Asian Journal of Chemistry Vol. 16, No. 1 (2004), 245–250

Conformation Analysis of Some 2,6-Diphenylthian-4-one Derivatives Using ^1H and ^{13}C NMR Spectral Data

N. BHAVANI* and S. ASHA
Department of Chemistry
Annamalai University, Annamalai Nagar-608 002, India

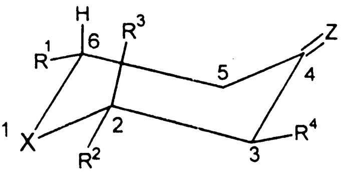
Four new thian-4-one derivatives, *viz.*, r-2,c-6-diphenylthian-4-one 1-oxide oxime (**1**), *t*-3-methyl-r-2,c-6-diphenylthian-4-one oxime (**2**), *t*-3-methyl-r-2,c-6-diphenylthian-4-one semicarbazone (**3**) and c-3-methyl-r-2,*t*-6-diphenylthian-4-one oxime (**4**) were synthesized and their ^1H and ^{13}C NMR spectra were recorded. In the light of the spectral data the conformations of these derivatives were derived. It has been found that compound (**1**) exists as an equilibrium mixture of chair form and boat form. In the boat form there is a possibility of intramolecular H-bonding between oxime hydrogen and S═O oxygen favouring it. Compounds (**2**) and (**3**) exist in chair form with —OH/—$NHCONH_2$ group **anti** to the methyl group and compound (**4**) exists in non-chair form.

Key Words: Conformational analysis, 2,6-Diphenylthian-4-one.

INTRODUCTION

The preparation of 2,6-diphenylthian-4-one was first reported by Arndt[1] and co-workers. Baliah[2] and Bhavani have reported the synthesis of both *t*-3-methyl-r-2,c-6-diphenylthian-4-one and c-3-methyl-r-2,*t*-6-diphenylthian-4-one by addition of hydrogen sulfide on 1,5-diphenyl-2-methyl-1,4-pentadien-3-one.

In the present paper the synthesis of four new thian-4-one derivatives



1. X = SO $R^1 = R^2 = Ph$ $R^3 = R^4 = H$ Z = NOH
2. X = S $R^1 = R^2 = Ph$ $R^3 = H, R^4 = CH_3$ Z = NOH
3. X = S $R^1 = R^2 = Ph$ $R^3 = H, R^4 = CH_3$ Z = $NNHCONH_2$
4. X = S $R^1 = R^3 = Ph$ $R^2 = H, R^4 = CH3$ Z = NOH

Scheme-1

(Scheme-1) and the conformational analysis of these derivatives with the aid of ^{1}H and ^{13}C NMR spectral data are reported.

EXPERIMENTAL

All the ketones were prepared by the reported[1, 2] procedure and their derivatives were prepared by condensing with respective bases.

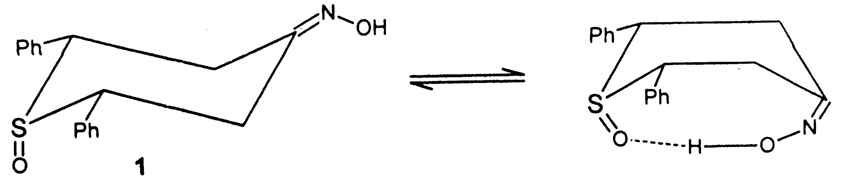
RESULTS AND DISCUSSION

It has been generally observed that in six membered ring ketoximes[3–6], the chemical shift difference between the two equatorial α-hydrogens is approximately 1 ppm, the *syn* α-hydrogen appearing at low field. This may be due to the interaction between N—O bond and the *syn* α(C—H) bond. This interaction induces a polarity in the α(C—H) bond so that the α-hydrogen acquires a slight positive charge and α-carbon a slight negative charge. The *syn* α-axial hydrogen is shielded compared to *anti* α-axial hydrogen. It is also shown that β-hydrogens *syn* to the —OH group are shielded. The shielding effect on the *syn* α-axial hydrogen and *syn* β-hydrogens may be due to the transfer of the negative charge on the *syn* α-carbon to the α-axial hydrogen and to the β-hydrogen through the *syn* β-carbon. Hence the effect of oximation is more pronounced on *syn* side, the carbon being shielded and hydrogen deshielded.

r-2, c-6-Diphenylthian-4-one 1-oxide Oxime

The parent ketone r-2, c-6-diphenylthian-4-one 1-oxide is found to exist in chair conformation with S=O group in axial orientation as evidenced from the downfield shift of H_{3a} and H_{5a} protons (0.8 ppm) compared to the sulfide ketone. This deshielding effect may be due to 1,3-interaction between the axial hydrogen and S=O axial. Though the equatorial sulfoxide may avoid this interaction, it will introduce dipole-dipole repulsion with the π electron clouds of the equatorial phenyl groups. Hence the S=O bond prefers axial orientation.

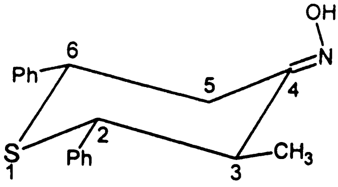
The various proton chemical shift assignments of the derivatives were made by comparison with the parent ketone chemical shifts. For ^{13}C assignments off-resonance decoupled spectra were used. Effect of oximation is observed in ^{1}H NMR chemical shift of r-2,c-6-diphenylthian-4-one 1-oxide oxime, the *syn* α-equatorial proton (H_{3e}) absorbs 1.1 ppm downfield compared to the *anti* α-equatorial proton (H_{5e}). The chemical shift difference (Table-1) between *syn* and *anti* α-axial protons (H_{3a} and H_{5a}) is 0.3 ppm. The smaller vicinal coupling constant for both the benzylic protons (13.7) compared to the ketone (13.9) may be due to flattening of the ring. The two benzylic carbons are shielded (*syn* benzylic 3.4 ppm and *anti* benzylic carbon 2.1 ppm) compared to the parent ketone. The chemical shift difference between the *syn* α-carbon and *anti* α-carbon is 8.1 ppm. Appearance of additional signals in ^{1}H and ^{13}C NMR spectra indicate the presence of more than one conformation for this oxime. It is more likely that the ring may adopt boat conformation in which there is a possibility of intramolecular H-bonding between oxime hydrogen and S=O oxygen. Thus the sulfoxide oxime exists as an equilibrium mixture of chair and boat forms.



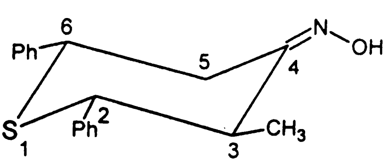
1

t-3-Methyl-r-2, c-6-diphenylthian-4-one oxime

Since the r-2,c-6-diphenylthian-4-one exists in chair form with the two phenyl groups in equatorial orientation, the methyl group in t-3-methyl-r-2,c-6-diphenylthian-4-one might also be expected to occupy the more stable equatorial position. The parent ketone is unsymmetrical, hence two configurational isomers (**2** and **2a**) are possible for t-3-methyl-r-2,c-6-diphenylthian-4-one oxime.



2



2a

A doublet at 4.1 ppm with J = 13.2 Hz is assigned to *anti* benzylic proton (H_2). The other benzylic proton which is *syn* to N—OH group appears as a broad doublet at 4.2 ppm with J = 15.2 Hz (this corresponds to $^{3}J_{6a,5a} + {}^{3}J_{6a,5e}$). A downfield shift of 0.9 ppm for H_{5e} indicates that N—OH group is *anti* to the methyl group. The large vicinal coupling constants of the two benzylic protons can be taken as evidence for the chair conformation of the ring. It can be seen from the ^{13}C chemical shifts (Table-2) of this oxime that the C-5 carbon resonates unfield compared to the C-3 carbon indicating that the C-5 carbon is *syn* to oxime —OH. Thus 3-methyl oxime is a single isomer existing in chair form with the oxime —OH *anti* to the methyl group (**2**). Moreover, the methyl protons give only one doublet supporting the presence of one isomer of the oxime.

t-3-Methyl-r-2,c-6-diphenylthian-4-one semicarbazone (3)

Since only one doublet is observed for methyl protons, this compound is also a single isomer. From the deshielded H_{5e} (*syn*) proton signal at 3.6 ppm it becomes clear that —NH—CO—NH_2 group is *anti* to the methyl group. ^{13}C NMR data show an upfield shift for C-5 carbon compared to the C-3 carbon indicating that C-5 carbon is *syn* to —NH—CO—NH_2 group.

In the two derivatives oxime (**2**) and semicarbazone (**3**), if the —OH or —NH—CO—NH_2 group is *syn* to the equatorial methyl group, then the two groups are coplanar leading to severe interaction between, them. To avoid this the oxime and semicarbazone are found as a single isomer with the —OH and —NH—CO—NH_2 group *anti* to the methyl group. Here again the ring must exist in chair form with two phenyl groups and methyl group in more stable equatorial orientation.

TABLE-1

^1H NMR DATA OF THIAN-4-ONES AND THEIR DERIVATIVES (δ In ppm, J in Hz)

Compound	Aromatic proton	H_2	H_6	H_{3a}	H_{3e}	H_{5a}	H_{5e}	Methyl protons	N=C–OH	NH_2	N–OH
r-2,c-6-Diphenylthian-4-one	7.4 (m)	4.33 (d) J = 12.2, 2.9	4.33 (dd) J = 12.2, 2.9	3.0 (t) J = 13.2, 12.2	2.9 (dd) J = 13.2, 2.9	3.0 (t) J = 13.2, 12.2	2.9 (dd) J = 13.2, 2.9	–	–	–	–
r-2,c-6-Diphenylthian-4-one 1-oxide	7.3 (m)	4.1 (dd) J = 13.9, 2.7	4.1 (dd) J = 13.9, 2.7	3.8 (t) J = 14.2	2.7 (d) J = 14.2, 2.7	3.8 (t) J = 14.2	2.7 (d) J = 14.2, 2.7	–	–	–	–
r-2,c-6-Diphenylthian-4-one 1-oxide oxime (1)	7.3 (m)	*syn* 3.9 (d) J = 13.7	*anti* 4.0 (d) J = 13.7	*syn* 3.3 (t) J = 14.2, 13.7	*syn* 3.8 (d) J = 13.2	*anti* 3.6 (t) J = 14.2, 13.7	*anti* 2.8 (d) J = 15.6	–	–	–	–
t-3-Methyl-r-2,c-6-diphenyl-thian-4-one	7.4 (m)	3.9 (d) J = 11.2	4.4 (dd) J = 12.5, 2.7	3.3–3.2 (m)	–	3.3–3.2 (m)	3.1 (dd) J = 12.7, 2.9	1.0 (d) J = 6.4	–	–	–
t-3-Methyl-r-2,c-6-diphenyl-thian-4-one oxime (2)	7.4 (m)	4.1 (d) J = 13.2	4.2 (d) J = 15.2	3.0 (dq)	–	2.5 (t) (b) J = 12.7	4.0 (d) J = 8.8	1.1 (d) J = 6.3	–	–	–
t-3-Methyl-r-2,c-6-diphenyl-thian-4-one semicarbazone (3)	7.4 (m)	3.9 (d) J = 10.7	4.2 (d) J = 10.8	2.9 (m)	–	2.6 (d) J = 12.7	3.6 (d) J = 11.7	0.9 (d) J = 6.8	9.5 (s)	6.2 (bs)	–
c-3-Methyl-r-2,t-6-diphenyl-thian-4-one	7.4 (m)	4.5 (d) J = 5.4	4.4 (dd) J = 8.6, 6.1	3.3 (t) J = 5.9, 6.3	–	3.1 (s)	3.2 (d) J = 2.4	1.2 (d) J = 6.8	–	–	–
c-3-Methyl-r-2,t-6-diphenyl-thian-4-one oxime (4)	7.5 (m)	4.3 (s)	4.4 (s)	3.5 (d) J = 6.3	–	3.2 (d) J = 5.3	3.3 (d) J = 5.4	1.3 (d) J = 6.8	–	–	8.5 (b)

dq: double quartet (not resolved), b: broad, bs: broad singlet, s: singlet, d: doublet, dd: doublet of doublet, m: multiplet.

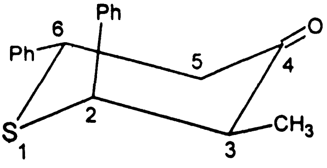
TABLE-2

^{13}C-CHEMICAL SHIFT (ppm) OF THIAN-4-ONES AND THEIR DERIVATIVES

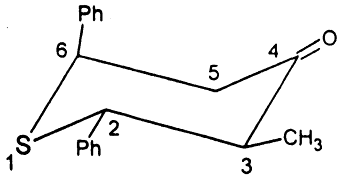
Compound	Benzylic carbons			*Ipso* carbons	Aromatic carbons	C═O	C═N	Me
	C-2, C-6	C-3	C-5					
r-2, c-6-Diphenylthian-4-one	48.5	50.5	50.5	139.3	128.9–127.1	208.0	–	–
r-2, c-6-Diphenylthian-4-one 1-oxide	62.9	37.9	37.9	143.3, 135.2	129.1–127.2	204.9	–	–
r-2, c-6-Diphenylthian-4-one 1-oxide oxime (1)	*syn* 59.5 *anti* 60.8	*syn* 19.2	*anti* 27.3	137.2	128.5, 128.0	–	152.6	–
t-3-Methyl-r-2, c-6-diphenyl-thian-4-one	55.4, 49.0	52.6	51.5	139.4, 138.6	128.8–127.2	209.6	–	12.1
t-3-Methyl-r-2, c-6-diphenyl-thian-4-one oxime (2)	55.0, 48.5	*anti* 47.1	*syn* 33.4	140.5, 139.6	127.9–126.9	–	156.9	14.6
t-3-Methyl-r-2, c-6-diphenyl-thian-4-one semicarbazone (3)	55.2, 47.0	*anti* 45,4	*syn* 35.9	140.5, 139.8	128.5–127.5	–	157.6, 150.6	14.2
c-3-Methyl-r-2, t-6-diphenyl-thian-4-one	51.2, 51.1	49.9	43.9	139.7, 139.6	128.7–127.2	210.6	–	13.6
c-3-Methyl-r-2, t-6-diphenyl-thian-4-one oxime (4)	48.9, 48.8	41.4	29.7	141.6, 141.2	128.8–127.3 (Six signals)	–	157.3	15.0

c-3-Methyl-r-2,t-6diphenylthian-4-one oxime

The parent ketones c-3-methyl-r-2,t-6-diphenylthian-4-one can have two chair forms (I) and (II).



I



II

For (II) the vicinal coupling constant between H_2 benzylic proton (axial) and H_3 proton (axial) should be around 10 Hz. But the observed coupling constant between these two protons is 5.4 Hz, less than the expected value. Hence the conformation (II) is excluded. For (I) the coupling constant $J_{2e,3a}$ should be *ca.* 4 Hz. Since the observed value is close to this, the compound should have the phenyl group at 2 position as axial. Ramalingam *et al.*[7] have proposed a flattened chair conformation for this ketone from single crystal X-ray analysis. The increased *cis* (a, e) coupling constant may be due to the flattening of the chair in the C-2, C-3 side.

The ^1H chemical shift data (Table-1) of oxime (4) indicate that there is no appreciable deshielding on the *syn* α-equatorial (H_{5e}) proton. Hence it is proposed that the oxime may exist in non-chair form where the effect of oximation is not pronounced on *syn* α-equatorial proton due to lack of coplanarity. The expected shielding is observed on the C-5 carbon (Table-2) indicating that it is *syn* to oxime OH. From the spectral data it is inferred that oxime (4) is also a single isomer, with the N—OH group *anti* to the methyl group, in order to avoid steric interaction with it. Since the parent ketone is known to exist in flattened chair form[7] the oxime may prefer a non-chair form.

REFERENCES

1. P. Arndt, P. Nachtwey and J. Pusch, *Ber.*, **58**, 1633 (1925).
2. V. Baliah, N. Bhavani and J. Chandrasekharan, *Indian J. Chem.*, **16B**, 942 (1978).
3. K. Pandiarajan, R.T. S. Mohan and M. Ul-Hasan, *Org. Magn. Reson.*, **24**, 312 (1986).
4. P. Geneste, R. Durand, C. Moreau and A. Pavia, *Org. Magn. Reson.*, **6**, 73 (1974).
5. P. Geneste, J.M. Kamenka and C. Brevard, *Org. Magn. Reson.*, **10**, 31 (1977).
6. G.C. Levy and G.L. Nelson, *J. Am. Chem. Soc.*, **94**, 4879 (1972).
7. K. Ramalingam, K.D. Berlin, R.A. Loghry, Dick Van der Helm and N. Satyamurthy, *J. Org. Chem.*, **44**, 447 (1979).

(*Received*: 16 April 2003; *Accepted*: 24 September 2003) AJC–3173