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# Synthesis and conformational studies of newly synthesized *cis*-2*r*,6*c*-distyryltetrahydro thiopyran-4-one and its oxime: Comparison of experimental and theoretical NMR spectral data

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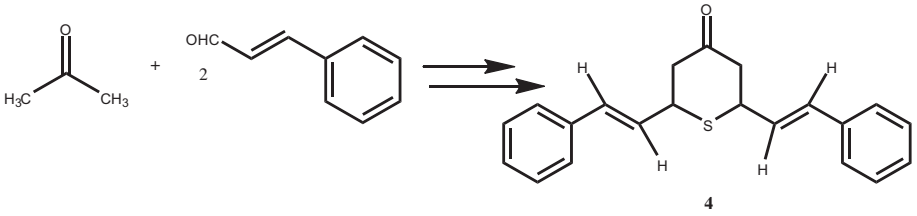
## HIGHLIGHTS

- *cis*-2*r*,6*c*-Distyryltetrahydro thiopyran-4-one and its oxime have been synthesized.
- Synthesis compounds have been characterized by using $^{1}H$, $^{13}C$ and 2D NMR spectra.
- Theoretical $^{1}H$ and $^{13}C$ have been calculated using DFT.
- Theoretical $^{1}H$ and $^{13}C$ NMR has been compared with observed $^{1}H$ and $^{13}C$ NMR spectra.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The *cis*-2*r*,6*c*-distyryltetrahydro thiopyran-4-one (**4**) was synthesized by the reaction of dicinnamylacetone with hydrogen sulphide. *cis*-2*r*,6*c*-distyryltetrahydro thiopyran-4-one oxime (**5**) was synthesized via oximination of **4**. The synthesized compounds were characterized by IR, NMR spectral studies and elemental analysis. The proton and carbon chemical shift values were unambiguously assigned using two dimensional NMR ($^{1}H$—$^{1}H$ COSY, HSQC, HMBC, NOESY) spectra. $^{1}H$ NMR and $^{13}C$ NMR chemical shifts of **4** were also obtained by the density functional theory (DFT) using 6-311++G(d,p) basis sets and the theoretical values were compared with experimental values.



## Introduction

The synthesis and biological activities of thiopyran containing molecules stand as an ever-expanding area of research in heterocyclic chemistry [1,2]. The thiopyran-4-one unit present in the thiochroman-4-one (**1**) (Fig. 1) heterocycles expresses potent biological activities [3]. Thiospiro-α-methylene-γ-butyrolactones (**2**) (Fig. 1) were reported for their significant biological activities [4]. Dithiomaltol (**3**) (Fig. 1) (Httma) and related ligands exhibited variety of biological activities such as metalloprotein protease inhibitors and as pro-oxidant cancer drugs [5]. These interesting activities have stimulated chemists to develop the chemistry of this class of compounds. Now days FT-IR and NMR spectroscopy combined with quantum chemical computations has been recently used as an effective tool in the vibrational analysis of drug molecules [6], biological compounds [7] and natural products [8]. This paper reports the synthesis and structural characterization of *cis*-2*r*,6*c*-distyryltetrahydro thiopyran-4-one and its oxime. The structures were elucidated on the basis of spectroscopic studies (IR, elemental analysis, and NMR). The complete assignment of the $^{1}H$ and $^{13}C$ NMR signals of **4** were achieved by 1D ($^{1}H$ and $^{13}C$) and 2D-

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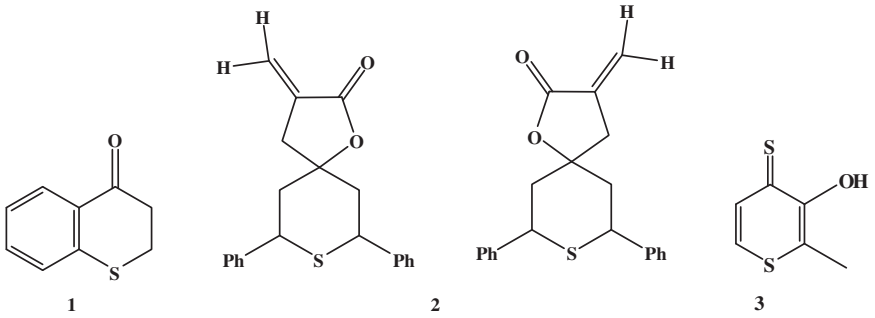



**Fig. 1.** Thiopyran-4-one unit containing potent biological activities heterocycles.

shift-correlated ($^1$H—$^1$H COSY, HSQC, HMBC and NOESY) NMR experiments. Whereas, compound **5** the assignment was made by using only $^1$H and $^{13}$C NMR experiments. Also the present work deals with DFT computations and the theoretical NMR spectral analysis of **4** are compared with experimental values.

## Experimental details

*cis*-2*r*,6*c*-Distyryltetrahydro thiopyran-4-one (**4**): To a boiling solution of sodium acetate (7.5 g), dicinnamylacetone (5 g) and 90% ethanol (40 mL), hydrogen sulfide gas was passed for 6–7 h. After completion of the reaction, the contents were cooled to 0 °C and the resinous mass formed was removed from the supernatant liquid by decantation. The supernatant liquid was kept at 0 °C for 2 days and the colorless crystals of *cis*-2*r*,6*c*-distyryltetrahydro thiopyran-4-one separated, filtered off, dried and recrystallized from petroleum ether to get the pure compound. mp 155–156 °C.

*cis*-2*r*,6*c*-Distyryltetrahydro thiopyran-4-one oxime (**5**): To a solution of **4** (50 mmol) and sodium acetate trihytrate (150 mmol) in boiling ethanol, hydroxylamine hydrochloride (60 mmol) was added. The mixture was heated under reflux for 15 min and poured into water, filtered and dried. The separated *cis*-2*r*,6*c*-distyryltetrahydro thiopyran-4-one oxime was recrystallized from ethanol. mp 168–169 °C.

The compounds were synthesized using the reaction shown in Scheme 1. The FT-IR spectrum of compounds **4** and **5** were recorded in the range of 4000–400 cm$^{-1}$ on AVATAR-330 FT-IR spectrophotometer (Thermo Nicolet) using KBr pellet technique at room temperature with a scanning speed of 30 cm$^{-1}$ min$^{-1}$ and a spectral resolution of 4.0 cm$^{-1}$. The $^1$H and $^{13}$C NMR spectral measurements were made in $CDCl_3$ in 5 mm NMR tubes. $^1$H and $^{13}$C NMR spectra were recorded at ambient temperature on a Bruker AMX 400 NMR spectrometer operating at 400.13 MHz for $^1$H and 100.62 MHz for $^{13}$C. The theoretical and experimental $^1$H and $^{13}$C spectra of compound **4** are shown in Fig. 2. The COSY spectrum of **4** is shown in Fig. 3.

## Computational details

The theoretical NMR spectra of **4** were performed with the Gaussian 03W software package [9] by using DFT method with B3LYP hybrid exchange–correlation functional [8,9] which have been previously shown to perform very well both for geometry optimizations and NMR spectra calculations [10]. The 6-311++G(d,p) basis set was used for calculations. In order to express the chemical shifts in ppm, the geometry of tetra methyl silane (TMS) molecule has been optimized and then its NMR spectrum was calculated by using the same method and basis set. The calculated Isotropic shielding constants $\sigma_i$ were then transformed to chemical shifts relative to TMS by $\delta_i = \sigma_{TMS} - \sigma_i$.

## Results and discussion

The compounds were synthesized using the reaction shown in Scheme 1. The numbering of carbon atoms in **4** also shown in 1.The protons are numbered accordingly. Thus, the proton on C-2 is denoted as H-2. The analytical and IR spectral data of compounds **4** and **5** are represented in Table 1. The $^1$H and $^{13}$C chemical shifts of compounds **4** and **5** are listed in Tables 2 and 3 respectively.

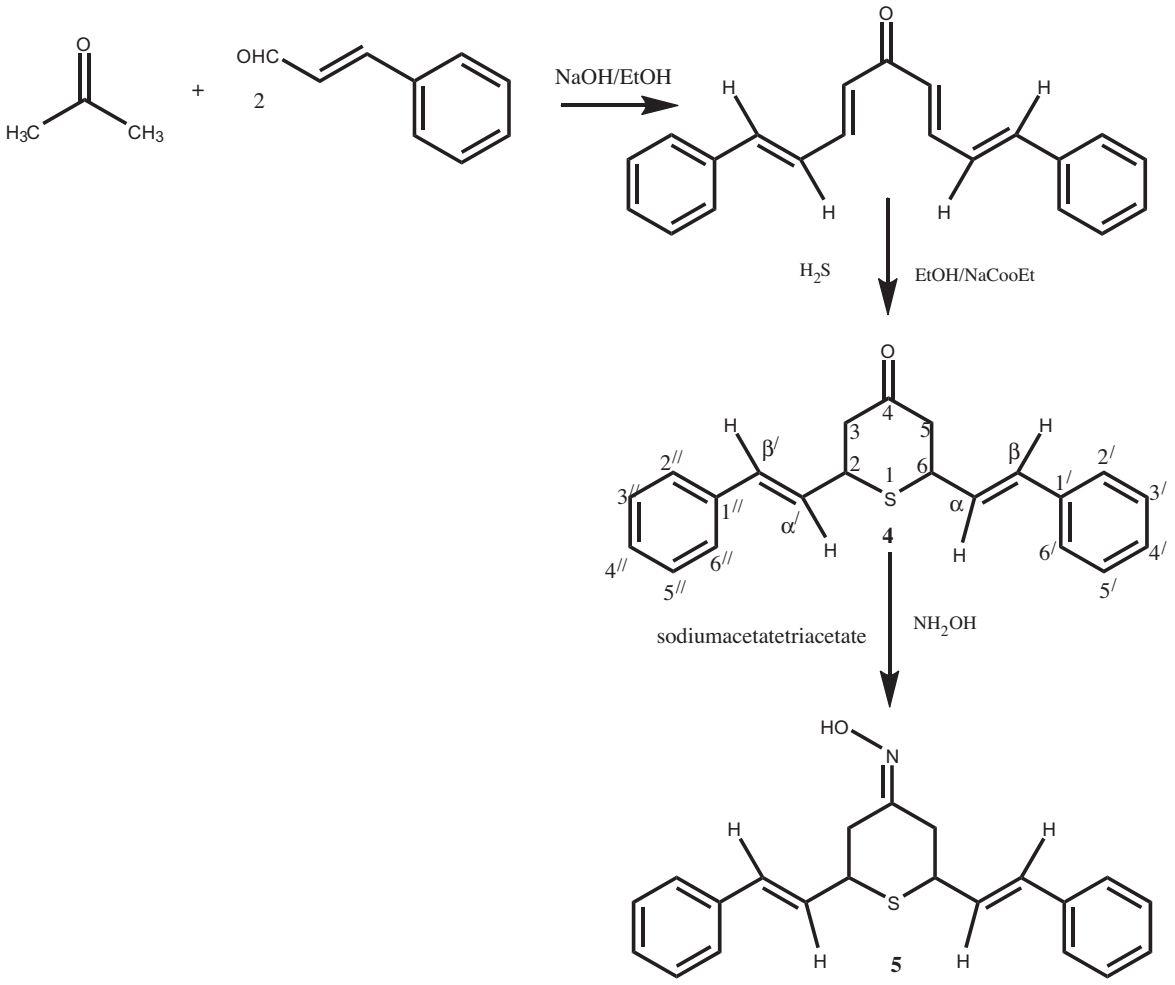
### *$^1$H NMR spectral analysis of cis-2r,6c-distyryltetrahydro thiopyran-4-one (**4**)*

In the $^1$H NMR spectrum of **4**, Aromatic protons appeared as a multiplet in the range 7.26–7.37 ppm [7.26($H'_4$ and $H''_4$), 7.32 ($H'_3$ and $H''_3$), 7.27($H'_2$ and $H''_2$)]. There are the signals at 6.15 and 6.63 ppm [$J$ = 15 Hz] due to the styryl protons [$H_\alpha$ and $H_\beta$]. On the basis of HOMOCOSY correlation, the signal at 6.15 ppm is due to $H_\beta$ proton [gives cross peak with 4.00 ppm (H-2) and 6.63 ppm ($H_\alpha$) Table 4]. The other signal at 6.63 ppm for $H_\alpha$ proton. The multiplet at 4.00 ppm is unambiguously assigned for benzylic protons at C-2 and C-6. This assignment is evident from the NOESY spectrum, where the signal shows strong NOE with the signal for methylene protons at C-3/C-5 and styryl protons. There are two double doublet at 2.86 and 2.72 ppm ($J$ = 5 Hz, 11.6 Hz) due to methylene protons. Among the two signals the one at 2.86 is due to H-3a and H-5a protons, whereas the other is due to H-3e and H-5e protons [11,12].

NOE spectrum of compound **4** (Table 4), gives useful information about the conformation of the styryl protons. The methylene protons at C-3 and C-5 have strong NOE with one of the styryl proton at 6.15 [$H_\beta$] than the other at 6.63 [$H_\alpha$]. Since the methylene protons are close proximity to $H_\beta$ proton. The styryl C=C bond has an E-configuration, which is evident from the scalar coupling between the H-α and H—β protons (15 Hz). The $^1$H chemical shifts for the **4** are listed in Table 2.

### *$^{13}$C NMR spectral analysis of cis-2r,6c-distyryltetrahydro thiopyran-4-one (**4**)*

In the $^{13}$C NMR spectrum of **4** there are three signals at 207.0, 136.6 and 132.6 ppm. In the HMBC spectrum of **4**, the signal at 207.0 ppm showed correlation with the axial and equatorial methylene protons only. Based on its position and the observed correlation, the signal could be readily assigned to the carbonyl carbon. The signal at 136.6 ppm showed correlation with the phenyl and styryl group protons and should be due to C-1′ and C-1″. The signal at 132.6 ppm showed correlation with benzylic and phenyl group protons and should be due to $C_\alpha$. The signal at 126.6 ppm, due to $C_\beta$, showed correlation with benzylic and methylene proton. The other three signals in aromatic region 128.6, 128.1 and




**Scheme 1.** Synthetic route of compounds.

127.3 ppm are due to meta(C-3′ and C-3″), para(C-4′ and C-4″), ortho(C-2′ and C-2″) respectively. The signal at 49.2 ppm showed correlation with carbonyl carbon and should be due to C-3 carbon. The remaining signal at 45.8 is due to C-2 carbon. These assignments were confirmed by the observed correlation in HSQC spectrum. The styryl group is shielded the α-carbon (C-2 and C-6) than the β-carbon (C-3 and C-5) comparing the corresponding thiopyran [13].

The assignment of H-α and H-β protons was obtained from HMBC spectrum as follows. The HMBC spectrum for **4** reveals interactions between the proton resonating at 6.15 ppm with carbons at 45.8, 49.2 and 136.6 ppm. As the signal at 49.2 ppm is due to the C-3carbon, the signal at 6.15 ppm can be unambiguously assigned to H-β. Consequently, the other proton resonating at 6.63 ppm can be assigned to H-α. This is also confirmed by the interaction between the proton at 6.63 ppm with the carbon at 45.8, 126.6 and 136.6 ppm in the HMBC spectrum. The $^{13}$C chemical shifts for the **4** are listed in Table 3.

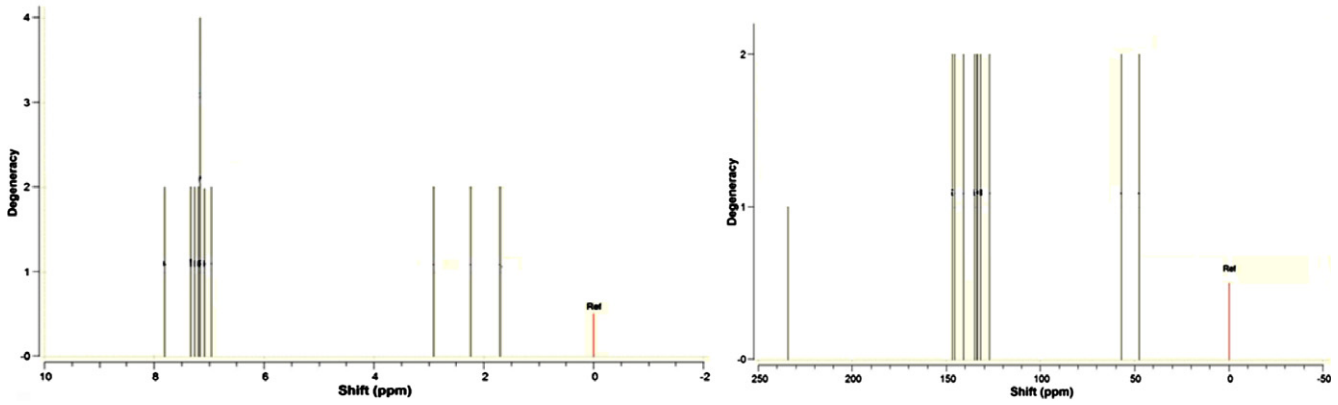
Generally dibenzalacetones afford both *cis* and *trans* thiopyrans when treated with hydrogen sulphide gas in the presences of sodium acetate in ethanol medium [14–17]. But this not the case with dicinnamylacetone which yields exclusively *cis* form due to the extended conjugation. The coupling constants reveal that the thiopyran ring exists in chair conformation with the equatorial orientation of aryl (styrene) group at C-2 and C-6. There are two possible chair conformations (**4a**, **4b**) with respect to orientation of protons in styrene group. The observed vicinal coupling constants for H-α (dd) are $J^3$ = 7.88 Hz; 15.7 Hz The observed vicinal coupling constant for H-2″ (d) is $J^3$ = 15.7 Hz. Which reveals that the protons H-2′ and H-2″ are in *trans* to each other and H-2 and H-2′ are *cis* to each other. Hence the compound **4** exists in chair conformation **4b**.

### *$^1$H and $^{13}$C NMR spectral analysis of cis-2r,6c-distyryltetrahydro thiopyran-4-one oxime (**5**)*

For compound **5**, the $^1$H and $^{13}$C chemical shifts are listed in Tables 2 and 3 respectively. The observed vicinal diaxial coupling constant $J_{\mathbf{5a,6a}}$ = 14.02 Hz, and the vicinal axial–equatorial coupling constant $J_{\mathbf{5e,6a}}$ = 2.95 Hz, whereas the germinal axial–equatorial coupling constants $J_{\mathbf{3a,3e}}$ and $J_{\mathbf{5a,5e}}$ are, respectively, 13.26 and 14.0 Hz (slightly varied due to the bulkier oximino group in place of the carbonyl carbon). Based on the obtained coupling constant values, normal chair conformation is proposed for compound **5** and depicted in Fig. 4. $J_{\mathbf{2a,3a}}$ **and** $J_{\mathbf{2a,3e}}$ are not resolved due to broadness of H-2a signal.

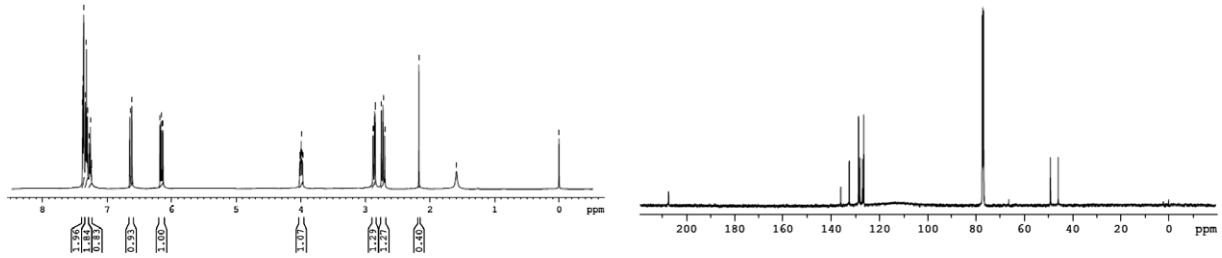
### *Effect of oximination*

Generally in six-membered heterocycles, decrease in electronegativity of a particular group in the ring skeleton shields the α-carbons and deshields the β- and γ-carbons [18]. Despite the less polar nature of the C=N than C=O bond, the electronegativity of the C=N—O—H group must be less than that of C=O group. All the $\Delta\delta$ ($\delta_{\text{thiopyran}} - \delta_{\text{oxime}}$) values for the thiopyran ring carbons of




$^{1}$H NMR spectrum of **4** in DFT method

$^{13}$C-NMR spectrum of **4** in DFT method




Observed $^{1}$H NMR spectrum of **4**

Observed $^{13}$C-NMR spectrum of **4**

**Fig. 2.** Computed and observed $^{1}$H, $^{13}$C and COSY spectra of **4**.

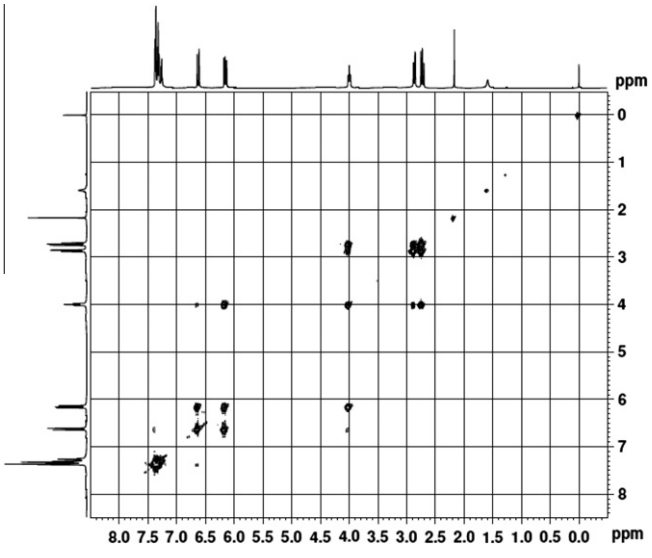



**Fig. 3.** Observed COSY spectrum of **4**.

the synthesized compound **5** are represented in Table 3. A perusal of the data in Table 3, Generally in ketoximes, the *syn* α-carbon is shielded than the *anti*-α-carbon, probably the chemical shift difference between the α-carbons is ($\Delta\delta_{\alpha}$) 7.6 ppm [19–22]. The difference in the chemical shift increases with a decrease in the dihedral angle between the C═N and C—α—H bonds. If the α-hydrogen lies in the NOC-α plane, the dihedral angle between them is zero. For such oximes the $\Delta\delta_{\alpha}$ value is around 7 ppm [22]. The $\Delta\delta_{\alpha}$ values of **5** are not much deviated from 7.0 ppm, because the compound **5** has appreciable possibility for the Chair conformation.

### *Theoretical NMR spectra*

Initially, molecular structures of the mentioned compounds are optimized. Then, gauge-including atomic orbital (GIAO) $^{13}$C and $^{1}$H chemical shift calculations of the compounds are made by using B3LYP method in conjunction with 6-311++G(d,p) basis set. The GIAO [23,24] method is one of the most common approaches for calculating nuclear magnetic shielding tensors. For the same basis set size GIAO method is often more accurate than those calculated with other approaches [25]. The NMR spectra calculations are performed by Gaussian 03 [9] program package. Chloroform ($CDCl_3$) is

**Table 1**
Analytical data for compounds **4** and **5**.

| Compds. | mp (°C) | Yield (%) | IR spectral data | Elemental analysis | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Calculated (%) | | | | Found (%) | | | |
| | | | | C | H | N | S | C | H | N | S |
| **4** | 155–156 | 75 | 1705, 2793 | 78.75 | 6.25 | – | 10.0 | 78.35 | 6.35 | – | 9.90 |
| **5** | 168–169 | 88 | 1640, 2803 | 75.22 | 6.27 | 4.18 | 9.55 | 75.10 | 6.29 | 4.25 | 9.33 |

**Table 2**
Computed and Observed $^{1}$H chemical shifts of **4** and **5** (with respect to TMS) (6-311++G(d,p)) ($\delta$, ppm).

| Protons | **4** (Experimental) | **4** (Theoretical) | **5** (Experimental) |
|---|---|---|---|
| H-2a | 4.00 | 2.91 | 3.91(d) |
| H-3a | 2.72 | 1.71 | 2.46(dd) |
| H-3e | 2.86 | 2.24 | 2.85(ddd) |
| H-5a | 2.72 | 1.71 | 2.11(dd) |
| H-5e | 2.86 | 2.24 | 3.80(dd) |
| H-6a | 4.00 | 2.91 | 3.86(dd) |
| H-β and H-β′ | 6.15 | 6.96 | 6.16 |
| H-α and H-α′ | 6.63 | 7.17 | 6.64 |
| Aromatic protons | 7.37(o), 7.32(m), 7.26(p) | 7.10(o), 7.17,7.20(p), 7.26,7.35(m) 7.83(o) | 7.24–7.49 |
| N—OH | – | – | 7.57 |

**Table 3**
Computed and observed $^{13}$C chemical shifts of **4** and **5** (with respect to TMS) (6-311++G(d,p)) ($\delta$, ppm).

| Carbons | **4** | | **5** (Experimental) | $\Delta\delta$ ($\delta_{\text{thiopyran}} - \delta_{\text{oxime}}$) |
|---|---|---|---|---|
| | Experimental | Theoretical | | |
| C-2 | 47.8 | 45.8 | 46.2 | −0.4 |
| C-3 | 57.2 | 49.2 | 39.5 | 9.7 |
| C-4 | 233.9 | 207.0 | 157.4 | 49.6 |
| C-5 | 57.2 | 49.2 | 31.9 | 17.3 |
| C-6 | 47.8 | 45.8 | 44.7 | 1.1 |
| C-β and C-β′ | 140.9 | 126.6 | 126.5 | 0.1 |
| C-α and C-α′ | 146.8 | 132.6 | 132.4 | 0.2 |
| Ipso carbons | 145.8 | 136.3 | 136.5 | −0.2 |
| Aromatic carbons | 127.0, 132.0 (o),133.4 (p), 133.9, 134.9 (m) | 127.3 (0), 128.6 (m), 128.1 (p) | 128.6, 128.1, 127.9, 127.3 | – |

**Table 4**
$^{1}$H–$^{1}$HCOSY, HSQC, HMBC, NOESY correlation spectral data of **4** ($\delta$, ppm).

| $^{1}$H NMR signals | Observed correlations | | | |
|---|---|---|---|---|
| | $^{1}$H–$^{1}$HCOSY | HSQC | HMBC | NOESY |
| 2.72 ($H_{3a}$ and $H_{5a}$) | 2.86, 4.00 | 49.2 (C-3) | 45.8, 126.6, 207.0 (C-4) | 2.86, 4.00, 6.15(S), 6.63(W) |
| 2.86 ($H_{3e}$ and $H_{5e}$) | 2.72, 4.00 | 49.2 (C-3) | 45.8, 126.6, 207.0 | 2.72, 4.00, 6.15(S), 6.63(W) |
| 4.00 ($H_2$ and $H_6$) | 2.72, 2.86, 6.15 | 45.8 (C-2) | 126.6 | 2.72, 2.86, 6.15, 6.63 |
| 6.15 ($H_\beta$) | 4.00, 6.63 | 126.6 ($H_\beta$) | 45.8, 49.2, 136.2 (C-1′) | 2.72(S), 2.86(W), 6.63, 7.37 |
| 6.63 ($H_\alpha$) [15 Hz] | 6.15 | 132.6 ($H_\alpha$) | 45.8, 126.6, 136.2 | 2.72, 2.86, 6.15, 7.37 |
| 7.26 ($H'_4$ and $H''_4$) | – | 128.1 (C-4′) | 128.6, 132.6, | – |
| 7.32 ($H'_3$ and $H''_3$) | – | 128.6 (C-3′) | 136.6, 128.1 | – |
| 7.37 ($H'_2$ and $H''_2$) | – | 127.3 (C-2′) | 127.3 | 2.86, 6.15(S), 6.63(W) |

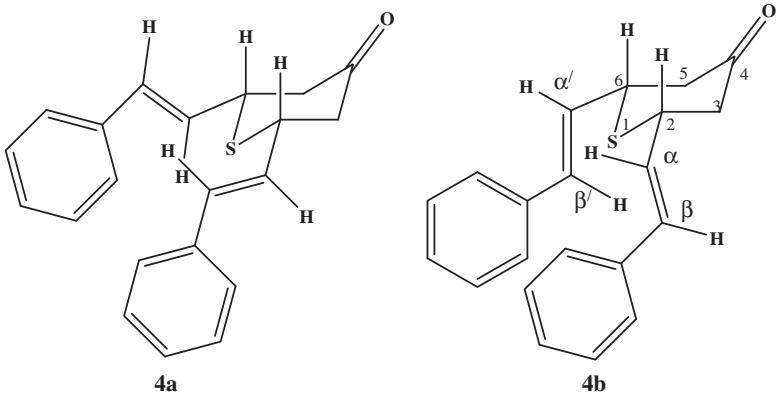



**Fig. 4.** Possible conformation of the compound **4**.

used as a solvent. Relative chemical shifts are estimated by using the corresponding TMS shielding in advance at the same theoretical level as the reference. $^{13}$C and $^{1}$H isotropic magnetic shielding (IMS) of any X carbon (or hydrogen) atom is made according to the value $^{13}$C IMS of TMS:CSx = IMSTMS − IMSx. Theoretical and experimental $^{1}$H and $^{13}$C NMR spectra chemical shifts of compound are gathered in Tables 2 and 3. $^{1}$H atom is the smallest of all atoms and mostly localized on periphery of molecules; therefore their chemical shifts would be more susceptible to intermolecular interactions in the aqueous solutions as compared to that for other hea-

vier atoms. Taking into account that the range of $^{13}C$ NMR chemical shifts for a typical aromatic compound usually is >100 ppm [10,26] the accuracy ensures reliable interpretation of spectroscopic parameters. In the present paper, $^{13}C$ NMR chemical shifts the ring in the title compound are >100 ppm, as they would be expected (in Table 3). The proton chemical shifts of H-2, H-3a and H-3e are deshielded. Likewise, the $^{13}C$ chemical shifts of C(3) and C(5) are also deshielded. This is due to the presences of electro negative oxygen and the electronic effects over carbon atoms in the ring. As seen in Tables 2 and 3, the calculated chemical shifts for $^{1}H$ are more sensitive to that of $^{13}C$. Isotropic $^{1}H$ and $^{13}C$ chemical shifts of molecules calculated by means of B3LYP method are closer to experimental data.

## 5. Conclusions

The synthesized compounds *cis*-2*r*,6*c*-distyryltetrahydro thiopyran-4-one and its oxime (**4** and **5**) were characterized by IR, NMR spectra and elemental analysis. All the spectral data support and confirm the formation of the target compounds. Well-pronounced oximination effect is Observed on thiopyran ring carbons and the associated protons. The oximination effect is extended up to ipso carbons. We have carried out DFT calculations on the structure of **4**. The calculated $^{1}H$ NMR and $^{13}C$ NMR by B3LYP/6-311++G(d,p) method were in good consistent with experimental results. The assignments made at higher level of theory with higher basis set with only reasonable deviations from the experimental values, seemed to be correct. This study demonstrated that scaled DFT/B3LYP calculations are powerful approach for understanding the NMR spectra of medium sized organic compounds.

## Acknowledgments

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