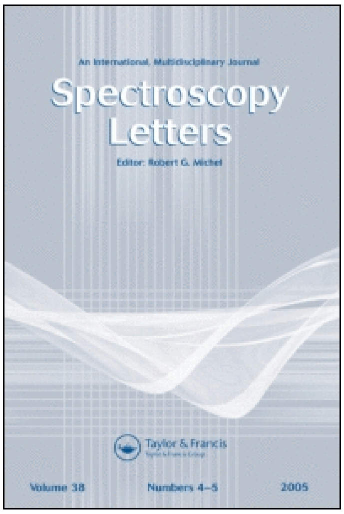


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

^{1}H and ^{13}C NMR Spectral Study of Some 2*r*-Aryl-6*c*-phenylthian-4-ones, Their 1-Oxides and 1,1-Dioxides

D. Devanathan[a]; K. Pandiarajan[a]
[a] Department of Chemistry, Annamalai University, Annamalai Nagar, India

To cite this Article Devanathan, D. and Pandiarajan, K.(2009) '^{1}H and ^{13}C NMR Spectral Study of Some 2*r*-Aryl-6*c*-phenylthian-4-ones, Their 1-Oxides and 1,1-Dioxides', Spectroscopy Letters, 42: 3, 147 — 155
To link to this Article: DOI: 10.1080/00387010902772153
URL: http://dx.doi.org/10.1080/00387010902772153

Spectroscopy Letters, 42:147–155, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010902772153

Taylor & Francis
Taylor & Francis Group

^{1}H and ^{13}C NMR Spectral Study of Some 2*r*-Aryl-6*c*-phenylthian-4-ones, Their 1-Oxides and 1,1-Dioxides

D. Devanathan,
and K. Pandiarajan

Department of Chemistry,
Annamalai University, Annamalai
Nagar, India

ABSTRACT Four 2*r*-aryl-6*c*-phenylthian-4-ones **1b**−**1e** and their 1-oxides **2b**−**2e** and 1,1-dioxides **3b**−**3e** have been newly synthesized. ^{1}H and ^{13}C NMR spectra have been recorded for all these compounds and 2*r*,6*c*-diphenylthian-4-one 1-oxide **2a**. ^{13}C NMR spectrum has been recorded for the sulfone **3a** of **1a**. For selected compounds ^{1}H-^{1}H COSY, HSQC, HMBC, and NOESY spectra have been recorded. The *vicinal* proton–proton coupling constants suggest that in all these compounds, the heterocyclic ring adopts chair conformation with equatorial orientations of the aryl and phenyl groups. Proton and carbon chemical shifts suggest that in the sulfoxides, the S = O bond is axial and enhances the J_{aa} value by some special effect. The S = O bond causes a significant upfield shift even on carbons without hydrogens. Significant solvent shifts also were observed.

KEYWORDS ^{13}C NMR, ^{1}H NMR, thian-4-one 1,1-dioxides, thian-4-one 1-oxides, thian-4-ones

INTRODUCTION

Nuclear magnetic resonance spectral study of organic compounds is of constant and continuous interest.[1−12] From the ^{1}H NMR spectral study of 2*r*,6*c*-diphenylthian-4-one **1a** and its sulfone **3a**, it has been found that the SO_2 function has a special influence on the *vicinal* diaxial coupling, apart from the general known electronegativity effect.[12] However, in this study[12] the sulfoxide **2a** was not included, and it could not be known whether axial or equatorial SO bond is responsible for the special effect. Furthermore, ^{13}C chemical shifts of sulfones have not been reported in this study.[12]

In the case of 2*r*,6*c*-diarylpiperidin-4-ones, the effects of *o*-substituents on the chemical shifts of the protons and carbons of the piperidine ring have been determined by comparing 2*r*,6*c*-di(*o*-substituted)phenylpiperidin-4-ones with the corresponding 2*r*,6*c*-diphenylpiperidin-4-ones.[3,4] The effects of *o*-substituents are considerable,[3,4] due to the steric interaction between the *ortho*-substituents with the nearby C−H bonds of the heterocyclic ring. However, a *meta* or *para* aromatic substituent can influence the chemical

Received 10 July 2008;
accepted 15 October 2008.

Address correspondence to
K. Pandiarajan, Department of
Chemistry, Annamalai University,
Annamalai Nagar 608002, India.
E-mail: profkpchem@yahoo.co.in

shifts of the protons and carbons of the ring only by the electrical charge placed on the *ipso* carbon by the mesomeric and inductive effect of the substituent, and such an effect has been found to be small in aryl-substituted compounds.[4,7,8] Such small effects could be investigated more reliably by studying heterocyclic compounds with a substituted phenyl group at C-2 and a phenyl group at C-6. The difference between the chemical shift of a carbon or proton in the phenyl side and that of the corresponding nucleus in the substituted phenyl side can be determined reliably. This paper reports the ^{1}H and ^{13}C NMR spectral study of four 2*r*-aryl-6*c*-phenylthian-4-ones **1b**–**1e**, their 1-oxides **2b**–**2e** and 1,1-dioxides **3b**–**3e**, where aryl is a *m*- or *p*-substituted phenyl group. For the sake of comparison, 2*r*,6*c*-diphenylthian-4-one 1-oxide (**2a**) and its 1,1-dioxide (**3a**) have also been included.

MATERIALS AND METHODS

Preparation of Compounds

Compounds **1b**–**1e** were prepared from the appropriate arylidenebenzalacetone following the literature procedure[13] used for the preparation of **1a**. Compounds **2** and **3** were prepared following the literature procedure.[13]

Recording of Spectra

^{1}H and ^{13}C NMR spectra of **2b** in $CDCl_3$ and **3b** in DMSO-d_6 were recorded on a Bruker DRX 500 NMR spectrometer operating at 500.03 MHz for ^{1}H and 125.75 MHz for ^{13}C. For all the other compounds, ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 400 spectrometer (Sophisticated Instrument Facility, Indian Institute of Science, Bangalore, India) operating at 400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C.

The following spectral parameters were used. ^{1}H: acquisition time = around 3.0 s, number of scans = 100, number of data points = 32 K, and spectral width = 5000 Hz. ^{13}C: acquisition time = around 0.5 s, number of scans = around 1000, number of data points = 32 K, and spectral width = around 30,000 Hz.

^{1}H-^{1}H COSY, phase-sensitive NOESY, HSQC, and HMBC spectra were recorded on a Bruker DRX 500 NMR spectrometer using standard parameters. The number of data points was 1 K. For NOESY spectrum, mixing time was 1000 ms.

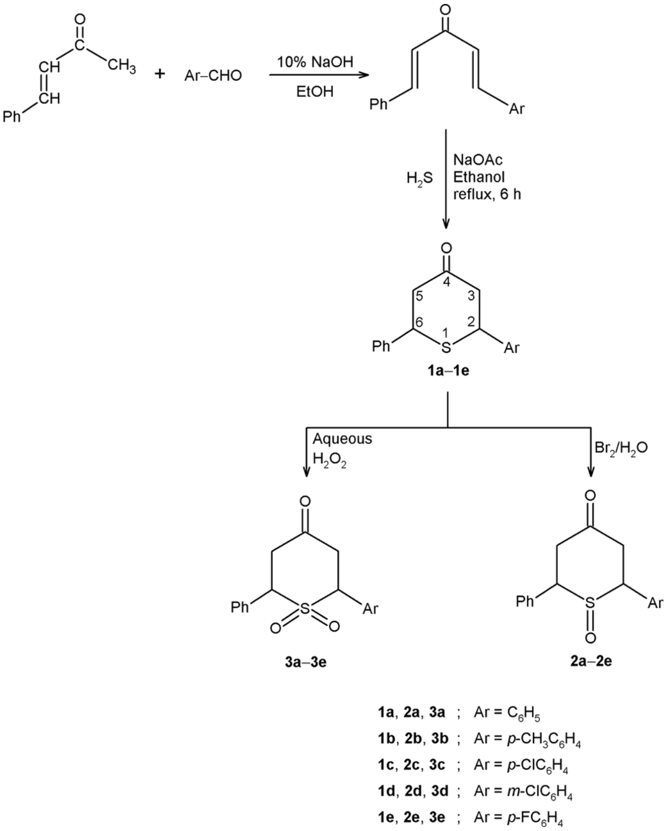
All NMR measurements were made using 5-mm tubes. For recording ^{1}H NMR spectra, solutions were prepared by dissolving about 10 mg of the compounds in 0.5 mL of the solvent. For recording ^{13}C and 2D NMR spectra, solutions were prepared by dissolving about 50 mg of the compound in 0.5 mL of the solvent.

Elemental analyses were performed on an Elementar Vario EL III CHNS/O analyzer (Sophisticated Analytical Instrument Facility, Central Drug Research Institute, Lucknow, India).

RESULTS AND DISCUSSION

The compounds were synthesized using the reactions shown in Scheme 1. The numbering of the carbons of the thiane ring is also shown in Scheme 1. The carbons of the substitutedphenyl group are numbered as C-1′, C-2′, C-3′, C-4′, C-5′, and C-6′. The carbons of the phenyl group are numbered as C-1″, C-2″, C-3″, C-4″, C-5″, and C-6″. Protons also are numbered accordingly.

Elemental analysis has been done for **1b**, **2d**, and **3b**. The physical data of the synthesized compounds



SCHEME 1 Synthesis of thian-4-ones, their 1-oxides and 1,1-dioxides.

TABLE 1 Physical Data for Compounds 1–3

Compound	IR band (C=O) (cm^{-1})	Melting point (°C)	Yield (%)
1a	1699	112	75
1b	1705	124	76
1c	1704	118	72
1d	1706	83	73
1e	1706	98	68
2a	1716	195	70
2b	1716	148	68
2c	1716	144	70
2d	1713	163	66
2e	1717	157	72
3a	1730	234	80
3b	1723	237	85
3c	1723	247	87
3d	1723	206	83
3e	1723	265	82

are given in Table 1, and the results of elemental analysis are given in Table 2. From X-ray crystallographic study,[14] it was found that **2e** adopts chair conformation **2eC** with the SO group axial and the *p*-fluorophenyl and phenyl groups in the equatorial positions.

For **2c**, **2d**, and **2e**, the NMR spectra were recorded in DMSO-d_6 as they are not soluble in $CDCl_3$. For **2a** and **3a**, the spectra were recorded in a mixture of CH_2Cl_2 and $CDCl_3$. For all the other compounds, the spectra were recorded in $CDCl_3$. For the sake of comparison, the spectra of **2b** and **3b** were recorded in DMSO-d_6 also.

For **1b**, chemical shifts of the four methylene protons (two axial and two equatorial) and the various proton–proton coupling constants could be determined by second-order analysis. However, for **1c**–**1e**, the multiplet for the methylene protons was more complex and could not be analyzed.

For sulfoxides and sulfones, the various proton chemical shifts and proton–proton coupling constants could be determined by first-order analysis. In the case of unsymmetric sulfones, long-range coupling was observed between the two equatorial protons.

TABLE 2 Results of Elemental Analysis of Typical Compounds 1b, 2d, and 3b

Compound	Experimental		Calculated for the molecular formula	
	% C	% H	% C	% H
1b	76.62	5.85	76.59	6.38
2d	63.54	4.90	64.15	4.71
3b	68.31	6.01	68.78	5.73

For all the unsymmetric compounds, separate signals were observed for the two benzylic carbons and the two methylene carbons. Separate signals were observed for chemically different aromatic carbons. From the observed correlations in the HMBC spectra of **1e**, **2b** (in $CDCl_3$), **2e**, and **3b** (in DMSO-d_6), the signals for aromatic and benzylic carbons in these compounds could be assigned unambiguously.

The assignments are explained taking **2b** as an example. In the ^1H NMR spectrum of **2b**, the aromatic protons of the *p*-tolyl group appeared as an **AB** quartet (instead of expected more complex **AA′BB′** spectrum) and the phenyl protons appeared as a broad singlet at 7.38 ppm. The other proton signals were assigned based on positions and multiplicities. In the ^{13}C NMR spectrum of **2b**, there were four weak signals at 205.0, 139.0, 135.5, and 132.4 ppm. In the HMBC spectrum of **2b**, the signal at 205.0 ppm showed correlation with the axial and equatorial methylene protons only. Based on its position and the observed correlation, this signal could be readily assigned to the carbonyl carbon. The signal at 139.0 ppm alone showed correlation with the methyl protons and should be due to C-4′. The signal at 135.5 ppm showed correlation with the phenyl protons and should be due to C-1″. The signal at 132.4 ppm showed correlation with one set of protons of the *p*-tolyl group at 7.19 ppm and should be due to C-1′. There were five signals for the other aromatic carbons at 129.9, 129.1, 128.9, 128.0, and 127.9 ppm. Based on intensity, the signal at 128.9 ppm was assigned to C-4″.

The signal at 129.9 ppm showed correlation with the methyl protons and should be due to C-3″ and C-5″. The signal at 129.1 ppm could, therefore, be assigned to C-3′ and C-5′. The signal at 127.9 ppm showed correlation with the protons of the *p*-tolyl group and should be due to C-2″ and C-6″. The signal at 128.0 ppm was, therefore, assigned to C-2′ and C-6′. Among the two signals for the benzylic carbons that at 62.8 ppm showed correlation with the aromatic protons of the *p*-tolyl group whereas that at 63.0 ppm showed correlation with the protons of the phenyl group. Hence, the signals 62.8 and 63.0 ppm were assigned to C-2 and C-6, respectively.

It was found that in all these cases (**1e**, **2b**, **3e**, and **3b**), C-1′ has a lower chemical shift than C-1″ and C-2 has a lower chemical shift than C-6. This can be attributed to the electron-releasing mesomeric effect of *p*-F or *p*-CH_3 substituent. Because C-1′ and C-2 are shielded by this electron-releasing effect, it should be expected that C-3 should have a lower chemical shift than C-5 in these compounds.

In all these cases, the assignments for the aromatic carbons were in accord with the known substituent effects.[15] For example, the chemical shifts of C-1′, C-2′, C-3′, and C-4′ were computed by adding the effects[15] of the methyl group to those of the corresponding carbons of the phenyl group as 132.6, 127.8, 129.8, and 138.2 ppm, respectively. These are in good agreement with the observed values. Hence, the signals of the aromatic carbons in all the other compounds were assigned based on substituent effects.[15] The chemical shifts of the aromatic carbons are listed in Table 3.

In the *m*-chlorophenyl compounds, C-1′ has a higher chemical shift than C-1″. This is because the resonance effect of the chlorine atom can put negative charge on C-2′, C-4′, and C-6′ but not on C-1′. Only electron-withdrawing inductive effect of the chlorine atom can influence the chemical shift of C-1′. Hence, in **1d, 2d**, and **3d** C-2 should have a higher chemical shift than C-6 and C-3 should have a higher chemical shift than C-5. The chemical shifts of benzylic carbons and methylene carbons were assigned based on these principles. The chemical shifts of carbons other than the aromatic carbons are listed in Table 4.

It was found that the chemical shift of H-2 is lower than that of H-6 in **1e** but higher than that of H-6 in **2e**. However, in **2b** (in $CDCl_3$) H-2 was found to have a lower chemical shift than H-6. From the NOESY spectrum, it was found that H-2 has a lower chemical shift than H-6 in **3b**. Hence, taking **2e** as an exceptional case, in the *p*-tolyl, *p*-fluoro, and *p*-chloro compounds H-2 should have a lower chemical shift than H-6. Also in the *m*-chlorophenyl compounds, H-2 should have a higher chemical shift than H-6.

In the ^1H-^1H COSY spectrum of **3b** (in DMSO-d_6) and **3d,** the benzylic proton with a higher chemical shift (H-6 for **3b** and H-2 for **3d**) correlated with methylene protons having higher chemical shifts. Also in the ^1H-^1H COSY spectrum of **2e,** H-2 correlated with the axial methylene proton having

TABLE 3 ^{13}C **Chemical Shifts (δ, ppm) of Aromatic Carbons of 1, 2, and 3**[a]

Compound	C-1′	C-1″	C-2′	C-2″	C-3′	C-3″	C-4′	C-4″
1a	139.1	139.1	126.8	126.8	128.4	128.4	127.6	127.6
1b	137.8	139.4	127.0	127.2	129.5	128.8	136.4	128.0
1c	137.9	139.1	128.5	127.2	129.0	128.9	133.9	128.2
1d[b]	141.3	139.1	127.4	127.1	134.7	128.9	128.2	128.3
1e	135.2	139.2	128.9	127.1	115.8 $J_{CF} = 21.4$ Hz	128.8	162.3 $J_{CF} = 247$ Hz	128.2
2a	138.5	138.5	130.7	130.7	131.7	131.7	131.5	131.5
2b	132.4	135.5	127.9	128.0	129.9	129.1	139.0	128.9
2b[c]	133.4	136.5	127.8	128.0	129.2	128.7	137.6	128.2
2c[c]	135.4	136.2	128.7	128.0	129.8	128.7	133.0	128.3
2d[b,c]	138.2	136.2	126.8	128.0	133.3	128.7	128.3	128.3
2e[c]	133.2	136.7	130.6	128.6	116.1 $J_{CF} = 21.3$ Hz	129.3	162.5 $J_{CF} = 241$ Hz	128.8
3b	125.3	128.5	128.9	129.3	129.7	129.5	139.9	129.7
3b[c]	127.7	130.8	128.6	129.2	129.6	129.8	138.6	129.0
3c	126.9	128.1	130.7	129.0	129.5	129.2	136.0	129.9
3d[b]	130.3	128.1	129.6	129.0	134.9	129.5	130.1	129.9
3e	124.2	128.2	131.3	129.0	116.1 $J_{CF} = 21.5$ Hz	129.5	163.5 $J_{CF} = 250$ Hz	129.9
4a[d]	142.6	142.6	126.4	126.4	128.6	128.6	127.7	127.7
5a[e]	140.6	140.6	125.4	125.4	128.1	128.1	128.0	128.0

[a] For **3a** only two signals were observed at 132.3 and 131.6 ppm.
[b] The chemical shifts of C-5′, C-6′ for **1d, 2d**, and **3d** are (130.1, 125.4; **1d**), (130.6, 127.8; **2d**), and (130.2, 127.7; **3d**).
[c] Values in DMSO-d_6.
[d] Data taken from Ref. 2.
[e] Data taken from Ref. 1.

TABLE 4 ^{13}C Chemical Shifts (δ, ppm) of Carbons other than Aromatic Carbons of 1, 2, and 3

Compound	C-2	C-3	C-4	C-5	C-6	Me
1a	48.2	50.2	206.8	50.2	48.2	—
1b	48.2	50.5	207.5	50.6	48.4	21.0
1c	47.7	50.3	207.2	50.4	49.5	—
1d	48.5	50.4	207.2	50.2	47.9	—
1e	47.7	50.4	207.6	50.6	48.5	—
2a	65.5	40.5	207.1	40.5	65.5	—
2b	62.8	38.0	205.0	38.2	63.0	21.2
2b[a]	59.9	37.1	204.7	37.2	60.1	20.6
2c[a]	60.6	37.7	204.4	37.5	59.9	—
2d[a]	60.2	36.9	204.3	36.7	59.6	—
2e[a]	59.9	37.5	205.0	37.8	60.6	—
3a	67.3	48.5	204.4	48.5	67.3	—
3b	64.3	45.8	202.2	45.8	64.4	21.1
3b[a]	61.6	43.3	204.3	43.3	61.7	20.7
3c	63.8	45.6	201.5	45.6	64.5	—
3d	64.6	45.7	201.4	45.6	63.8	—
3e	63.8	45.7	201.6	45.7	64.5	—
4a[b]	61.0	50.2	207.8	50.2	61.0	—
5a[c]	78.6	49.5	205.2	49.5	78.6	—

[a] Values in DMSO-d_6.
[b] Data taken from Ref. 2.
[c] Data taken from Ref. 1.

a lower chemical shift. In all these cases, the chemical shifts of the methylene protons of C-3 are in accord with the electronic effect of the aromatic substituents. However, in the case of **2d**, H-2 (benzylic proton with lower chemical shift) correlated with axial methylene proton having higher chemical shift. Considering this as an exceptional case, the chemical shifts of the methylene protons at C-3 should be in accord with the electronic effect of the aromatic substituents on C-1′. The signals for benzylic protons and methylene protons were assigned based on these principles. The proton chemical shifts are listed in Table 5. The various proton-proton coupling constants are listed in Table 6. For the sake of comparison, the spectral data for 2*r*,6*c*-diphenylpiperidin-4-one (**4a**) and 2*r*,6*c*-diphenyloxan-4-one (**5a**) are also given in Tables 3, 4, 5, and 6.

The *vicinal* coupling constants of all the compounds are in accord with chair conformation for the thiane ring with equatorial orientations of the aryl and phenyl groups. The chemical shifts of the benzylic protons, methylene protons, benzylic carbons, and methylene carbons in **2b** (in DMSO-d_6), **2c,** and **2d** are very close to those in **2e**. Also the

TABLE 5 Proton Chemical Shifts (δ, ppm) of 1, 2, and 3

Compound	H-2	H_{3a}	H_{3e}	H_{5a}	H_{5e}	H-6	Me	Aromatic
1a	4.30	3.02	2.94	3.02	2.94	4.30	—	7.22–7.39
1b	4.29	3.02	2.93	3.02	2.94	4.31	2.33	7.28 (H-2′, H-6′) 7.17, (H-3′, H-5′), 7.30–7.40 (others)
1c	4.34	2.90–3.10				4.36	—	7.30–7.42
1d	4.31	2.91–3.06				4.28	—	7.26–7.34
1e	4.30	2.91–3.06				4.31	—	7.04 (H-3′, H-5′), 7.26–7.37 (others)
2a	4.14	3.77	2.70	3.77	2.70	4.14	—	7.34–7.50
2b	4.09	3.74	2.67	3.75	2.67	4.10	2.34	7.26 (H-2′, H-6′), 7.19 (H-3′, H-5′), 7.38 (others)
2b[a]	4.70	3.52	2.45	3.53	2.45	4.73	2.29	7.25 (H-2′, H-6′), 7.21 (H-3′, H-5′), 7.36–7.42 (others)
2c[a]	4.74	3.50	2.50	3.53	2.50	4.78	—	7.37–7.49
2d[a]	4.81	3.55	2.55	3.55	2.55	4.75	—	7.36–7.47
2e[a]	4.79	3.52	2.61	3.54	2.61	4.74	—	7.25 (H-3′, H-5′), 7.35–7.50 (others)
3a	4.56	3.73	2.95	3.73	2.95	4.56	—	7.37–7.41
3b	4.53	3.74	2.96	3.75	2.98	4.54	2.36	7.34 (H-2′, H-6′), 7.23 (H-3′, H-5′), 7.40–7.50 (others)
3b[a]	5.03	3.60	2.96	3.63	2.99	5.06	2.29	7.23 (H-2′, H-6′), 7.22 (H-3′, H-5′), 7.37 (others)
3c	4.54	3.70	2.97	3.75	2.99	4.56	—	7.38–7.44
3d	4.56	3.75	3.00	3.70	2.97	4.52	—	7.35–7.45
3e	4.55	3.70	2.98	3.75	2.98	4.55	—	7.12 (H-3′, H-5′), 7.26–7.44 (others)
4a[b]	4.09	2.60−2.70		2.60−2.70		4.70	—	7.26–7.49
5a[c]	4.84	2.73	2.69	2.73	2.69	4.84	—	7.32–7.47

[a] Values in DMSO-d_6.
[b] Data taken from Ref. 4.
[c] Data taken from Ref. 27.

TABLE 6 **Proton–Proton Coupling Constants (Hz) of 1, 2, and 3**

Compound	$J_{2a,3a}$	$J_{2a,3e}$	$J_{5a,6a}$	$J_{5e,6a}$	$J_{5a,5e}$	$J_{3a,3e}$
1a	12.40	2.80	12.40	2.80	13.20	13.20
1b	12.59	2.74	12.61	2.78	13.80	13.86
1c[a]	11.83	3.63	12.12	3.26	—	—
1d[a]	11.98	3.58	12.41	3.27	—	—
1e[a]	11.67	3.70	12.11	3.47	—	—
2a	13.80	2.30	13.80	2.30	14.54	14.54
2b	14.03	2.74	13.94	2.83	14.51	14.44
2b[b]	14.00	3.00	14.00	3.00	14.50	14.50
2c[b]	14.25	2.93	14.18	2.93	—	—
2d[b]	13.75	2.96	13.80	2.89	13.30	13.30
2e[b]	13.91	2.86	13.92	2.94	14.70	14.38
3a	14.10	3.00	14.10	3.00	14.58	14.58
3b[c]	14.14	3.13	14.15	3.08	14.60	14.43
3b[b,d]	11.50	3.50	11.70	3.70	13.00	13.00
3c[c]	14.20	3.39	14.19	3.32	14.54	14.60
3d[c]	14.06	3.30	14.00	3.30	14.53	14.70
3e	14.08	3.09	14.08	3.09	—	—
5a[e]	11.70	2.56	11.70	2.56	14.20	14.20

[a] Reporting coupling constants are apparent value.

[b] Values in DMSO-d_6.

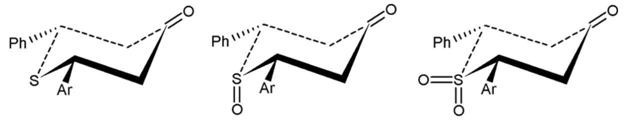
[c] The long range coupling constant for **3b, 3c**, and **3d** are (3.08; **3b**), (3.29; **3c**), (3.22; **3d**).

[d] The lines were broad and error in the coupling constants may be 15–20%.

[e] Data from Ref. 27.

chemical shifts of the benzylic protons, methylene protons, benzylic carbons, and methylene carbons in **2a** are close to those in **2b** (in $CDCl_3$). Hence, in all the sulfoxides, S=O should be axial. The conformations of all the compounds are shown in Fig. 1.

The conformation of S=O bond has been investigated in various six-membered saturated heterocyclic compounds.[16–21] Generally, in six-membered cyclic sulfoxides, S=O is axial.[16] However, replacement of a methylene group at the *β*-position by a heteroatom or the replacement of a *β*-axial hydrogen by a methyl group increases the population of the S=O equatorial conformation.[17,18] The replacement of α-methylene group by sulfur results in a greater predominance of the S=O axial conformation.[19–21] In the current case, the S=O equatorial conformation **2C′** will have the phenyl and aryl groups in the axial positions. Hence, this cannot make a significant contribution to **2** in solution.



Ar = C_6H_5	**1aC**	**2aC**	**3aC**
Ar = *p*-MeC_6H_4	**1bC**	**2bC**	**3bC**
Ar = *p*-ClC_6H_4	**1cC**	**2cC**	**3cC**
Ar = *m*-ClC_6H_4	**1dC**	**2dC**	**3dC**
Ar = *p*-FC_6H_4	**1eC**	**2eC**	**3eC**

FIGURE 1 **Conformations of thian-4-ones, their 1-oxides and 1,1-dioxides.**

From Tables 3, 4, and 5, it is seen that the chemical shifts of the carbons and protons of the thiane ring are influenced by the *meta*- and *para*-substituents in the aromatic ring.

From Table 4, it is seen that the chemical shifts of the benzylic carbon increase in the order **1a** < **4a** < **2a** < **3a** < **5a**. Lambert et al.[22] have found that in pentamethyleneheterocycles **6,** the chemical shifts of the α-carbon increases steeply with increase in the electronegativity of the heteroatom X. A similar effect is reflected in the trend **1a** < **4a** < **5a**. The observed chemical shifts of the benzylic carbons suggest that the electronegativities of SO and SO_2 groups are slightly higher than that of nitrogen but much lower than that of oxygen.

However, the chemical shifts of the benzylic protons increase in the order **4a** < **2a** < **1a** < **3a** < **5a**. This order is not consistent with the order of electronegativity. The chemical shift of the benzylic proton in **1a** is higher than that expected based on electronegativity alone. The observed trend suggests that the benzylic protons are deshielded by the magnetic anisotropic effect to a greater extent by the C—S bond than by the C—N bond. Also, the axial SO bond may shield the benzylic proton by its magnetic anisotropic effect.

Lambert et al.[22] have found that the chemical shift of the *β*-carbon in **6** is not significantly affected by the electronegativity of the heteroatom X. A similar observation is made for **1a, 4a**, and **5a**. However, in **2a** the methylene carbon (*β*-carbon) is significantly shielded. Also, the axial methylene proton is significantly deshielded in **2a** compared with that in **1a**, whereas the equatorial methylene proton in **2a** is shielded relative to that in **1a**. These observations can be explained as follows: The S=O bond interacts with the axial C–H bonds at C-3 and C-5 inducing a polarization in them. A partial positive charge is placed on the axial hydrogens, and an equivalent negative charge is placed on the methylene carbon. This causes a significant deshielding on the axial proton and a shielding on the methylene carbon. This is a *γ-gauche* effect of the oxygen atom on the methylene carbon. The partial negative charge on the methylene carbon induces a shielding on the equatorial methylene proton.

In **3a**, the shielding on the methylene carbon is only small. However, the axial methylene protons in **2a** and **3a** have almost the same chemical shift. Also, the equatorial methylene proton in **3a** is deshielded relative to that in **1a** and **2a**. The small shielding on the methylene carbon in **3a** suggests that the interaction between the axial S=O bond and the axial C–H bonds at C-3 and C-5 is much less than that in **2a**. Perhaps due to dipolar interaction between the two S=O bonds in **3a**, the polarity of the axial S=O bond is significantly decreased. Also, the magnetic anisotropy of the CSO_2 function may have a deshielding effect on both the methylene protons.

It is interesting to note that in the sulfoxides and sulfones of 3-arylidene-1-thioflavan-4-one epoxides, an axial proton at C-3 has almost the same chemical shift in sulfoxides (with S=O axial) and sulfones, whereas an equatorial proton at C-3 has a higher chemical shift in the sulfone than in the corresponding sulfoxide.[5] These observations have been corroborated with *ab initio* calculations of the anisotropic effects of the oxirane ring and the SO and SO_2 groups in these compounds.[5]

Comparison of the chemical shifts of the *ipso* carbons in **1b, 2b**, and **3b** suggest that S=O bond significantly shields the *ipso* carbons. This may be a *γ-gauche* effect of the oxygen atom on the *ipso* carbons. However, such *γ-gauche* effect on carbon without hydrogen is generally much less. For example, in **4b** the *ipso* carbon of the phenyl group at C-2 is shielded relative to that of the phenyl group at C-6 only by 0.9 ppm.[2] In **5b**, such a shielding is only 1.0 ppm.[1] Probably the oxygen on the sulfur exercises a significant *γ-gauche* effect on carbons by a mechanism apart from inducing a polarization of a C−H bond.

It has been found by Karplus[23] by valence bond calculations that the *vicinal* coupling constant between two protons will have a maximum value for any system when the torsional angle between them is 180°. Karplus also has pointed out that the *vicinal* coupling constants should decrease with increase in the electronegativities of the substituents in the C−C segment.

The J_{aa} values of **1a** and **5a** are in accord with the electronegativities of S and O atoms. Based on electronegativity effect, the J_{aa} values in **2a** and **3a** should be expected to be lower than that in **1a**. However, the J_{aa} values in **2a** and **3a** are significantly higher than that in **1a**. Haasaunt and co-workers[24] have proposed a general equation for calculating the *vicinal* coupling constant for any torsional angle using the appropriate electronegativities of various substituents on the C-C segment. Using this equation, the J_{aa} values in **1a** and **3a** have been calculated as 12.2 and 11.5 Hz, respectively.[12] Such a calculation was not done for **2a** due to the unavailability of suitable electronegativity of value the axial SO group. However, such a calculated value should be in between 11.5 and 12.2 Hz. The observed J_{aa} value is much higher than the probable calculated value. Hence, it is obvious that the axial S=O bond enhances the J_{aa} value by a special effect.

Heydenreich et al.[25] by using theoretical calculations and experimental measurements have found that the ^3J(C,H) coupling constants via –S−, –SO−, and $–SO_2–$ groups increase in the order $SO_2 < SO < S$. In the current work, the *vicinal* coupling does not occur through the sulfur function. It is interesting to note that the SO and SO_2 functions on the C-C segment increases the *vicinal* coupling constant J_{aa} but has little influence on J_{ae}.

Abraham et al.[26] have measured the ^{1}H chemical shifts of 124 compounds in DMSO-d_6 and $CDCl_3$. They have determined the ^{1}H solvent shift $\Delta\delta[\delta(\text{DMSO-}d_6)-\delta(CDCl_3)]$ for all these cases. They have also calculated the ^{1}H solvent shifts by theoretical methods. The solvent effects have been discussed in terms of solvent-solute interactions. It has been found that for protic hydrogens, hydrogen bonding is the dominant interaction, and for the remaining protons, solvent anisotropy and electric field effects are the major factors. However, in this study no sulfoxide or sulfone has been included. The ^{1}H and ^{13}C solvent shifts for **2b** and **3b** are listed in Tables 7 and 8.

TABLE 7 ^{1}H Solvent Shifts for 2b and 3b

	$\Delta\delta$, δ(DMSO-d_6)−δ($CDCl_3$)						
Compound	H-2	H-3a	H-3e	H-5a	H-5e	H-6	CH_3
2b	0.61	−0.22	−0.22	−0.22	−0.22	0.63	−0.05
3b	0.50	−0.14	0.00	−0.12	0.01	0.32	−0.07

TABLE 8 ^{13}C Solvent Shifts for 2b and 3b

	$\Delta\delta$, δ(DMSO-d_6)−δ(CDCl$_3$)					
Compound	C-2	C-3	C-4	C-5	C-6	CH$_3$
2b	−2.9	−0.9	−0.3	−1.0	−2.9	−0.6
3b	−2.7	−2.5	2.1	−2.5	−2.7	−0.4

The benzylic carbon is shielded and the benzylic proton is deshielded in DMSO-d_6 compound with that in CDCl$_3$. This can be explained as follows: In the sulfoxides and sulfones, the benzylic protons should be slightly acidic. Because this, the C(benzylic)−H bond should be polar to some extent so that the benzylic carbon gets a partial negative charge and the benzylic proton gets a partial positive charge. This polarity is probably increased in DMSO-d_6 compound with that in CDCl$_3$ resulting in a shielding of the benzylic carbon and a deshielding of the benzylic hydrogen.

The methylene carbons also are shielded in DMSO-d_6 compared with that in CDCl$_3$. This shows that the C(methylene)−H bonds also are polarized to a greater extent in DMSO-d_6 than in CDCl$_3$. However, the ^{1}H solvent shifts in the methylene protons are either small or slightly negative. This may be due to a magnetic anisotropic effect of the surrounding solvent molecules.

The current study shows that *meta*- and *para*-substituents in the aromatic ring of 2*r*-aryl-6*c*-phenylthians induce measurable change on the chemical shifts of carbons and protons of the thiane ring. This study also reveals some special effects of SO and SO$_2$ groups. This study also shows the use of NMR in studying molecules with nuclei differing in their chemical shifts by very small magnitude.

ACKNOWLEDGMENTS

The authors are thankful to SIF, Indian Institute of Science, Bangalore, for recording all the NMR spectra. The authors are also thankful to SAIF, Central Drug Research Institute, Lucknow, for providing elemental analysis data.

REFERENCES

1. Ramalingam, K.; Berlin, K. D.; Satyamurthy, N.; Sivakumar, R. Carbon-13 shifts in 1-hetera-2,6-diaryl-4-cyclohexanones and a few corresponding 1-hetera-4-cyclohexanols. *J. Org. Chem.* **1979**, *44*, 471–478.
2. Hasan, M. U.; Arab, M.; Pandiarajan, K.; Sekar, R.; Mako, D. Conformational analysis and ^{13}C NMR spectra of some 2,6-diarylpiperidin-4-ones. *Magn. Reson. Chem.* **1985**, *23*, 292–295.
3. Pandiarajan, K.; Sabapathy Mohan, R. T.; Krishnakumar, R. PMR & ^{13}C NMR spectral studies of some 2,6-diarylpiperidin-4-ones. *Indian J. Chem. B* **1987**, *26*, 624–627.
4. Pandiarajan, K.; Sekar, R.; Anandharaman, R.; Ramalingam, V.; Marko, D. Conformational studies of some piperidin-4-ones using PMR spectroscopy. *Indian J. Chem. B* **1991**, *30*, 490–493.
5. Kovacs, J.; Toth, G.; Simon, A.; Levai, A.; Koch, A.; Kleinpeter, E. ^{1}H, ^{13}C, ^{17}O NMR and quantum-chemical study of the stereochemistry of the sulfoxide and sulfone derivatives of 3-arylidene-1-thioflavan-4-one epoxides. *Magn. Reson. Chem.* **2003**, *41*, 193–201.
6. Srinivasan, M.; Perumal, S.; Selvaraj, S. A^{1,3}-Strain mediated epimerization of 2e,3e,5e,6e-tetraarylpiperidin-4-one oximes. *Magn. Reson. Chem.* **2004**, *42*, 1056–1059.
7. Pandiarajan, K.; Sabapathy Mohan, R. T.; Gomathi, R.; Muthukumaran, G. Synthesis and NMR spectral study of some *t*(3)-aryl-*r*(2),*c*(4)-bisethoxycarbonyl-*t*(5)-hydroxy-*c*(5)-methylcyclohexanones. *Magn. Reson. Chem.* **2005**, *43*, 430–434.
8. Pandiarajan, K.; Sabapathy Mohan, R. T.; Murugavel, K.; Hema, R. Synthesis and conformational study of some *r*(2),*c*(4)-bis(isopropoxycarbonyl)-*t*(3)-aryl-*c*(5)-hydroxy-*t*(5)-methylcyclohexanones using NMR spectra. *J. Mol. Struct.* **2008**, *875*, 226–235.
9. Coelho, P. J.; Fernandes, I. C.; Carvalho, L. M. ^{1}H and ^{13}C NMR signal assignments of some new spiro[7*H*-benzo[*de*]anthracenenaphthopyrans]. *Magn. Reson. Chem.* **2008**, *46*, 295–298.
10. Singh, G. S.; Pheko, T. Azetidin-2-one versus chroman-2-one: application of ^{1}H-^{13}C COSY NMR and mass spectroscopy in structure elucidation-class of compounds. *Spectrosc. Lett.* **2008**, *41*, 15–18.
11. Pedersoli, S.; Lombardi, L.; Hoehr, N. F.; Rittner, R. Assignments of ^{1}H and ^{13}C NMR spectral data for benzoylecgonine, a cocaine metabolite. *Spectrosc. Lett.* **2008**, *41*, 101–103.
12. Pandiarajan, K.; Christopher Newton Benny, J. ^{1}H NMR spectral study of some 2,6-diphenylthian-4-ones and their 1,1-dioxides. *Indian J. Chem. B* **2003**, *42*, 1711–1715.
13. Baliah, V.; Chellathurai, T. Conformational studies on heterocyclic compounds: part I – preparation & stereochemistry of some substituted tetrahydrothiapyran-4-ones & tetrahydrothiapyran-4-ols. *Indian J. Chem. B* **1971**, *9*, 424–429.
14. Thiruvalluvar, A.; Balamurugan, S.; Butcher, R. J.; Pandiarajan, K.; Devanathan, D. 2-(4-Fluorophenyl)-6-phenyltetrahydro-2H-thiopyran-4-one 1-oxide. *Acta Crystallogr. E* **2007**, *63*, 04486.
15. Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*; 6th ed, Wiley: New York, 1998; 229 pp.
16. Johnson, C. R.; McCants, D. Jr. The stereochemistry of oxidation of sulfur. Oxidation of 4-substituted thianes to sulfoxides. *J. Am. Chem. Soc.* **1965**, *87*, 1109–1114.
17. Van Acker, L.; Anteunis, M. Difference in the conformational preference of the sulfur-oxygen bond in 1,3-dithiane 1-oxides and 1,3-oxathiane 3-oxides. *Tetrahedron Lett.* **1974**, *2*, 225–228.
18. Khan, S. A.; Lambert, J. B.; Hernandez, O.; Carey, F. A. Oxides of 1,3-dithiane and 1,3,5-trithiane. The diamagnetic anisotropy of carbon-sulfur bonds. *J. Am. Chem. Soc.* **1975**, *97*, 1468–1473.
19. Harpp, D. N.; Gleason, J. G. Conformational analysis of sulfur-containing heterocycles. A dipolar effect. *J. Org. Chem.* **1971**, *36*, 1314–1316.
20. Bass, S. W.; Evans, S. A. Jr. Carbon-13 nuclear magnetic resonance spectral properties of alkyl disulfides, thiosulfinates and thiosulfonates. *J. Org. Chem.* **1980**, *45*, 710–715.
21. Juaristi, E.; Guzman, J.; Kane, V. V.; Glass, R. S. Conformational preference of the S→O bond. ^{1}H and ^{13}C NMR studies of the mono-S-oxides of 1,2-, 1,3- and 1,4-dithianes. *Tetrahedron* **1984**, *40*, 1477–1485.
22. Lambert, J. B.; Netzel, D. A.; Sun, H. N.; Lilianstrom, K. K. Carbon-13 chemical shifts of the pentamethylene heterocycles. *J. Am. Chem. Soc.* **1976**, *98*, 3778–3783.
23. Karplus, M. Contact electron-spin coupling of nuclear magnetic moments. *J. Chem. Phys.* **1959**, *30*, 11–15.

24. Haasnoot, C. A. G.; de Leeuw, F. A. A. M.; Altona, C. The relationship between proton-proton NMR coupling constants and substituent electronegativities-I an empirical generalization of the Karplus equation. *Tetrahedron* **1980**, *36*, 2783–2792.
25. Heydenreich, M.; Koch, A.; Kovacs, J.; Toth, G.; Kleinpeter, E. Electronic influences on $^3J(C,H)$ coupling constants via –S–, –S(O)– and $-SO_2-$: their determination, calculation and comparison of detection methods. *Magn. Reson. Chem.* **2004**, *42*, 667–670.
26. Abraham, R. J.; Byrne, J. J.; Griffiths, L.; Perez, M. ^1H chemical shifts in NMR: part 23, the effect of dimethyl sulphoxide *versus* chloroform solvent on ^1H chemical shifts. *Magn. Reson. Chem.* **2006**, *44*, 491–509.
27. Gurumani, V.; Pandiarajan, K.; Swaminathan, M. Conformational studies of some 1-hetera-2,6-diphenylcyclohexan-4-one oximes using NMR spectra – evidence for boat form contributions to *trans*-2,6-diphenyl systems. *Bull. Chem. Soc. Japan* **1997**, *70*, 29–35.