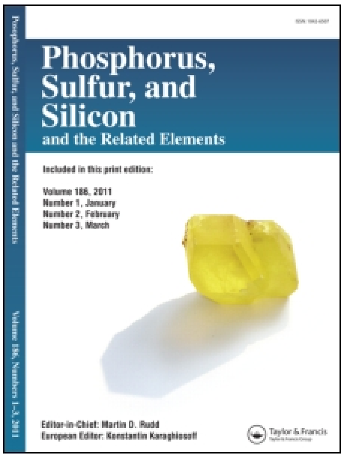

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AN INFRA-RED SPECTROSCOPIC STUDY OF SOME SUBSTITUTED 1,3-THIAZOLIDIN-4-ONES

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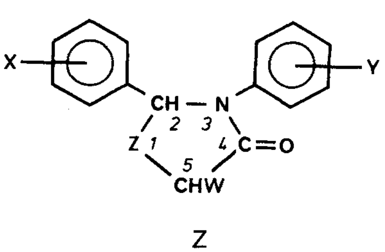
The infra-red spectra of a series of 2,3-diaryl-1,3-thiazolidin-4-ones were measured and the majority of the absorption bands assigned. The value of the carbonyl stretching frequency was related to the availability of the lone pair on the nitrogen atom of the thiazolidinone ring. The effects of S-oxidation of these compounds on their spectra were examined. The spectra of 3-benzyl-2-phenyl-1,3-thiazolidin-4-one, 3-butyl-2-phenyl-1,3-thiazolidin-4-one, 5-methyl-2,3-diphenyl-1,3-thiazolidin-4-one and 3-phenyl-2-thioxo-1,3-thiazolidin-4-one were also investigated.

Key words: 1,3-Thiazolidin-4-ones; 1-oxides; 1,1-dioxides; infra-red spectroscopy.

INTRODUCTION

Despite the large number of references, listed in reviews, which discuss the ir spectra of 1,3-thiazolidin-4-ones with doubly-bonded substituents at C(2)[1–3] and a discussion of the factors affecting the carbonyl stretching frequencies of 2,3-disubstituted and 2,3,5-trisubstituted 1,3-thiazolidin-4-ones by Vigorita and Chimirri,[4] no adequate discussion of the ir spectra of the 2,3-diaryl-1,3-thiazolidin-4-ones (**1**) has appeared in the literature. An investigation of the spectra of these compounds was, therefore, undertaken and was then extended to include the effects of oxidation to the 1-oxides (**2**) and 1,1-dioxides (**3**). 3-Benzyl-2-phenyl-1,3-thiazolidin-4-one (**4a**), 3-butyl-2-phenyl-1,3-thiazolidin-4-one (**4b**), 5-methyl-2,3-diphenyl-1,3-thiazolidin-4-one (**1v**) and 3-phenyl-2-thioxo-1,3-thiazolidin-4-one (**5**) were also investigated for comparison.



	Z
1	S
2	SO
3	SO_2

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†Author to whom correspondence should be addressed.

2,3-Diaryl-1,3-thiazolidin-4-ones (**1**):

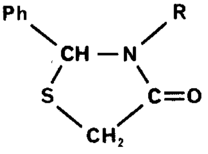
Compound	W	X	Y	Compound	W	X	Y
1a	H	H	H	**1l**	H	3-NO$_2$	H
1b	H	4-OMe	H	**1m**	H	4-NO$_2$	H
1c	H	4-Me	H	**1n**	H	H	4-OH
1d	H	3-Me	H	**1o**	H	H	4-OMe
1e	H	3-OMe	H	**1p**	H	H	4-Me
1f	H	4-Cl	H	**1q**	H	H	4-Cl
1g	H	4-Br	H	**1r**	H	H	4-Br
1h	H	3-F	H	**1s**	H	H	3-Br
1i	H	3-Cl	H	**1t**	H	H	4-CO$_2$H
1j	H	3-Br	H	**1u**	H	H	3-NO$_2$
1k	H	4-CN	H	**1v**	Me	H	H

2,3-Diaryl-1,3-thiazolidin-4-one-1-oxides (**2**):

Compound	W	X	Y	Z	Compound	W	X	Y	Z
2a	H	H	H	O	**2e**	H	4-Cl	H	O
2b	H	4-OMe	H	O	**2f**	H	3-Br	H	O
2c	H	4-Me	H	O	**2g**	H	H	4-OMe	O
2d	H	3-OMe	H	O	**2h**	H	H	3-Br	O

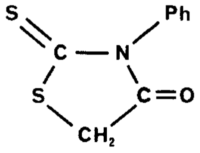
2,3-Diaryl-1,3-thiazolidin-4-one-1,1-dioxides (**3**):

Compound	W	X	Y	Z
3a	H	H	H	O$_2$
3b	H	4-Br	H	O$_2$
3c	H	3-Br	H	O$_2$



4a R = Bz

4b R = Bu



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RESULTS AND DISCUSSION

Ir absorption bands characteristic of aromatic C—H out-of-plane bending (680–900 cm^{-1}), CH$_2$ scissoring (1450–1470 cm^{-1}), aromatic C═C stretching (*ca.* 1500 and *ca.* 1600 cm^{-1}), >C═O stretching (1640–1735 cm^{-1}), aliphatic C—H stretching (2830–3000 cm^{-1}) and aromatic C—H stretching (3020–3130 cm^{-1}) were observed in the spectra of nearly all of the compounds investigated. In addition, an assortment of other bands was observed which characterised the functional groups in individual compounds (Tables I–IV).

Aromatic C—H Bending Bands

The arrangement of the C—H out-of-plane bending bands in the 680–900 cm^{-1} region has often been reported as varying with substitution patterns in aromatic systems although the frequency ranges quoted by different authors tend to vary somewhat.[5-7] Those quoted by Williams and Fleming[6] were found to be present in the spectra of most of the diaryl compounds examined although the number of bands in this region was found to be quite large owing to the presence of two aromatic rings. Tentative assignments of these bands are given in Tables I–IV although in some compounds other weaker bands were present in addition to those tabulated and in the spectra of the S-oxides one of the bands assigned to C—H bending may, in fact, have been due to C—S stretching.

Absorptions in the regions 680–720 cm^{-1} (m-s), 730–770 cm^{-1} (m-s) and *ca.* 900 cm^{-1} (w-m) were attributed to the five adjacent hydrogens of the monosubstituted ring.

Generally, more C—H bending bands were observed in the spectra of compounds with a *meta*-substituted ring than in those of compounds having a *para*-substituted ring. This was explained by the greater asymmetry of the *meta*-substituted ring, with the three adjacent and one isolated hydrogen atoms giving rise to bands at 775–810 cm^{-1} (m-s) and 855–880 cm^{-1} (w-m), respectively. In contrast, in the spectra of most *para*-substituted compounds, these bands were replaced by a single band at 830–850 cm^{-1} (m-s) which tended to occur at a slightly lower frequency in compounds (other than the oxides) with the substituent in the *N*-ring than in those with it in the *C*-ring.

No attempt was made to identify the aromatic C—H in-plane deformations in the 950–1225 cm^{-1} region as most of the compounds displayed many bands in this region, ranging in intensity from weak to strong. However, the aromatic C—Me in-plane bending band was identified as a medium band at 300–320 cm^{-1} in the spectra of compounds **1c**, **1d** and **2c**.

It was not possible to relate substitution patterns to the frequencies of the overtone and combination bands[5,7] at 1650–2000 cm^{-1} as these were very weak and sometimes obscured by the carbonyl absorption.

CH_2 and CH_3 Deformation Bands

Bands associated with the symmetrical deformation of the thiazolidinone CH_2 group (scissoring) were observed with, usually, medium intensity in the 1450–1470 cm^{-1} range. Two CH_2 scissoring bands were observed in the spectra of compounds **4a** and **4b**, both of which have more than one CH_2 group. For most of the compounds examined there seemed to be no overlap of the CH_2 scissoring bands with the aromatic C=C stretching bands discussed below except, possibly, with the weak band in the 1430–1465 cm^{-1} region which has been reported elsewhere[5] but whose presence could not be positively demonstrated in the spectra discussed here.

Asymmetrical deformation of the CH_3 group of methyl and methoxy compounds was observed as the medium band in the 1410–1455 cm^{-1} region. Neither the symmetrical CH_3 deformation band nor the CH_2 rocking band could be identified since the regions in which these bands usually occur (1370–1390 cm^{-1} and 720–810 cm^{-1}, respectively) were obscured by the presence of other bands. The band at 1310 cm^{-1} (m-s) in the spectrum of compound **4b** may have been due to CH_2 wagging. It seemed likely that the band at *ca.* 1220 cm^{-1} (m) in the spectra of most of the compounds apart from the oxides was due to twisting of the CH_2 group.

TABLE Ia

Infra-red spectra of diarylthiazolidinones with a substituent in the *C*-phenyl ring

Com-pound	Aromatic C—H out-of-plane bending				CH_3 asym def	CH_2 sc	CH_2 tw?	Ar db str	>C=O str	Al C—H str in OMe	Other Al C—H str	Ar C—H str
	[a]	[b]	[c]	[d]								
1a	690s, 715s, 740s, 900m					1455s	1220s	1490s, 1590s	1670 vs		2920m-s, 2965m-s	3035m
1b	695m-s, 760m-s, 900w-m	845m-s			1455m	1465m	1235m-s	1495s, 1515s, 1585m, 1600m-s, 1615s	1690vs	2840w-m	2890m, 2930m, 2960m, 2980m-s	3020w-m
1c	700s, 760s, 910m	835m			1425m	1460w-m	1215w-m	1495s, 1500s, 1520m, 1600m-s, 1615w-m	1690vs		2900m, 2930w-m, 2980m-s	3030w-m
1d	695s, 755m-s, 770m-s, 900w-m		880w	790m	1415w-m	1455w-m	1225m	1490m-s, 1500m-s, 1595m-s, 1605m	1692vs		2900w-m, 2930w-m, 2980m	3030w-m
1e	690m-s, 750m-s, 900w		875w-m	775m-s	1440m	1460m	1220m-s	1490s,[e] 1585m-s, 1590m, 1610m-s	1674vs		2925w-m, 2950w-m	3050w-m
1f	695s, 750s, 765m-s, 900w	845m-s				1460m	1220m-s	1470m, 1495s, 1580m, 1595m-s	1674vs		2860w-m, 2930m	3035w-m
1g	700s, 750s, 770m-s, 895w	840m				1465m	1220m-s	1495s, 1500s, 1580m, 1595m-s	1676vs		2920m	
1h	685s, 740m-s, 770m-s, 900w-m		875w-m	780m-s		1450m	1220m-s	1480m-s, 1490m-s, 1585m-s, 1610m	1662vs		2910m	3020w
1i	690m-s, 695m-s, 750s, 765m, 900w-m		880w-m	805m		1455w-m	1220m-s	1470w-m, 1490m-s, 1570w-m, 1595m-s	1676vs		2930w-m	3060w-m
1j	685m-s, 695m-s, 750s, 760m, 895w-m		870w	805m		1455m	1220m-s	1465m, 1490m-s, 1560w-m, 1570m, 1590m	1674vs		2920m	3050m
1k	690s, 750s, 770m-s, 900w	850m-s				1455w-m	1220m-s	1480w-m, 1495s, 1595m-s, 1610m-s	1674vs, 1684vs		2920w, 2980w	3030w-m
1l	685m-s, 720s, 745m-s, 905w-m			800m		1450w-m	1220m	1475m, 1490m-s, 1590m	1674vs		2860w-m, 2930w-m, 2985w-m	3070w-m, 3085w-m
1m	700s, 740s, 770s, 900w-m	840m-s				1460m	1215m-s	1465m, 1475m, 1495s, 1600m-s, 1605m-s	1688vs		2930m	3085m

[a] Monosubstituted ring. [b] p-Disubstituted ring. [c] m-Disubstituted ring (isolated H). [d] m-Disubstituted ring (3 adjacent H). [e] Close doublet.

Compound	Other absorptions
1a	—
1b	535m-s C—O—C i-p def. 1035m-s or 1105m-s sym C—O—C str. 1265s asym C—O—C str.
1c	315m Ar C—Me i-p ben.
1d	305m Ar C—Me i-p ben.
1e	540m C—O—C i-p def. 1055m sym C—O—C str. 1230m-s asym C—O—C str.
1f	480m C—Cl str & ring def. 1100m X-sensitive band.
1g	1075m-s X-sensitive band.
1h	295s o-o-p C—F ben? 390m or 415m i-p C—F ben. 535m-s C—F str & ring def. 1210m-s X-sens. band?
1i	1075m X-sensitive band.
1j	1065w-m X-sensitive band
1k	400w i-p C—CN bend. 555m-s combination of i-p C≡N def & o-o-p ar ring def. 2220m-s C≡N str.
1l	535m NO_2 i-p ben. 1345vs NO_2 sym str. 1520vs NO_2 asym str.
1m	545m NO_2 i-p ben. 865m-s C—NO_2 str. 1350vs NO_2 sym str. 1525vs NO_2 asym str.

TABLE Ib

Infra-red spectra of diarylthiazolidinones with a substituent in the *N*-phenyl ring

Compound	Aromatic C—H out-of-plane bending				CH_3 asym def	CH_2 sc	CH_2 tw?	Ar db str	>C═O str	Al C—H str in OMe	Other Al C—H str	Ar C—H str
	[a]	[b]	[c]	[d]								
1n	710m, 730m, 900w	840m				1450m	1225m	1490w-m, 1515s, 1595w-m, 1610w-m	1642vs		2950w-m	3030w-m
1o	690s, 775m, 900w	830m			1420m or 1440m	1455m-s	1210m-s	1510s, 1605m	1668vs	2840w-m	2920w-m, 2960w-m	3030w-m
1p	690m, 720m-s, 900w-m	825m			1450m	1450m	1215m-s	1485m-s, 1505s, 1600m-s	1668vs		2850m, 2920m-s	3030m, 3050m
1q	700m-s, 735m, 765m, 895w	830s				1455w-m	1215m	1495s, 1595w-m	1680vs, 1688vs		2920w-m	3070w-m
1r	700s, 735s, 765m, 900w	835s				1455m	1220m-s	1490s, 1590m, 1600w-m	1680vs		2920w-m	3040w-m
1s	700s, 750m, 900w-m		855w-m	790m-s		1455m	1215m-s	1480s, 1570m-s, 1585m-s	1670vs		2925m	3035w-m, 3070m
1t	700m-s, 765m-s, 900w-m	860m-s				1455m	1215m	1495w-m, 1510m-s, 1575m, 1600s	1678vs, 1692vs		masked by O—H str	3130m?
1u	700s, 735s, 905m		860w-m	790m-s		1455m	1210m-s	1485m-s, 1585m, 1615m	1690vs		2915m	3095m

[a–e]For meanings of footnotes see Table Ia.

Compound	Other absorptions	Compound	Other absorptions
1n	1240m or 1270m-s C—OH str. 1360m OH def. 3120m, b O—H str.	**1s**	1070m X-sensitive band.
1o	535m C—O—C i-p def. 1025m-s sym C—O—C str. 1240s or 1250s asym C—O—C str.	**1t**	545w-m CO_2 o-o-p roc. 615w, 620w CO_2 ben. 950w-m,b OH def. 1240s, 1265s C—O str. 1430m-s OH def? *ca.* 2500-*ca.* 3100m intermolecular H-bonded O—H str.
1p	320w Ar C—Me i-p ben.		
1q	450w-m C—Cl str & ring def. 1090m-s X-sensitive band.	**1u**	540m NO_2 i-p ben. 870m-s C—NO_2 str. 1350vs NO_2 sym str. 1515vs NO_2 asym str.
1r	1075m-s X-sensitive band.		

Taylor gives a similar assignment for the band at 1205–1210 cm^{-1} (m) which occurs in the spectra of certain 2-substituted 1,3-thiazolidin-4-ones.[8]

Aromatic C=C Stretching Bands

In the spectra of many of the compounds the aromatic C=C stretching bands were observed as two pairs of narrow bands at *ca.* 1500 cm^{-1} and *ca.* 1600 cm^{-1} resulting from four skeletal vibrations of the aromatic rings. In most cases, the lower frequency pair of bands was the stronger and for each pair the more intense band was usually the one of higher frequency. In a number of cases more than four bands were observed and in others one or more bands were broadened or split into a narrow doublet of bands. This was to be expected in a system with more than one aromatic ring; indeed it was surprising that the spectra of so many of the compounds showed just the four main bands. In several spectra, including that of compound **1a**, only the main two bands at *ca.* 1500 cm^{-1} and *ca.* 1600 cm^{-1} were observed and in others some of the bands were probably concealed by other absorptions such as the asymmetrical NO_2 stretching band of the nitro compounds or the >C=O stretching band.

>C=O Stretching Bands

For all of the compounds the >C=O stretching band was observed as a very strong band in the 1640–1735 cm^{-1} region.

Two bands were observed in the spectrum of compound **1t** with its two carbonyl groups. As the usual >C=O stretching frequency range for aromatic carboxylic acids is 1680–1700 cm^{-1},[9] it seemed likely that the higher frequency, stronger carbonyl absorption at 1692 cm^{-1} was due to the carbonyl of the COOH group. This would also be in accord with the fact that acid >C=O absorptions are often somewhat more intense than those due to amides.

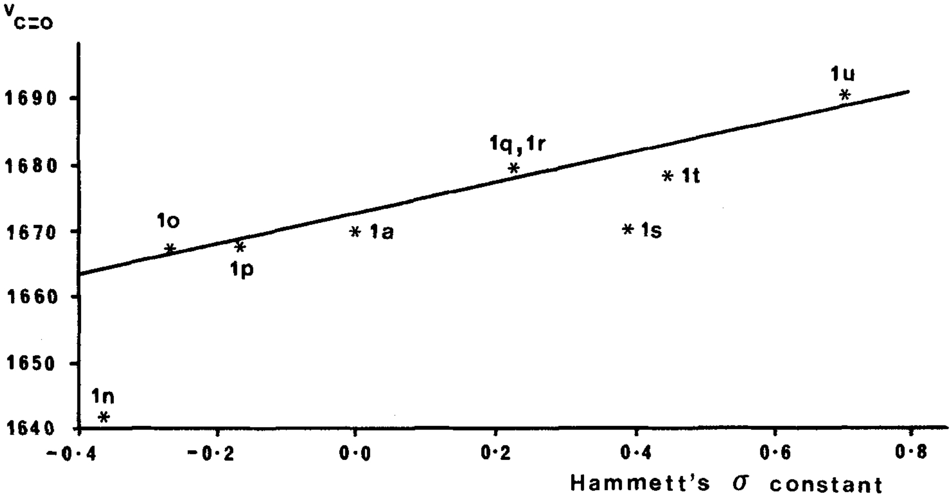


FIGURE 1 Graph of carbonyl stretching frequency, $\nu_{C=O}$, against Hammett's σ constant for compounds with a substituent in the *N*-aryl ring. (Compounds **1n** and **1s** were omitted in calculating the line of best fit.)

TABLE II

Infra-red spectra of the 1-oxides

Compound	Aromatic C—H out-of-plane bending				CH_3 asym def	CH_2 sc	Ar db str	>C═O str	Al C—H str in OMe	Other Al C—H str	Ar C—H str	>S—O str
	[a]	[b]	[c]	[d]								
2a	690m-s, 710w-m, 755m, 900w					1455w-m	1490m-s, 1595m	1680vs		2910w-m, 2945w-m	3030vw	1065s
2b	680m-s, 750s, 900w-m	850m-s			1430w-m	1450m	1485s, 1490s, 1505s, 1575m-s, 1595m, 1610m-s	1708vs	2830w-m	2925w-m, 2950w-m	3070w-m	1050vs
2c	690m-s, 700m, 740m, 755s, 770m-s, 890m or 910w-m	835s			1415w-m	1455m	1490s,[e] 1510m-s, 1595m-s[e]	1696vs		2930m, 2995m	3070w-m	1050vs
2d	700m, 760m, 770m, 895w-m		875w	795w-m	1445w-m	1460w-m	1500s, 1590m, 1600m-s, 1610m-s	1696vs	2840w	2940w-m, 2960w-m	3060w	1060vs
2e	700s, 760s, 770m-s, 910w	850s				1465m	1500vs, 1585w-m, 1600s	1704vs		2930m, 2990m	3075m	1060vs
2f	690m-s, 700s, 750m, 770s, 900w-m		870w-m	800m-s, 810m		1460m	1475m-s, 1495s, 1575m-s, 1595s	1706vs		2930m	3060m-s	1060vs
2g	690m, 700m-s, 720m, 765m, 890w	840m-s			1440m-s	1455m-s	1465m?, 1490m-s, 1505vs, 1580w-m,[e] 1605m	1698vs	2830w-m	2910m-s, 2995m	3040w-m	1050vs
2h	700s, 720m-s, 900w-m		875w-m	775s, 795m		1460m-s	1480s, 1500m, 1575m-s, 1585m-s	1686vs		2910m-s, 2940m-s, 2980m	3075m	1060vs

[a–e] For meanings of footnotes see Table Ia.

Compound	Other absorptions	Compound	Other absorptions
2a	—	**2e**	470m or 490m C—Cl str & ring def. 1100s X-sensitive band.
2b	510m or 530m C—O—C i-p def. 1020s sym C—O—C str. 1260s asym C—O—C str.	**2f**	—
2c	300m or 320m Ar C—Me i-p ben.	**2g**	510m or 550m C—O—C i-p def. 1030s sym C—O—C str. 1240vs asym C—O—C str.
2d	505w-m or 550w C—O—C i-p def masking sym C—O—C str. 1265s asym C—O—C str.	**2h**	—

TABLE III

Infra-red spectra of the 1,1-dioxides

Compound	Aromatic C—H out-of-plane bending [a]	[b]	[c]	[d]	CH_2 sc	Ar db str	>C=O str	Al C—H str	Ar C—H str
3a	690m, 700m-s, 730w-m, 755m-s, 895w or 905w				1455m	1500m-s,[e] 1600m	1692vs	2850w-m, 2930m-s, 3000m	3060w-m
3b	690s, 745m-s, 890w	830m			1455w-m	1485s,[e] 1585m-s	1700vs	2930m, 2995w-m	3060w-m
3c	685s, 695s, 740s, 750m, 900m			775m-s, 795m, 810m	1460m	1480m-s, 1500s, 1580m, 1595m-s	1698vs, 1716vs	2930s, 3000m-s	3060m

[a–e]For meanings of footnotes see Table Ia.

Compound	$>SO_2$ sym str	$>SO_2$ asym str	$-SO_2$ sc	X-sensitive band
3a	1130s, 1145m-s	1325s, 1340s	545m or 570m	
3b	1125s, 1135s	1345vs	560m-s	1070s
3c	1120s, 1140vs	1315vs, 1335vs	545m-s or 555s	1075m-s

TABLE IV

Infra-red spectra of compounds **1v**, **4a**, **4b** and **5**

Compound	Ar C—H o-o-p ben[a]	CH_3 asym def	CH_2 sc	CH_2 tw?	Ar db str	>C=O str	Al C—H str	Ar C—H str	Other absorptions
1v (W = Me, X = Y = H)	690m-s, 710m, 760m-s, 890vw or 915w	1445m	1455m		1495s, 1590m-s	1674vs	2930m	3030m, 3070m	
4a	695m, 705s, 735w-m, 755m, 895w		1455w-m, 1460w-m	1220w-m	1495m, 1605w-m	1671vs	2920w-m	3020w-m	
4b	710s, 735s, 900w-m	1435s	1450m-s, 1470m-s	1225m-s	1500m (other band masked)	1664vs	2865m-s, 2925s, 2955s	3030w-m	1310m-s CH_2 wag?
5	685s, 750m-s, 880m		1450m	masked	1480w-m, 1490m-s, 1580w-m	1734vs	2910w-m, 2960m	3050w-m	1215-1235vs >C=S str?

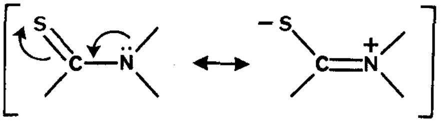
[a] For meanings of footnotes see Table Ia.

The splitting of the carbonyl band in the spectra of compounds **1k** and **1q** may have been due to conformational effects.

An approximately linear relationship was found between the >C=O stretching frequency ($\nu_{C=O}$) and Hammett's σ constant for compounds with a substituent in the *N*-phenyl group ($r = 0.816$; $n = 9$). Omitting compounds **1n** and **1s** gave the improved relationship, $\nu_{C=O} = 22.18\sigma + 1672.5$ ($r = 0.943$; $n = 7$) (Figure 1). It was not possible to explain the anomalously low carbonyl stretching frequencies of **1n** and **1s**. Although, in the former case, it was tempting to invoke intermolecular hydrogen bonding as part of the explanation, since this was also present for **1t** which correlated well, it seemed likely that other factors were also important.

The above mentioned correlation appeared to suggest that the value of the >C=O stretching frequency was, to some extent, governed by competition for the *N* lone pair, with increasing electron withdrawal by the substituent in the *N*-phenyl group being accompanied by increases in >C=O stretching frequency.

In line with this suggestion, a large increase in >C=O stretching frequency compared with the average value of the diaryl compounds was observed for compound **5**. This compound showed the highest >C=O stretching frequency of all the compounds examined (1734 cm^{-1}) and this was readily explained by the presence of the electron-withdrawing thioxo group which competes strongly for the *N* lone pair (I). Replacement of the *N*-aryl group by a benzyl or butyl group (compounds **4a** and **4b**, respectively) and, hence, removal of any competition for the *N* lone pair, resulted in >C=O stretching frequencies (1671 and 1664 cm^{-1}, respectively) fairly similar to that of the parent compound (**1a**) (1670 cm^{-1}). These findings are in reasonable accord with those of Vigorita and Chimirri who reported similar results for a varied selection of 2,3,5-trisubstituted 1,3-thiazolidin-4-ones.[4]



I

C—H Stretching Bands

Aliphatic and aromatic C—H stretching bands were observed as weak to medium bands in the 2830–3000 cm^{-1} and 3020–3130 cm^{-1} regions, respectively, the latter bands generally being somewhat weaker than the former. In all but one of the methoxy compounds, the band at 2830–2840 cm^{-1} (w-m) was identified as C—H stretching in the methyl group.

Other Absorption Bands

In the spectra of the 1-oxides (Table II), the >SO stretching band was observed as a very strong absorption at 1050–1065 cm^{-1}. Since no obvious splitting of this band was observed, this, together with evidence from NMR,[10] seemed to indicate that only one isomer was present.

The spectra of the 1,1-dioxides (Table III) showed medium to strong absorptions due to >SO_2 symmetrical stretching at 1120–1145 cm^{-1} and due to >SO_2 asymmetrical stretching at 1315–1345 cm^{-1}. Most of these absorptions were split into two bands. The asymmetrical stretching bands were slightly stronger than the symmetrical stretching bands in accordance with their larger fluctuating dipoles. In addition to these stretching bands, a variable intensity band at 545–570 cm^{-1} in the spectra of the dioxides appeared to result from $>SO_2$ scissoring.

The spectra of the nitro compounds showed bands due to symmetrical and asymmetrical $—NO_2$ stretching at *ca.* 1350 cm^{-1} (vs) and *ca.* 1520 cm^{-1} (vs), respectively, $C—NO_2$ stretching at *ca.* 870 cm^{-1} (m-s) and NO_2 in-plane bending at *ca.* 540 cm^{-1} (w-m).

Symmetrical and asymmetrical C—O—C stretching of the Ar-O-Me group of the methoxy compounds were observed as, usually, strong bands at 1020–1055 cm^{-1} and 1230–1265 cm^{-1}, respectively, the asymmetrical band being the stronger. In addition, in-plane deformation of the C—O—C group generally gave a medium intensity band at 505–550 cm^{-1}.

Evidence for intermolecular hydrogen bonding was seen in the spectra of compounds **1n** and **1t**. In the case of the former compound, the OH stretching band was seen at the low value of 3120 cm^{-1} as a broad, medium intensity band, both the low frequency and the width of which indicated the presence of intermolecular association. The broad, medium band with peaks at 1225 and 1240 cm^{-1} (and, possibly, the strong band at 1270 cm^{-1}) was probably caused by stretching of the C—OH bond and the medium band at 1360 cm^{-1} by OH deformation. (Socrates[11] lists both of these bands as combinations of the C—OH stretch and the OH deformation).

For compound **1t** the OH stretching band at *ca.* 2500–*ca.* 3100 cm^{-1} (m) showed the presence of extensive hydrogen bonding, evidence for dimerisation being provided both by the position of this band and by the presence of an $O—H\cdots O$ out-of-plane deformation band at 950 cm^{-1} (w-m, b). The exceptionally low tlc Rf value and partition coefficient of this compound which we found in other experiments yet to be reported can, therefore, be explained in terms of the strong intermolecular hydrogen bonding present between the carboxyl group and the silica or water.

Although somewhat weaker than usual, it seemed likely that the weak to medium 545 cm^{-1} band in the spectrum of compound **1t** was produced by CO_2 rocking. A weak band with peaks at 615 and 620 cm^{-1} was characteristic of CO_2 bending in a *para*-substituted carboxylic acid.

In the spectrum of compound **1k** the C≡N stretching band occurred as a medium to strong absorption at 2220 cm^{-1}. In addition, other characteristic bands were seen at 400 cm^{-1} (w) and 555 cm^{-1} (m-s). Socrates indicates that the former band results from in-plane bending of the C—CN bond and the latter band from a combination of in-plane C≡N deformation and an out-of-plane deformation of the aromatic ring.[12]

It seemed likely that the very strong band with peaks at 1215 and 1235 cm^{-1} in the spectrum of compound **5** was the >C═S stretching band. However, because of the very wide range over which >C═S stretching absorptions can occur, this assignment remained questionable.

In the spectra of most of the Cl and Br compounds a sharp X-sensitive band[5] was observed at 1065–1100 cm^{-1} (m-s). Although it was not possible to identify positively this band in the spectrum of compound **1h**, the sharp band at 1210 cm^{-1} (m-s) seemed a likely candidate.

The band produced by C—halogen stretching in combination with ring deformation was seen as a medium to strong band at 535 cm^{-1} in the spectrum of compound **1h** and as a medium band in the 450–490 cm^{-1} region in the spectra of several of the chlorine compounds.

EXPERIMENTAL

Compounds **1a–1u**, **2**, **3** and **4** were prepared and their identities confirmed as described by us previously.[10] Compound **1v** was prepared in a similar way to compounds **1a–1u** except that 2-mercaptopropanoic acid was used in place of mercaptoethanoic acid.

Compound **5** was prepared by adding mercaptoethanoic acid (0.1 mol) to a solution of phenyl isothiocyanate (0.1 mol) in methanol (100 ml) and warming the mixture to 45°C for 5 min. Cooling and partial evaporation of the resulting solution yielded yellow crystals which were recrystallised to constant melting point from methanol.

Infra-red spectra were obtained using a Pye-Unicam SP3-300 spectrophotometer calibrated against polystyrene at 1601 cm^{-1}. The samples were examined as KBr wafers. Carbonyl stretching frequencies were recorded to ± 1 cm^{-1}, other frequencies below 2000 cm^{-1} to ± 5 cm^{-1} and those over 2000 cm^{-1} to ± 10 cm^{-1}.

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