Thian-4-one (**1a**) and a series of related compounds (**1b**,**c**) and (**2**)—(**7**) were recently prepared as starting materials for the synthesis of thiathromboxane analogues.[1,2] As little has been published on the solution-,[3–7] and particularly the solid-state, ^{13}C n.m.r. of these types of compound we undertook such a study. The results of this investigation, which are summarised in Tables 1 and 2, proved extremely interesting, especially with respect to (a) keto–enol tautomerism and (b) aromaticity of thiin-4-ones.

Tautomerism.—All the compounds studied are, in principle, capable of keto–enol tautomerism except for those of types (**3**) and (**7**). However, an enol form is only likely to exist to any appreciable extent when a methoxycarbonyl group is bonded to an sp^3 carbon adjacent to the ketone group, *i.e.* for systems (**4**) and (**6**). Although the compounds are mostly known in the keto form, (**4b**),[8] (**4c**), and (**6c**) are actually in the enol form in solution and compounds (**4a**)[9] and (**6a**)[8] are known to exist as tautomeric mixtures in solution. Carbon-13 n.m.r. is one of the best tools for studying such tautomerism because resonances expected for a keto carbonyl group are well to high frequency of those typical for CHOH carbons. Of course, the position of equilibrium for such tautomerism depends greatly on the physical state of the system, in particular on the solvent. A change of phase to the solid state is expected in general to result in the stabilisation of one or other of the forms. Heretofore most n.m.r. studies of tautomerism have been made for solutions, but the recently developed techniques for high-resolution n.m.r. of solids allow keto–enol investigations to be extended to the solid state. This ability to follow the effect of phase-changes considerably enhances the value of n.m.r. Few such studies have been reported to date.[10–12]

Results and Discussion

(1) *Solution Spectra.*—The assignments in Tables 1 and 2 were based on (i) comparison with published[3,6,13,14] data and (ii) the chemical shift changes known[3,7b,15] to occur at the adjacent α and β sp^3 carbon atoms, on oxidation of a sulphide, *i.e.* shielding of the α-carbon and deshielding of the β-carbon. The unambiguous complete assignment of ^{13}C absorptions to the enolic compounds (**4a**—**c**) and (**6a**,**c**) proved difficult. In compounds [**4a** (enol form), **b**, and **c**] the C-4 and C-7 'carbonyl' absorptions all occur in the range δ 169.0—171.8 p.p.m. and so are difficult to assign. The C-2 and C-6 methylene groups of (**4a**—**c**) also have similar chemical shifts making assignment difficult. The assignments shown in Table 2 were eventually made on the basis of ^{13}C (fully coupled) $\{^1H\text{-NOE}\}$ difference experiments and/or ^{13}C–^1H two-dimensional shift-correlation studies.

For compounds [**6a** (enol form), **c**] the 'carbonyl' absorptions C-4 and C-7 were difficult to assign with certainty as were the peaks due to vinylic atoms C-5 and C-6 in sulphone (**6c**).

(2) *Solid-state N.m.r. Spectra.*—Assignments of the solid-state spectra, listed in Tables 1 and 2, were assisted by non-quaternary suppression (NQS), sometimes known as dipolar dephasing, experiments (see Figure 1). These utilise a pulse sequence which involves a pre-acquisition delay (following cross-polarisation) under proton-coupled conditions. Signals from carbon atoms with relatively large linewidths are discriminated against, so that only resonances arising from quaternary or mobile carbons are normally observed. Figure 1 shows a typical example of spectra with and without NQS.

Apart from the effects of keto–enol tautomerism, the solid-state spectra sometimes differ in two other ways from those of solutions. First, some or all of the chemical shifts may differ markedly. This can arise either from intramolecular effects (molecular geometry changes forced by crystal packing) or from intermolecular interactions (especially if hydrogen-bonding is involved). A second difference between solid and solution may be in the doubling of some signals for the solid state. This may result from the 'freezing' of intramolecular motion, or, as for some of the present systems, from the existence of two crystallographic sites for a given type of carbon. The latter may, in turn, relate to a lowering of relevant molecular symmetry in the solid [which, for the molecules studied here, is only possible for systems (**1**) and (**3**)] or from the existence of non-congruent molecules in the unit cell.

Since solid-state linewidths are typically of the order of 0.6 p.p.m. and referencing procedures differ for the solution and solid states, chemical shift variation of <2 p.p.m. with change of phase is not regarded as significant. Nevertheless, a number of the chemical shifts change by 4 p.p.m. or more from the solution to the solid-state (for the same tautomer): specifically C-2 for (**3a**) (average Δδ 5.8 p.p.m.); C-4 for (**4a**) (average Δδ 4.8 p.p.m.); C-5 for (**4b**) (Δδ 7.4 p.p.m.); C-2 for (**5a**) (Δδ 4.7 p.p.m.); C-4 for (**6b**) (Δδ 4.0 p.p.m.); C-2 for (**7a**) (Δδ 9.2 p.p.m.); and C-3 for (**7a**) (Δδ 6.4 p.p.m.). Of course, greater reliance can be placed on changes in intramolecular shift differences (between signals for different carbons) than on changes in absolute shifts. In this context the C-2 to C-3 shift difference for (**7a**) is particularly noteworthy, since it is 11.9 p.p.m. in the solution state and 27.5 p.p.m. for the solid. The resonances for the other carbons of (**7a**) change little (maximum 1.6 p.p.m.) with the phase change, which strongly suggests a localised direct effect such as may be

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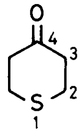
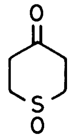
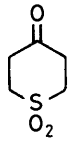
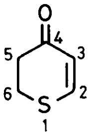
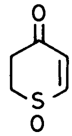
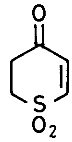
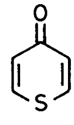
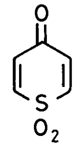
Table 1. ^{13}C N.m.r. data (p.p.m.) for compounds (**1**)—(**3**)[a,b]

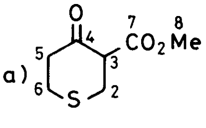
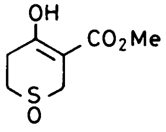
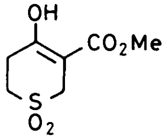
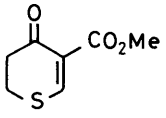
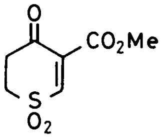
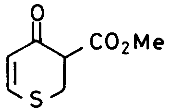
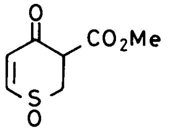
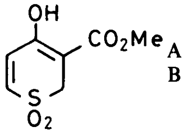
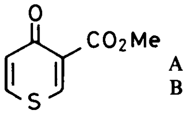
Compounds			Chemical shifts and assignments				
(1a)		A[c]	207.9 (s) [C-4]	44.0 (t) [C-3, C-5]	29.9 (t) [C-2, C-6]		
(1b)		A	204.8 (s) [C-4]	47.0 (t) [C-2, C-6]	32.2 (t) [C-3, C-5]		
(1c)		A[3,d]	203.1 [C-4]	48.2 [C-2, C-6]	37.7 [C-3, C-5]		
(2a)		A	193.3 [C-4]	146.4 [C-2]	123.4 [C-3]	37.3 [C-5]	27.3 [C-6]
(2b)		A	192.2 [C-4]	151.2 [C-2]	130.3 [C-3]	48.8 [C-6]	31.6 [C-5]
(2c)		A[e]	192.6 [C-4]	143.7 [C-2]	133.7 [C-3]	50.1 [C-6]	36.2 [C-5]
(3a)		A	179.5 (s) [C-4]	137.9 (d) [C-2, C-6]	131.5 (d) [C-3, C-5]		
		B	179.3 [C-4]	144.2 143.2 [C-2, C-6]	130.2 129.2 [C-3, C-5]		
(3c)		A[e]	179.1 (d) [C-4]	142.2 (d) [C-2, C-6]	131.8 (d) [C-3, C-5]		
		B	182.5 181.7 [C-4]	144.6 144.0 [C-2, C-6]	132.2 131.5 [C-3, C-5]		

[a] A = solution-state spectrum; B = solid-state spectrum. [b] Solution spectra in $CDCl_3$ unless otherwise stated. [c] Consistent with data in refs. 3 and 4. [d] In $(CD_3)_2SO$. [e] In $(CD_3)_2CO$.

attributed to a change of π-electron density in the C-2–C-3 bond. Unfortunately the crystal structure of this compound is not known. There seems to be little consistency regarding the carbons giving large chemical shift changes with phase other than for (**7a**).

Of the 11 compounds studied in the solid state, six show no doubling of peaks, indicating that the asymmetric unit of the crystal structure is a single molecule. The spectrum of compound (**3a**) shows doubling of peaks due to C-2/C-6 and C-3/C-5 but not that arising from C-4. This suggests loss of molecular symmetry in the solid state but not the existence of different molecular crystallographic sites. On the other hand, for compound (**3c**) the peaks due to C-4, C-2/C-6, and C-3/C-5 are doubled (see Figure 2), suggesting non-congruent molecules in the unit cell rather than loss of molecular symmetry. However, it is possible that the same interpretation applies for (**3a**) but that a potential splitting for the resonance due to C-4 is unresolved. Of course, the compounds with methoxycarbonyl substitution do not have the molecular symmetry of (**3a** and **c**), so any peak doubling necessarily shows there are non-

Table 2. ^{13}C N.m.r. data (p.p.m.) for compounds (**4**)—(**7**)[a,b]

Compound		Chemical shifts and assignments						
(**4a**) 	A keto[d]	203.3 (s) [C-4]	172.4 (s) [C-7]	58.6 (d) [C-3]	52.3 (q) [C-8]	43.5 (t) [C-5]	32.4 (t) [C-2]	30.3 (t) [C-6]
	A enol[d]	171.7 (s) [C-4]	169.0 (s) [C-7]	97.2 (s) [C-3]	51.7 (q) [C-8]	30.8 (t) [C-5]	24.6 (t) [C-6]	23.4 (t) [C-2]
	B keto	208.9 207.2 [C-4]	171.7 [C-7]	57.9 [C-3]	52.2 [C-8]	44.3 43.1 [C-5]	30.2 [C-2]	28.2 [C-6]
(**4b**) 	A[d]	171.8 (s) [C-7]	170.8 (s) [C-4]	89.1 (s) [C-3]	52.1 (q) [C-8]	44.4 (t) [C-2]	42.5 (t) [C-6]	21.8 (t) [C-5]
	B	172.2	168.2	90.7	53.1	42.3	40.0	29.2
(**4c**) 	A[d]	170.8 (s) [C-7][c]	169.5 (s) [C-4][c]	92.3 (s) [C-3]	52.4 (q) [C-8]	47.5 (t) [C-2]	46.4 (t) [C-6]	29.4 (t) [C-5]
	B	171.0	169.3 167.4	94.1 92.8	56.0 53.7	47.0 46.2	44.9	30.4 29.3
(**5a**) 	A	189.2 (s) [C-4]	163.4 (s) [C-7]	156.5 (d) [C-2]	124.9 (s) [C-3]	52.0 (q) [C-8]	37.7 (t) [C-5]	27.2 (t) [C-6]
	B	190.0	163.0	161.2	122.8	51.8	36.8	26.0
(**5c**) 	A[e]	189.0 (s) [C-4]	163.0 (s) [C-7]	143.4 (d) [C-2]	136.4 (s) [C-3]	53.4 (q) [C-8]	50.1 (t) [C-6]	36.6 (t) [C-5]
	B	191.3	163.8	140.0	137.9	55.1	50.5	36.6
(**6a**) 	A keto	188.4 (s)	168.7 (s)	146.1 (d)	123.3 (d)	52.4 (d)	52.2 (q)	29.4 (t)
	A enol	171.4 (s)[c] [C-4]	166.4 (s)[c] [C-7]	137.7 (d) [C-6]	119.6 (d) [C-5]	85.9 (s) [C-3]	51.7 (q) [C-8]	23.8 (t) [C-2]
	B keto	190.4	170.7	147.8	123.8	53.3	51.2	27.4
(**6b**) 	A[e]	188.9 (s) [C-4]	167.3 (s) [C-7]	143.8 (d) [C-6]	132.7 (d) [C-5]	53.1 (q) [C-8]	52.2 (d) [C-3]	51.9 (t) [C-2]
	B	192.9	167.8	142.0	132.7	55.4	51.0[f]	51.0[f]
(**6c**) 	A[e]	169.9 (s) [C-4][c]	160.9 (s) [C-7][c]	136.8 (d) [C-6][c]	132.5 (d) [C-5][c]	94.6 (s) [C-3]	52.8 (q) [C-8]	48.0 (t) [C-2]
	B	169.9 168.5	158.8 157.9	135.4 134.8	133.7 132.4	95.7	56.1 53.6	47.1 45.6
(**7a**) 	A	175.8 (s) [C-4]	164.4 (s) [C-7]	144.5 (d) [C-2]	135.8 (d) [C-6]	133.9 (d) [C-5]	132.6 (s) [C-3]	52.7 (q) [C-8]
	B	175.1	166.0	153.7	137.3	133.4	126.2	53.9

[a] A = solution-state spectrum; B = solid-state spectrum. [b] Solution spectra are in $CDCl_3$ unless stated otherwise. [c] Assignment uncertain. [d] Assignments confirmed by ^{13}C (fully coupled) {^{1}H-NOE} difference spectra and/or ^{13}C–^{1}H shift correlation. [e] In $(CD_3)_2CO$. [f] Coincident absorptions.

congruent molecules in the unit cell. This occurs for (**4a**) (but only doubling for C-4 and C-5 is detectable), (**4c**) (all peaks doubled except for C-7 and C-6), and (**6c**) (all peaks doubled except for C-3). This crystallographic information is not otherwise available since no results from single-crystal *X*-ray work have been reported for the compounds studied here in the solid state. Such structures must be known before the magnitude of n.m.r. splittings can be properly interpreted. The largest splitting magnitudes are for the methyl carbons of (**4c**) and (**6c**) (2.3 and 2.5 p.p.m., respectively).

(3) *Keto–Enol Tautomerism.*—The data in Table 2 are of interest with respect to the keto–enol tautomerism of 3-methoxycarbonylthian-4-ones. The carbonyl group of the ring in

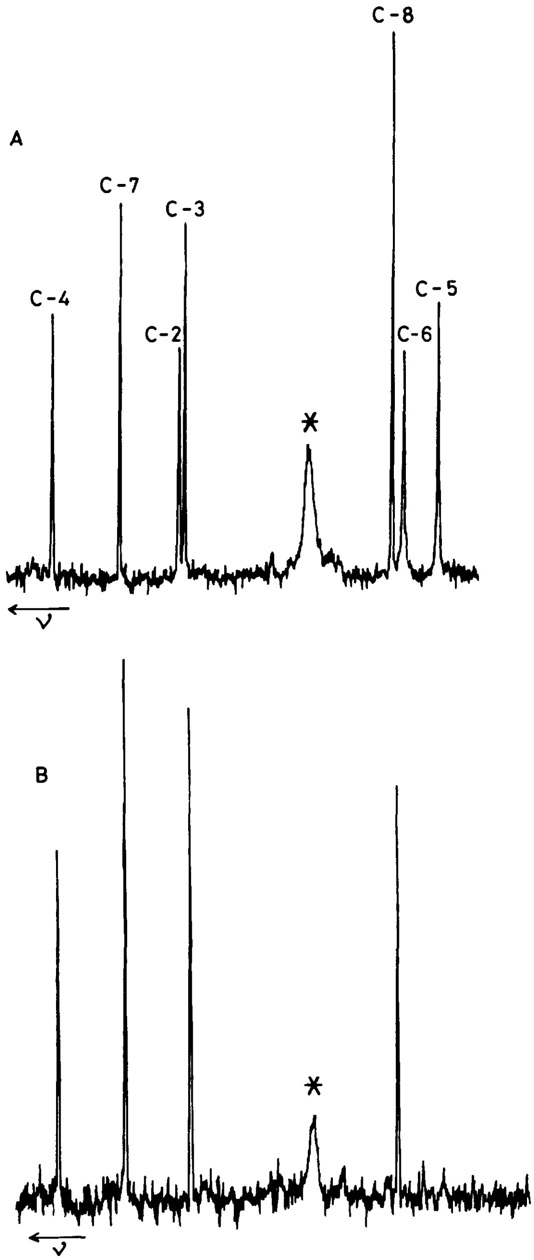


Figure 1. Carbon-13 n.m.r. spectra (at 50 MHz) of solid 3-methoxycarbonyl-5,6-dihydrothiin-4-one 1,1-dioxide (**5c**), obtained using magic-angle rotation. The peak marked with an asterisk arises from the delrin material in the base of the rotor. A, Normal cross-polarisation spectrum, obtained using the flip-back procedure; B, non-quaternary suppression spectrum, obtained using a decoupling window of 40 μs. Spectrometer conditions: 2 000 transients; contact time 2 ms; recycle delay 4 s; proton decoupler power equivalent to 60 kHz

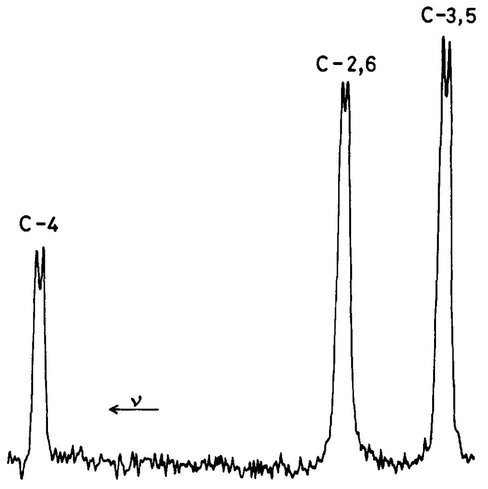
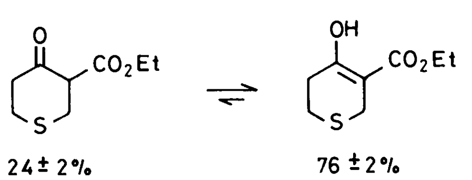


Figure 2. Carbon-13 n.m.r. spectra (at 50 MHz) of solid thiin-4-one 1,1-dioxide (**3c**), illustrating peak-splittings arising from crystallographic inequivalence. Spectrometer conditions: cross-polarisation (with flip-back) and magic-angle rotation; 6 000 transients; contact time 1 ms; recycle delay 10 s; proton decoupler power equivalent to 60 kHz

the keto form of the system studied here invariably gives a resonance at higher frequency than δ 175 p.p.m. Indeed, in the absence of conjugation the relevant peak is in the region δ 200—210 p.p.m., but the existence of one double bond in the ring lowers the shift to δ 188—195 p.p.m., with a further double bond [as in compound types (**3**) and (**7**)] causing a further lowering by *ca.* 14 p.p.m. The CHOH carbon for the enol forms of (**4**) and (**6**) resonate at δ 168—175 p.p.m. Characterisation as keto or enol is thus completely clearcut. Assignment of tautomeric form is easily confirmed because the conversion of the sp^3 carbon at the methoxycarbonyl substituent position of a keto form into an sp^2 carbon for an enol form causes a shift change of *ca.* 35 p.p.m. The signal due to this carbon (C-3) can be readily recognised in the solid-state spectrum as arising from a quaternary carbon (when the enol form exists) by means of the non-quaternary suppression experiment. Figure 3 contrasts the solid-state spectra of (**4a**) (keto form) and (**4b**) (enol form).

3-Ethoxycarbonylthian-4-one has been studied by ^1H n.m.r.–i.r. and shown to exist predominantly in the enol form in CCl_4 at ambient temperature.[9]



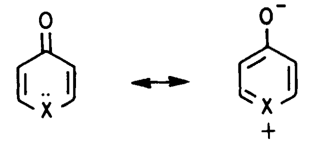
We found that the methyl β-keto ester (**4a**) tautomerises in solution, the ^{13}C spectrum showing a mixture of both tautomers. The solid-state ^{13}C spectrum, however, shows only peaks due to the keto tautomer and provides a means of identifying all the keto and enol signals in the solution spectra. We also found, perhaps not surprisingly, that the oxidation level of sulphur influences the extent of enolisation. The oxide and dioxide of β-keto ester (**4a**) [*viz.* (**4b** and **c**)] are 100% enolised in both solution and solid states.

The monounsaturated sulphide (**6a**) also exists in the keto form in the crystalline state but tautomerises in solution. In this system, however, the keto form predominates at equilibrium. The corresponding sulphone (**6c**) on the other hand is 100% enolised in both solution and solid states. A more surprising observation is that sulphoxide (**6b**) apparently exists only in the keto form (for both solution and solid states), in complete contrast to its saturated analogue (**4b**). It should be noted, however, that acetone was used as a solvent for (**6b,c**) in these studies, whereas chloroform was used for (**4a**—**c**) and (**6a**).

(4) *Aromaticity of Thiin-*4*-ones.*—A number of chemical, physical, and theoretical studies have been carried out to determine whether or not 4-pyrone (**8**)[16] and thiin-4-one (**3a**)[17] can be considered aromatic, *i.e.* to establish whether

zwitterionic structures make a significant contribution to the overall bonding pictures.

(3a) X = S
(8) X = O



N.m.r. studies have been of particular interest with regard to induced diamagnetic ring currents.[18] ^1H N.m.r. spectroscopy shows that the ring protons of 4-pyrone (8) are deshielded by 1 p.p.m. compared with those of its 2,3-dihydro derivatives.[16a,19,20] A more detailed study reached the conclusion that substituted pyrones and benzene have comparable ring currents.[16b] The ^{13}C spectra of kojic acid and related pyrone derivatives have been reported[21] and in this study the authors also conclude that a degree of aromaticity is present in the pyrone system. Despite these numerous claims, however, it should be noted that Beak *et al.* have classified 4-pyrone as non-aromatic on the basis of magnetic susceptibility measurements.[22]

In going from 4-pyrone to its sulphur-containing counterpart, thiin-4-one (**3a**), high-frequency shifts of the ring protons are observed, possibly indicating increased ring currents and greater aromaticity in the sulphur-containing compounds.[23] Chemical studies have also led to the conclusion that 4-pyrone and thiin-4-one possess a degree of aromatic stabilisation.[24] However, no one seems to have approached the question of the potential aromaticity of thiin-4-ones by comparing their ^{13}C spectra with those of their saturated counterparts. The results in Tables 1 and 2 enable this comparison to be carried out. Pertinent data are gathered in Table 3. It has been suggested[21] that the difference in chemical shifts between C-2 and C-3 may reflect the degree of aromaticity of the system; a small $\Delta\delta_{2,3}$ indicating an evening of charge distribution due to aromatic delocalisation.[21] This effect can be clearly seen from the data in Table 3.

Dihydrothiin-4-one (**2a**) shows $\Delta\delta_{2,3}$ value of 23 p.p.m. which decreases to 10 p.p.m. on oxidation to the sulphone and removal of the mesomeric shielding influence of sulphur on C-3. In contrast, thiin-4-one (**3a**) shows an extremely small value of 6 p.p.m. (compared with 41 p.p.m. for kojic acid),[21] which increases to 10 p.p.m. in the non-aromatic sulphone (**3c**).

A similar trend is observed in the substituted series (Table 3); large $\Delta\delta_{2,3}$ and $\Delta\delta_{5,6}$ differences in the monounsaturated sulphides (**5a**) and (**6a**) respectively but dramatically smaller differences for the potentially aromatic compound (**7a**). However, it should be noted that in the solid state $\Delta\delta_{2,3}$ for (**3a**) is 14.0 p.p.m. (on average) and for (**7a**) it is 27.5 p.p.m., whereas $\Delta\delta_{5,6}$ for (**7a**) in the solid state is only 3.9 p.p.m. Clearly other factors than aromaticity affect these shift differences.

The resonances of the carbonyl carbons for the compounds shown in Table 3 might also be expected to give an indication of the aromatic nature of (**3a**) and (**7a**). However, although there is a significant decrease on going from the saturated sulphide (**1a**) to the mono- and di-unsaturated analogues (**2a**) and (**3a**) (207.9 $\longrightarrow$ 193.3 $\longrightarrow$ 179.5 p.p.m.), a similar trend can be observed from the corresponding sulphones (**1c**) $\longrightarrow$ (**2c**) $\longrightarrow$ (**3c**). The carbonyl chemical shifts for (**4a**)—(**7a**) follow a similar pattern. So although the carbonyl resonances for (**3a**) and (**7a**) are highly shielded this information cannot be taken as proof of their aromatic character.

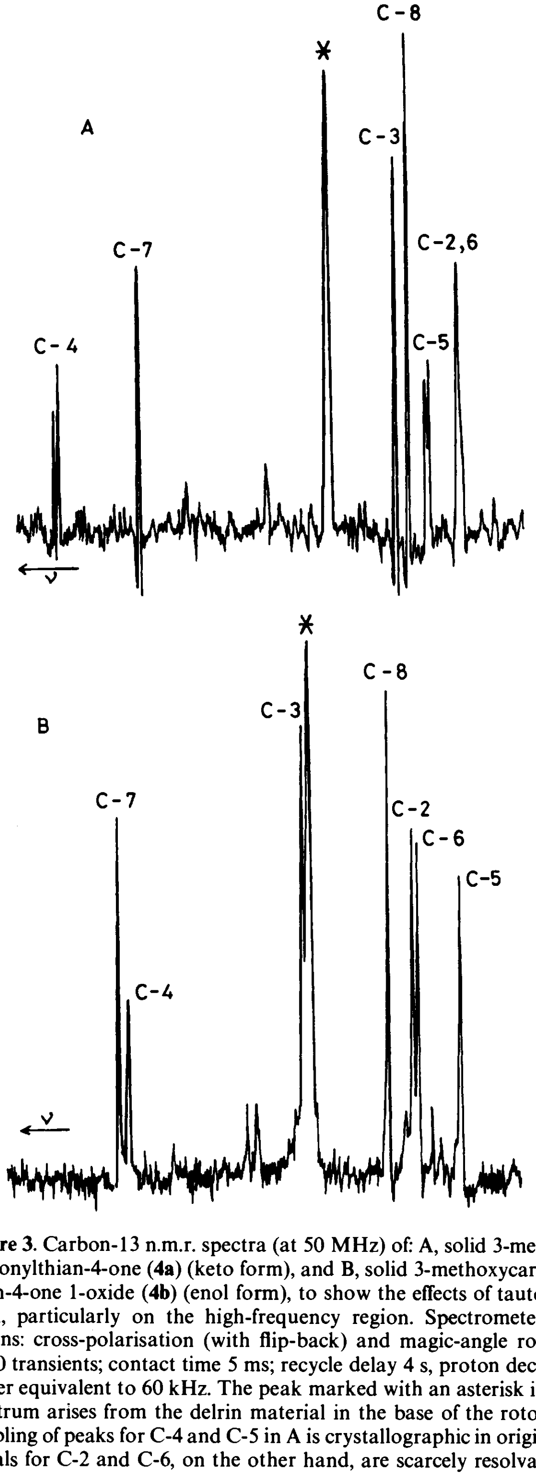
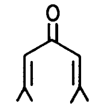
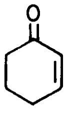
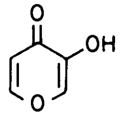
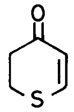
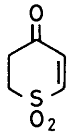
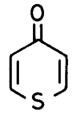
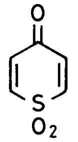
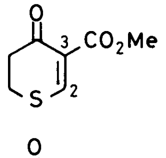
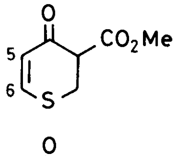
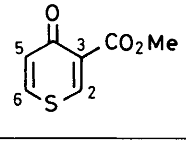


Figure 3. Carbon-13 n.m.r. spectra (at 50 MHz) of: A, solid 3-methoxycarbonylthian-4-one (**4a**) (keto form), and B, solid 3-methoxycarbonylthian-4-one 1-oxide (**4b**) (enol form), to show the effects of tautomeric form, particularly on the high-frequency region. Spectrometer conditions: cross-polarisation (with flip-back) and magic-angle rotation; 1 000 transients; contact time 5 ms; recycle delay 4 s, proton decoupler power equivalent to 60 kHz. The peak marked with an asterisk in each spectrum arises from the delrin material in the base of the rotor. The doubling of peaks for C-4 and C-5 in A is crystallographic in origin. The signals for C-2 and C-6, on the other hand, are scarcely resolvable

Finally, it should be noted that Tarbell and Hoffman[25] studied the i.r. spectra of a series of thiin-4-ones [including (**3a,c**) and (**7a**)] as Nujol mulls. They noted that thiin-4-one (**3a**) and ester (**7a**) do not display the expected conjugated carbonyl absorption bands at *ca.* 1 660 cm^{-1} in their i.r. spectra whereas the corresponding sulphone (**3c**) shows sharp bands in the conjugated carbonyl and double bond regions. This was taken as further evidence for the aromatic nature of (**3a**) and (**7a**). We should like to point out that the i.r. spectra of unsaturated thian-4-ones exhibit remarkable solvent dependence (Table 4). As can be seen, the monounsaturated sulphide (**5a**) exhibits only a weak enone absorption as a Nujol mull but shows an additional stronger band in dichloromethane solution. The thiin-4-one (**7a**) also shows entirely different i.r. absorptions when the spectra are recorded as a Nujol mull or as a solution

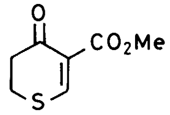
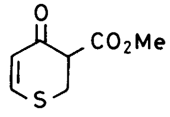
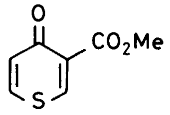
Table 3. $\Delta\delta_{2,3}$ and/or $\Delta\delta_{5,6}$ Data for a series of α,β-unsaturated ketones (solution state)

Compound	$\Delta\delta_{2,3}$ (p.p.m.)	$\Delta\delta_{5,6}$ (p.p.m.)
	29[21]	
	29[21]	
		41[21]
(2a) 	23	
(2c) 	10	
(3a) 	6	
(3c) 	10	
(5a) 	32	
(6a) 		23
(7a) 	12	2

in dichloromethane. Caution should therefore be exercised when drawing conclusions from the i.r. spectra of this type of compound.

Experimental

Table 4. I.r. absorptions (cm^{-1}) in 1 500—1 700 region *

Compound	Nujol mull	Solution (CH_2Cl_2)
(5a) 	1 725 1 645 (w) 1 570	1 730 1 700 1 675 1 530 (w)
(6a) 	1 730 1 655 1 550	1 740 1 665 1 550
(7a) 	1 690 1 615 1 510	1 740 1 715 1 625 1 520 (w)

* Strong unless stated (w = weak).

Column chromatography was performed using silica gel 60 (Merck 7734). I.r. spectra were recorded using a Perkin-Elmer 297 spectrophotometer and mass spectra on a Kratos MS25. ^{1}H N.m.r. spectra were obtained using a JEOL PMX 60 instrument. Solution ^{13}C n.m.r. spectra were recorded at *ca.* 30 °C on a JEOL FX 100 spectrometer at 25.05 MHz (8 K data points, 6 024 Hz sweep width) using 5 mm o.d. tubes, tetramethylsilane as internal standard, and solvent deuterium as internal lock.

Solid-state ^{13}C spectra were obtained at 50.3 MHz in high-resolution using the cross-polarisation–high-power decoupling–magic-angle rotation suite of techniques. Either a Bruker CXP 200 spectrometer or a purpose-built system with Bruker probes was used. Rotors were of the Andrew-Beams type, constructed with a conical delrin base and a cylindrical MACOR top (the latter containing the sample). To aid assignments the non-quaternary suppression (dipolar dephasing) pulse sequence,[26] which selects signals from quaternary and mobile methyl carbons, was employed. Typically, contact times of 2—5 ms were needed, with recycle delays of 4 s. The number of transients acquired was between 1 000 and 2 000, with values in the upper half of that range for the non-quaternary suppression experiments. The pre-acquisition delay for the non-quaternary suppression spectra was set to 40 μs.

Preparation of Starting Materials.—The sulphides (**1a**),[27] (**2a**),[28] (**4a**),[27] (**5a**),[8] (**6a**),[8] and (**7a**)[29] were all prepared using straightforward literature procedures. Thiin-4-one (**3a**)[25,27] was made by treatment of its dihydro-analogue (**2a**)[28] with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. The sulphoxides and sulphones were prepared by oxidation of the corresponding sulphides: compounds (**2b**),[30] (**2c**),[31] and (**4b**)[8] were obtained following the literature procedures indicated: compounds (**1b**)[32] and (**4c**)[27] were prepared using *m*-chloroperbenzoic acid in place of the oxidant in the literature procedure. Compounds (**3c**),* (**5c**), (**6b**), and (**6c**) were also obtained by *m*-chloroperbenzoic acid oxidation of the corresponding sulphides. Sulphone (**1c**) was not prepared, since published n.m.r. data are available.[3]

Attempts to prepare sulphoxides from sulphides (**3a**) and (**5a**) resulted in mixtures of starting material and sulphones (**3c**) and (**5c**) containing only small amounts of the corresponding sulphoxides which could not be isolated in a pure state. 3-Methoxycarbonylthiin-4-one (**7a**) is inert to oxidation, which is surprising in view of the relative ease with which thiin-4-one (**3a**) undergoes oxidation to sulphone (**3c**). Fehnel and Carmack[27] were unsuccessful in their attempts to prepare the sulphone derived from (**7a**) by an alternative route.

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* See ref. 27 for an alternative synthesis.

Thiin-4-*one* (**3a**).—A solution of 2,3-dihydrothiin-4-one (**2a**) (2.28 g, 20 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (4.54 g, 20 mmol) in 1,4-dioxane (60 ml) was heated under reflux for 20 h. The mixture was cooled to room temperature and filtered to remove the precipitated quinol. The filtrate was concentrated *in vacuo* and partitioned between saturated sodium hydrogen carbonate solution and ethyl acetate. The aqueous phase was extracted with two more portions of ethyl acetate and the combined extracts were washed with saturated sodium hydrogen carbonate solution, dried (MgSO$_4$), and the solvent removed *in vacuo* to give a brown crystalline solid. Further purification by column chromatography (ethyl acetate–dichloromethane, 1:1) gave the title compound as crystals (1.84 g, 82%), m.p. 102—104 °C (lit.,[25] 110—111.5 °C).

Thiin-4-*one* 1,1-*Dioxide* (**3c**).—*m*-Chloroperbenzoic acid (5.07 g, 0.025 mol) was added in a single portion to a solution of thiin-4-one (**3a**) (1.12 g, 0.01 mol) in dichloromethane (100 ml). The mixture was stirred at ambient temperature for 30 min and the solvent was removed *in vacuo*. The solid residue was washed thoroughly with cold diethyl ether (100 ml) and then recrystallised from diethyl ether to give the title compound (**3c**) as a crystalline solid (0.53 g, 37%), m.p. 174—177 °C (lit.,[27] 173—174 °C).

3-*Methoxycarbonyl*-5,6-*dihydrothiin*-4-*one* 1,1-*Dioxide* (**5c**).—Solid *m*-chloroperbenzoic acid (*ca.* 85%; 2.03 g, 10 mmol) was added to a solution of the sulphide (**5a**) (0.86 g, 5 mmol) in dichloromethane (20 ml). After stirring the mixture at room temperature for 15 min, the solvent was removed *in vacuo* to give a solid which was washed with diethyl ether. Two recrystallisations of the semi-solid residue from diethyl ether gave the *sulphone* (**5c**) as a crystalline solid (0.367 g, 36%), m.p. 111—112 °C; $\nu_{max.}$ (Nujol mull) 3 040, 3 020, 1 740, 1 695, 1 300, and 1 130 cm^{-1}; δ(CDCl$_3$) 7.60 (1 H, s, br), 3.92—3.68 (2 H, m), 3.76 (3 H, s), and 3.36—3.10 (2 H, m) (Found: C, 41.2; H, 3.8; S, 15.4. C$_7$H$_8$O$_5$S requires C, 41.2; H, 3.95; S, 15.7%).

3-*Methoxycarbonyl*-2,3-*dihydrothiin*-4-*one* 1-*Oxide* (**6b**) *and* 3-*Methoxycarbonyl*-2,3-*dihydrothiin*-4-*one* 1,1-*Dioxide* (**6c**).—Solid *m*-chloroperbenzoic acid (*ca.* 85%, 2.03 g, 10 mmol) was added to a solution of the sulphide (**6a**) (0.86 g, 5 mmol) in dichloromethane (25 ml). After stirring the mixture at room temperature for 30 min, the solvent was removed *in vacuo* to give a solid which was washed with diethyl ether. Recrystallisation of the semi-solid residue from carbon tetrachloride gave the sulphoxide (**6b**) as a crystalline solid (110 mg, 12%); δ[(CD$_3$)$_2$C=O] 7.40 (1 H, d, *J* 11 Hz), 6.50 (1 H, d, *J* 11 Hz), 4.40—3.85 (3 H, m), and 3.72 (3 H, s).

Concentration of the mother liquor followed by recrystallisation from diethyl ether gave the sulphone (**6c**) as a crystalline solid (222 mg, 22%), $\nu_{max.}$ (Nujol mull) 3 060, 1 665, 1 595, 1 310, and 1 130 cm^{-1}; δ[(CD$_3$)C=O] 12.15 (1 H, s), 7.15 (1 H, d, *J* 10 Hz), 6.75 (1 H, d, *J* 10 Hz), 4.15 (2 H, s), and 3.75 (3 H, s). The two compounds were not sufficiently stable for microanalytical data to be obtained.

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