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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

Venkataraman Gurumani, Karuppiah Pandiarajan,* and Meenakshisundaram Swaminathan

Department of Technology, Annamalai University, Annamalainagar - 608002, India

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^{1}H NMR spectra have been recorded for *cis*- and *trans*-2,6-diphenyltetrahydrothiopyran-4-ones (**1** and **5**), *cis*- and *trans*-2,6-diphenyltetrahydropyran-4-ones (**2** and **6**), 3-methyl- and 3-ethyl-2,6-diphenyltetrahydropyran-4-ones (**3** and **4**) and their oximes (**7** — **12**) at 270 MHz. For the oximes, ^{13}C NMR spectra have also been recorded. The coupling constants suggest that the oximes **7**, **8**, **9**, and **10**, which have the phenyl groups in *cis* orientation, largely exist in chair conformations with equatorial disposition of the substituents. Analysis of the vicinal coupling constants of *trans*-2,6-diphenyltetrahydrothiopyran-4-one oxime (**11**) suggests that boat forms **11c** and **11d** must make significant contributions to it. Moreover, chair conformation **11a**, which has the axial phenyl group in the *syn*-side, should be more populated than chair conformation **11b**, which has the axial phenyl group in the *anti*-side. These conclusions are corroborated using ^{13}C chemical shifts. The NOESY spectrum of **11** gives definite evidence for the contribution of **11c**. The coupling constants of **12** suggest that the chair conformation **12a** with axial phenyl group in the *syn*-side should be more populated than chair conformation **12b** with the axial phenyl group in the *anti*-side. By analogy boat form should contribute to **12** also.

NMR spectroscopy has been widely used in stereochemical studies. For example, the conformation of bicyclo[5.2.1]decane-2,6-dione has been investigated$^{1)}$ using NMR techniques. Recently, from the vicinal coupling constants of 1,2-ethanediol, it has been found that in solution *anti* rotamer should be an important contributor to this molecule.$^{2)}$

Considerable work has been carried out on the NMR spectra of ketoximes$^{3—8)}$ and the configurations and conformations of the oximes have also been determined using NMR techniques. It has been found$^{3—5)}$ that in ketoximes the α-carbon *syn* to the OH group is shielded relative to the *anti* α-carbon and the magnitude of this shielding, denoted as $\Delta\delta_\alpha$, has been used for determining the conformations of oximes. Indeed a twist-boat conformation has been assigned to *trans*-2,6-di-*t*-butylcyclohexanone oxime, based on a small $\Delta\delta_\alpha$ for this compound.$^{5)}$

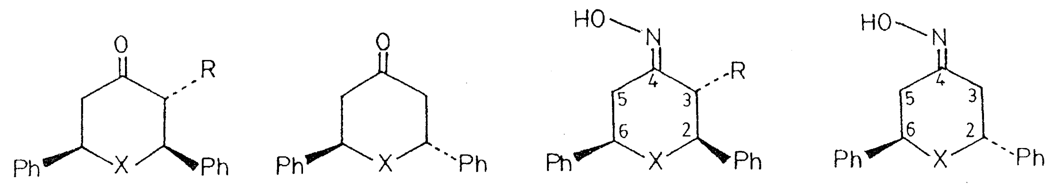
Conformations of several 2,6-diarylpiperidin-4-one oximes have been studied$^{7)}$ using ^{1}H and ^{13}C NMR spectra. For the oximes of 2,6-diarylpiperidin-4-ones and their 3-alkyl derivatives, chair conformation has been assigned and for the oximes of 3,5-dimethyl-2,6-diarylpiperidin-4-ones with *cis* methyl groups an asymmetric non-chair conformation has been assigned.$^{7)}$ In continuation of the study on 2,6-diarylpiperidin-4-one oximes, we thought that it will be worthwhile to investigate the corresponding oxygen and sulfur analogues. This is because in such cases *cis*- and *trans*-diphenyl compounds are available, whereas in the case of piperidin-4-ones only the *cis*-diphenyl compounds have been synthesized. For the *trans*-2,6-diphenyl compounds, in addition to two different chair conformations, boat forms also may contribute and it is worth finding which ones are more important. Study of these oximes is particularly advantageous in that these compounds give well separated signals for the heterocyclic ring protons. Such data enable one to measure the vicinal coupling constants to a desirable accuracy. In this paper we report a detailed ^{1}H and ^{13}C NMR spectral study of ketones **1**—**6** and their corresponding oximes **7**—**12** (Chart 1).

Experimental

The ketones were prepared according to the procedures described in the literature: **1**,$^{9)}$ **2**,$^{10)}$ **4**,$^{12)}$ **5**,$^{9)}$ and **6**.$^{13)}$ The oximes were prepared according to the procedure of Baliah et al.$^{14)}$ The compounds were recrystallized from suitable solvents and the melting points of the ketones$^{9—13)}$ and oximes$^{15)}$ were in excellent agreement with the reported values.

NMR Measurements. ^{1}H NMR spectra: Proton NMR spectra at 270 MHz were recorded on a Bruker WH-270 NMR spectrometer operating at a field of 6.35 Tesla. Samples were prepared by dissolving about 10 mg of material in 0.5 ml of chloroform-*d* containing 1% TMS. About a hundred FIDs were accumulated for each sample. Spectral width was 3000 Hz and the data points were 16 K. For **12** the spectrum was also recorded at 400 MHz on a Bruker AMX-400 NMR spectrometer with 4000 Hz spectral width and 16K data points.

^{13}C NMR spectra: Proton decoupled ^{13}C spectra were recorded on a Bruker WH-270 NMR spectrometer operating at 67.89 MHz for ^{13}C nucleus using 10 mm sample tubes. Samples were prepared by dissolving 0.5 g of the material in 2.5 ml of chloroform-*d* containing a few drops of TMS. The experimental parameters were as follows: spectral width, 18600 Hz; data points, 32K; pulse angle 45°; and number of transients, 5000.



(1) X=S, R=H
(2) X=O, R=H
(3) X=O, R=CH_3
(4) X=O, R=C_2H_5

(5) X=S
(6) X=O

(7) X=S, R=H
(8) X=O, R=H
(9) X=O, R=CH_3
(10) X=O, R=C_2H_5

(11) X=S
(12) X=O

Chart 1.

2D spectra: C–H HETCOR and NOESY spectra of **11** were recorded on a Bruker AMX-400 spectrometer using standard experimental parameters.

Results and Discussion

For **1**, **2**, **5**, and **6**, ABX spectra were obtained for the heterocyclic ring protons, the benzylic proton being the X-part and the methylene protons forming the AB part. The vicinal coupling constants could be readily obtained by a second-order analysis.16)

In the cases of **3** and **4**, the signal due to the proton at C-3 overlapped with those due to the methylene protons at C-5 and therefore, J_{5a6a} and J_{5e6a} could not be evaluated. However, the value of J_{2a3a} and the sum of J_{5a6a} and J_{5e6a} were obtained.

In all the oximes studied the *syn*-side protons formed an AMX system and the coupling constants could be readily extracted. For the oximes **7**, **8**, and **11**, *anti*-side protons formed an ABX system and the vicinal coupling constants were determined by a second-order analysis. For oxime **12** the *anti*-side methylene protons appeared only as a doublet and the *anti*-side benzylic proton appeared only as a triplet even at 400 MHz, due to a very small chemical shift difference between the *anti*-methylene protons. Therefore, only the sum of the vicinal coupling constants could be determined. For oximes **11** and **12**, the assignments were confirmed by selective decoupling of the benzylic protons.

The proton chemical shifts of ketones and oximes are furnished in Table 1. The coupling constant data are given in Table 2. The measured coupling constants may have 2—20% error depending on the broadening of the lines.17) The error would be within 2% when the spectral lines are sharp. In the present study, very sharp spectral lines were observed in all cases and the reported coupling constants should be accurate to within 2%. The coupling constants are given to three significant figures. For **12** the coupling constants and chemical shifts obtained from 270 and 400 MHz spectra are in excellent agreement.

The ^{13}C chemical shifts were assigned as follows; the signal in the range 155—160 ppm could be readily assigned to the hydroxylimino carbon C-4. The signals in the range 125—142 ppm must be due to the aromatic carbons.

The aromatic carbons except *ipso* carbons should be expected to absorb around 128 ppm, at which benzene absorbs. Therefore, the signals in the range 125—129 ppm were assigned to these carbons. The weak signals around 140—142 ppm could be assigned to *ipso* carbons. The signals in the range 25—90 ppm could be assigned to the heterocyclic ring carbons and those in the range 10—20 ppm could be

Table 1. Proton Chemical Shifts (δ/ppm) of Ketones and Oximes

Compd	H_2	H_{3a}	H_{3e}	H_{5a}	H_{5e}	H_6	Alkyl	Aryl	N–OH
1	4.30	3.02	2.94	3.02	2.94	4.30	—	7.22 to 7.39	—
2	4.84	2.73	2.69	2.73	2.69	4.84	—	7.32 to 7.47	—
3	4.34	a)	—	a)	a)	4.82	0.87	7.13 to 7.45	—
4	4.45	b)	—	b)	b)	4.80	1.18,1.58,c)0.79	7.23 to 7.47	—
5	4.31	3.13d)	3.01e)	3.13d)	3.01e)	4.31	—	7.20 to 7.31	—
6	5.05	2.84d)	2.76e)	2.84d)	2.76e)	5.05	—	7.17 to 7.36	—
7	4.20	2.77	2.92	2.37	3.96	4.14	—	7.26 to 7.48	8.04
8	4.72	2.46	2.71	2.12	3.67	4.66	—	7.26 to 7.55	8.12
9	4.29	2.65	—	2.19	3.79	4.67	0.96	7.26 to 7.49	9.44
10	4.44	2.57	—	2.19	3.81	4.68	1.36,1.62,c)0.92	7.26 to 7.49	9.39
11	4.12	3.01d)	2.98e)	3.52d)	3.10e)	4.34	—	7.24 to 7.49	8.27
12	4.79	2.73d)	2.73e)	3.39d)	2.86e)	5.16	—	7.26 to 7.54	8.23

a) Peaks overlap and were in the range 2.69 to 2.86. b) Peaks overlap and were in the range 2.61 to 2.87. c) For the methylene protons of the ethyl group. d) Hydrogen *cis* to phenyl. e) Hydrogen *trans* to phenyl.

Table 2. Vicinal Coupling Constants (Hz) of Ketones **1**—**6** and Oximes **7**—**12**

Compd	About C(2)–(3) bond			About C(5)–(6) bond		
	J_{cis}	J_{trans}	J_{total}	J_{cis}	J_{trans}	J_{total}
1	2.86	12.6	15.5	2.86	12.6	15.5
2	2.56	11.7	14.2	2.56	11.7	14.2
3	—	10.4	—	—	—	14.3
4	—	10.4	—	—	—	14.4
5	4.46	8.19	12.7	4.46	8.19	12.7
6	5.07	6.74	11.8	5.07	6.74	11.8
7	2.41	12.2	14.6	2.36	12.3	14.7
8	2.11	11.6	13.7	2.42	11.8	14.2
9	—	10.2	—	2.53	11.8	14.3
10	—	10.3	—	2.33	11.7	14.0
11	3.59	10.0	13.6	4.54	7.32	11.9
12	—	—	12.6	5.52	5.03	10.5
	—	—	12.7[a]	5.53[a]	5.21[a]	10.7[a]

[a] Values from 400 MHz spectrum.

assigned to the side chain alkyl carbons. Among the four signals for the heterocyclic ring carbons, two upfield signals could be assigned to the α-carbons (carbons α to the C=N–OH group). Among these two signals, the upfield signal could be assigned to the *syn* α-carbon.[3—5,8]

In the 3-alkyl substituted oximes **9** and **10**, C-2 should appear at a lower field than C-6 due to the β-effect of the alkyl group. Since it has been shown[8] that in *cis*-2,6-diphenylpiperidin-4-one oxime the *syn* β-carbon appears at a slightly higher field than the *anti* β-carbon, in oximes **7**, **8**, **11**, and **12**, among the two signals for the benzylic carbons the upfield signal was assigned to the *syn* benzylic carbon. For **11** the assignments were confirmed using C–H HETCOR spectrum. The ^{13}C chemical shifts of the oximes are given in Table 3. The ^{13}C chemical shift differences between the α-carbons are listed in Table 4.

Oximes of *cis* Ketones. In oximes **7** and **8**, the vicinal coupling constants in the *syn*-side are very nearly the same as those in the *anti*-side. One vicinal coupling constant is about five times that of the other. The larger value must correspond to J_{aa} and the lower value must correspond to J_{ae}. Hence, these compounds should largely exist in chair conformations with equatorial orientations of the phenyl groups. The coupling constants in **8** are lower than those in **7**, probably due to the electronegativity of oxygen being greater than that of sulfur.

Table 4. ^{13}C Chemical Shift Difference between the α-Carbons ($\Delta\delta_\alpha$) in Oximes **7**—**12** and Ketones[25] **1**—**6**

Oxime	Ketone	($\delta_{anti}-\delta_{syn}$)/ppm		
		Oxime	Ketone	(Oxime − Ketone)
7	**1**	7.8	0	7.8
8	**2**	6.6	0	6.6
9	**3**	9.6	1.5	8.1
10	**4**	15.8	7.5	8.3
11	**5**	7.7	0	7.7
12	**6**	7.9	0	7.9

In oximes **9** and **10**, the J_{aa} value in the *syn*-side is about 1.5 Hz higher than that in the *anti*-side. A similar observation has been made in the case of 2,6-diarylpiperidin-4-ones.[18] This has been attributed to a flattening of the ring about the C(2)–C(3) bond, which probably occurs to decrease the *gauche* interaction between the phenyl and methyl groups.

The vicinal coupling constants of **7** and **8** are slightly lower than those of the corresponding ketones. In the oximes the ring torsional angles about C(2)–C(3) and C(5)–C(6) bonds may be slightly lower than those in the corresponding ketones.

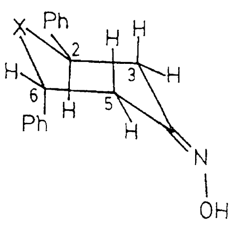
For oximes from symmetric ketones, the $\Delta\delta_\alpha$ value increases with the decrease in the torsional angle between the C=N and C_α–H bonds.[3—6] In the chair conformations of six-

Table 3. ^{13}C Chemical Shifts (δ/ppm) of the Oximes

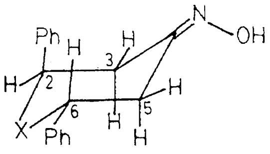
Compd	C-2	C-3	C-4	C-5	C-6	Alkyl	Aromatic carbons	
							ipso Carbonx	Others
7	49.4	41.0	158.6	33.2	47.9	—	140.3, 140.4	128.8, 128.0, 127.4
8	79.7	39.6	156.5	33.0	78.4	—	141.6, 141.8	128.6, 127.9, 125.9
9	86.8	43.1	159.2	33.5	78.7	11.1	140.4, 141.8	128.5, 127.8, 127.5, 125.9
10	85.3	49.7	157.7	33.9	78.6	18.5 (CH_2) 11.6 (CH_3)	140.4, 141.8	128.5, 128.3, 127.7, 127.6 125.9
11	43.6	38.9	157.7	31.2	43.1	—	141.0, 141.4	128.7, 128.6, 127.7, 127.5
12	73.1	36.8	155.7	28.9	72.9	—	140.3, 141.1	128.6, 127.9, 127.8, 127.0 126.6

membered ring oximes, the torsional angle between C=N and C_{α}–H_e bonds is nearly 0°. For such oximes the $\Delta\delta_{\alpha}$ value is around 7 ppm. The $\Delta\delta_{\alpha}$ value of **7** and **8** do not deviate much from 7.0 ppm, suggesting that these compounds largely exist in chair conformations.

Oximes of *trans* Ketones. For oxime **11**, two nonequivalent chair conformations, **11a** and **11b**, are possible (Chart 2). In addition we consider boat forms **11c**, **11d**, **11e**, and **11f**, and twist-boat form **11g** (Charts 3, 4, and 5). Among the two vicinal coupling constants in one side the larger one is taken as J_{trans} and the smaller one is taken as J_{cis}. The reverse assignment could be ruled out as follows: In a reverse assignment, the J_{cis} values in the two sides should be 10.0 and 7.3 Hz. These values should correspond to conformation **11e** or **11f**, with a greater distortion at the *syn* side. However, the two J_{trans} values are not much different and such a conformation could thus be ruled out. Recently,[19] it has been shown that **5** exists in boat conformation **5c** analogous to **11c**, from its vicinal coupling constants, taking J_{trans} to be larger than J_{cis}. A reverse assignment would suggest conformation **5e** for **5** (Chart 6). However, such a possibility could be ruled out since the dipole moment of **5** (5.54 aCpm) is only slightly higher than that of **1**[20] (4.87 aCpm). In **5e** the angle between the directions of the moments due to the carbonyl (9.77 aCpm)[20] and sulfide (6.17 aCpm)[20] functions should be acute. If this angle is taken as 90°, the calculated dipole moment is 11.56 aCpm. Therefore, the dipole moment of **5e** should be greater than 11.56 aCpm. Since the observed moment of **5** is considerably lower than that expected for **5e**, **5e** cannot be the major conformation of **5**. This conclusion must apply to **11** also. Therefore, the higher values could be assigned to the coupling constants between *trans* protons and the lower values could be assigned to those between *cis* protons.

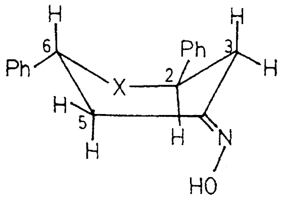


11a, X = S
12a, X = O

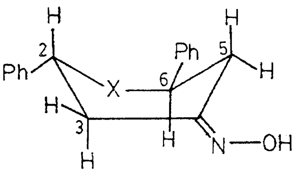


11b, X = S
12b, X = O

Chart 2.

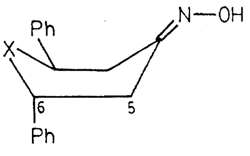


11c, X = S
12c, X = O

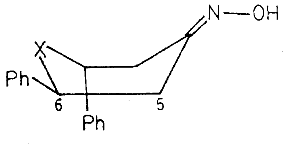


11d, X = S
12d, X = O

Chart 3.

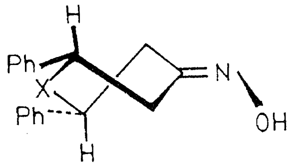


11e, X = S
12e, X = O



11f, X = S
12f, X = O

Chart 4.

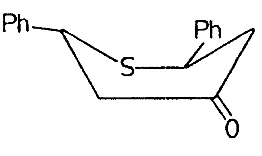


11g, X = S
12g, X = O

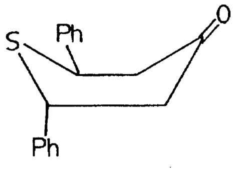
Chart 5.

Using the equation of Haasnoot et al.,[21] we found that a 5° degree variation in the torsional angle in the range 180° cannot significantly alter the vicinal coupling constant whereas a similar change in the torsional angle in the range 60° markedly affects the value of the coupling constant. Because of this, though **11a** and **11b** are likely to be more flattened than the chair conformation of **7**, their J_{aa} value may be taken as 12.3 Hz (average of the two J_{aa} values of **7**) but their J_{ee} value may be considerably less than 2.4 Hz (observed J_{ae} of **7**). Thus, for **11a** and **11b** the value of $J_{trans(\mathrm{total})}$ should be somewhat less than 14.7 Hz (12.3+2.4). The observed $J_{trans(\mathrm{total})}$ value of **11** is 17.3 Hz, which is considerably higher than that expected for chair conformation **11a** or **11b**. However, the observed J_{cis} values are not too high. Indeed $J_{cis(\mathrm{total})}$ of **11** is less than that of the corresponding ketone **5** but $J_{trans(\mathrm{total})}$ of **11** is higher than that of **5**. This suggests that boat forms with high $J_{trans(\mathrm{total})}$ values but not too high $J_{cis(\mathrm{total})}$ values should contribute to **11** in solution. Only **11c** and **11d** meet these requirements.

Moreover, for **11** the observed $J_{trans(syn)}$ value is very much lower than the $J_{trans(anti)}$ value. Only in the chair conformations **11a** and **11b** the two J_{trans} values could differ largely. Therefore, the lower $J_{trans(syn)}$ value should be due to a lower contribution of J_{aa} and a greater contribution of J_{ee} to it. In other words, conformation **11a** should be more populated than conformation **11b**. Thus we conclude that **11** exists in



5c



5e

Chart 6.

solution as an equilibrium mixture of **11a**, **11b**, **11c**, and **11d**.

The vicinal coupling constants in **11c** should be almost equal to the corresponding vicinal coupling constants in **11d**. Thus, in **11c** and **11d** $J_{trans(anti)}$ value may be taken as the same and this may be designated as $J^{boat}_{trans(anti)}$. Let X_a, X_b, and X_{boat} be the mole fractions of **11a**, **11b**, and boat forms. If we assume reasonable values for $J^{boat}_{trans(syn)}$ and $J^{boat}_{trans(anti)}$ and take J_{aa} as 12.3 Hz and J_{ee} as less than 2.4 Hz, X_a, X_b, and X_{boat} could be calculated using equations **1** and **2**, since the sum of X_a, X_b, and X_{boat} should be one.

$$X_aJ_{ee} + X_bJ_{aa} + X_{boat}J^{boat}_{trans(syn)} = 7.3[J^{obs}_{trans(syn)}] \cdots 1,$$
$$X_aJ_{aa} + X_bJ_{ee} + X_{boat}J^{boat}_{trans(anti)} = 10.0[J^{obs}_{trans(anti)}] \cdots 2.$$

Calculations were made assuming J_{ee} as 2.0, 1.5, and 1.0 Hz. Various values were assume for $J^{boat}_{trans(anti)}$. The value of $J^{boat}_{trans(syn)}$ was taken as one Hz less than the assumed value of $J^{boat}_{trans(anti)}$ since the observed $J_{cis(syn)}$ is higher than the observed $J_{cis(anti)}$ by 0.9 Hz. When J_{ee} was taken as 2.0 Hz and $J^{boat}_{trans(anti)}$ was taken as 12 Hz the calculated values of X_a, X_b, and X_{boat} are 0.45, 0.21, and 0.34, respectively. Use of lower values for J_{ee} and $J^{boat}_{(trans)}$ couplings was found to decrease the values of X_a and X_b and increase the value of X_{boat}. Moreover, the value of X_a was found to be more than twice that of X_b. Though it is not possible to obtain the relative populations more precisely, it is certain that the boat forms should contribute significantly to **11**, and **11a** should be more populated than **11b**.

Using the β-effects of axial and equatorial phenyl groups[22] on the C-13 chemical shifts, the $\Delta\delta_\alpha$ values for **11a** and **11b** were computed as 12.1 and 3.1 ppm, respectively. The $\Delta\delta_\alpha$ value for the boat forms may be taken as that of *trans*-3, 5-di-*t*-butylcyclohexanone oxime, i.e., 3.5 ppm.[5] The observed $\Delta\delta_\alpha$ value of **11**, is 7.7 ppm, which is consistent with the conformational equilibrium suggested by the vicinal coupling constants.

The NOESY spectrum of **11** is shown in Fig. 1. From the signals in the vertical direction, five NOEs could be identified between protons not involved in direct coupling. NOE-1 is between H-6 and the ortho protons of the (C-6)-phenyl group. Such an NOE could occur in **11b**, **11c**, and **11d**. In **11b**, **11c**, and **11d** the (C-6)-phenyl group should be almost coplanar with H-6. Two such equivalent conformations are possible. However, such conformations have been shown to be interconvertable at a fast rate.[23] In each conformation, one of the ortho protons will experience NOE with H-6. NOE-2

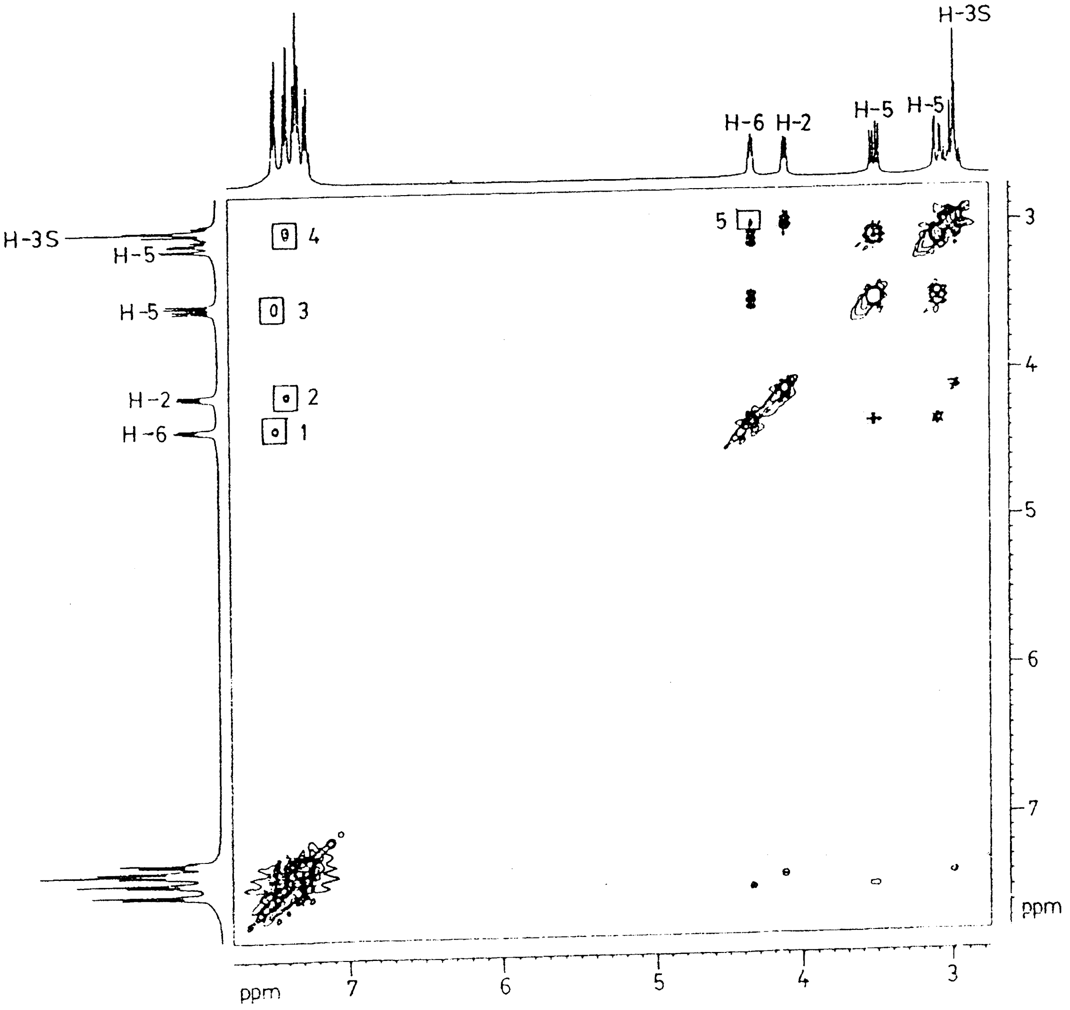
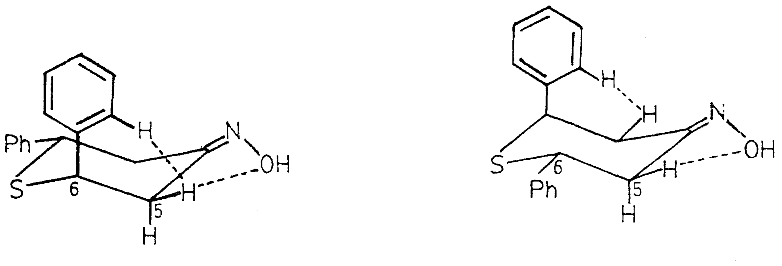


Fig. 1. Phase-sensitive NOESY spectrum of **11**. The spectrum was recorded with a mixing time of 400 ms.



(11a) (11b)

Fig. 2. Nonbonded interactions involving the equatorial methylene hydrogens in the chair conformations of **11** and **12**.

is between H-2 and the ortho protons of (C-2)-phenyl group. Such an NOE could occur in **11a**, **11c**, and **11d**.

It is seen that the ortho protons of the (C-6)-phenyl group have significant NOE with H-5, which has large coupling with H-6 (NOE-3). Similarly, NOE-4 is between the ortho protons of (C-2)-phenyl group and H-3 which has a large coupling with H-2. If the larger vicinal coupling constants are taken as J_{cis}, the possible conformations are only **11e** and **11f**, in which the ortho protons of the axial-like phenyl group should have NOE with the adjacent proton *cis* to the phenyl group. However, the *cis* proton should then have only a smaller vicinal coupling, which is not the case. Therefore, **11e** and **11f** could be ruled out and the large coupling must correspond only to J_{trans}.

The NOEs 3 and 4 could be accounted for as follows: In the chair conformation the ortho protons of an equatorial phenyl group have significant NOE with the adjacent axial protons (proton *cis* to the phenyl group) but only a negligible NOE with the adjacent equatorial proton (proton trans to the phenyl group).[24] In **11c** and **11d**, the phenyl groups are adopting equatorial-like orientations. Therefore, in **11c** and **11d** also the ortho protons of the phenyl groups must have significant NOE only with the adjacent proton *cis* to the phenyl groups. It is easily seen that the ortho protons of the axial phenyl group in **11a** and **11b** must have significant NOE with the adjacent equatorial proton, which is *cis* to the phenyl group.

NOE-5 is between H-6 and H-3, which has large coupling with H-2. Such an NOE could occur in **11c**. Similarly, in **11d** there should be NOE between H-2 and H-5 which has large coupling with H-6. However, such an NOE is not observed. Therefore, **11d** could be only a minor contributor. This should be expected since in **11d** the N–O bond should be almost eclipsing the bond between the *syn*-α-carbon and bowspirit hydrogen, whereas in **11c** the N–O bond lies between two C–H bonds.

For **12**, the sum of the vicinal coupling constants in the *anti* side is much greater than that in the *syn* side, suggesting that **12a** should be more populated than **12b**. Since the coupling constants in the *anti* side could not be determined independently, it is not possible to get reliable evidence for boat form contribution to **12**. However, by analogy the boat form should be expected to contribute to **12** also.

The greater stability of **11a** over **11b** and of **12a** over **12b** can be explained as follows. If one considers chair conformations **11a**, **11b**, **12a**, and **12b** there are two steric interactions, one between the OH group and the *syn*-equatorial methylene hydrogen and the other between the *ortho*-hydrogen of the phenyl group and the adjacent equatorial methylene hydrogen (Fig. 2). In **11a** and **12a** both these interactions could be relieved by either a change in the torsional angle about C(5)–C(6) bond or by a small change in H–C–H bond angle. However, in **11b** and **12b**, such a kind of distortion has to occur at both sides to decrease the two interactions. Thus, in **11b** and **12b** there could be more internal strain than in **11a** and **12a**, and this makes **11a** more stable than **11b** and **12a** more stable than **12b**.

Conclusions

Oximes **7**—**10**, having the phenyl groups in *cis* orientation, exist largely in chair conformations. However, for the *trans*-oximes **11** and **12**, boat forms must make significant contributions in solution. Moreover, for **11** and **12**, chair conformation with an axial phenyl group in the *syn* side is more populated than that with an axial phenyl group in the *anti* side. For **11** boat form **11c** seem to be a significant contributor. The greater stability of **11a** over **11b** and of **12a** over **12b** suggests that change in stereochemistry at one center may influence the conformational preference at a remote center significantly. Since **11c** seems to be more stable than **11d** NO···CH eclipsing interaction should be repulsive. For **11** the conclusions reached from vicinal coupling constants have been corroborated with ^{13}C chemical shifts as well as NOESY spectrum. This adduces further evidence for the versatility of NMR as a powerful tool in studying conformational equilibria.

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References

1) R. J. Abraham, A. E. Rowan, J. M. Bakke, and J. E. Braeden, *J. Chem. Soc., Perkin Trans. 2*, **1991**, 1471.

2) S. R. Salman, R. D. Ferrani, P. W. Sanderson, and J. C. Lindon, *Magn. Reson. Chem.*, **31**, 585 (1992).

3) G. C. Levy and G. L. Nelson, *J. Am. Chem. Soc.*, **94**, 4897 (1972).

4) G. E. Hawkes, K. Herwig, and J. D. Roberts, *J. Org. Chem.*, **39**, 1017 (1974).

5) P. Geneste, R. Durand, J. M. Kamenka, H. Beierbeck, R. Martino, and J. K. Saundes, *Can. J. Chem.*, **56**, 1940 (1978).

6) P. Geneste, J. M. Kamenka, and C. Brevard, *Org. Magn. Reson.*, **10**, 31 (1977).

7) K. Pandiarajan, R. T. Sabapathymohan, and Misbah Ul Hasan, *Magn. Reson. Chem.*, **24**, 312 (1984).

8) J. M. McGill and R. Johnson, *Magn. Reson. Chem.*, **31**, 273 (1993).

9) F. Arndt, P. Natchtwey, and J. Pusch, *Ber. Dtsch. Chem. Ges. B*, **58B**, 1637 (1925).

10) R. Cornubert, R. Delmas, S. Montil, and J. Viriot, *Bull. Soc. Chim. Fr.*, **1950**, 400.

11) F. R. Japp and W. Maitland, *J. Chem. Soc.*, **1904**, 1484.

12) V. Baliah and G. Mangalam, *Indian J. Chem., Sect. B*, **16B**, 213 (1978).

13) P. Petrenko-Kritschenko and D. Plotnikoff, *Ber. Dtsch. Chem. Ges.*, **30**, 2802 (1897).

14) V. Baliah, M. R. Lakshmanan, and K. Pandiarajan, *Indian J. Chem., Sect. B*, **17B**, 72 (1978).

15) N. Chandrasekar, K. Ramalingam, M. D. Herd, and K. D. Berlin, *J. Org. Chem.*, **45**, 4352 (1980).

16) J. A. Pople, H. J. Bernstein, and W. G. Schneider, *Can. J. Chem.*, **35**, 65 (1957).

17) Y. Cheualier, *Magn. Reson. Chem.*, **24**, 404 (1986).

18) K. Pandiarajan, R. Sekar, R. Anantharaman, V. Ramalingam, and D. Marko, *Indian J. Chem., Sect. B*, **30B**, 490 (1991).

19) K. Pandiarajan, R. Sekar, T. Rangarajan, and R. Sarumathi, *Indian J. Chem., Sect. B*, **32B**, 535 (1993).

20) V. Baliah and K. Pandiarajan, *Indian J. Chem., Sect. B*, **16B**, 807 (1978).

21) C. A. G. Haasnoot, F. A. A. M. De Leeuw, and C. Altona, *Tetrahedron*, **36**, 2783 (1980).

22) E. L. Eliel and M. Manoharan, *J. Org. Chem.*, **46**, 1959 (1981).

23) K. Pandiarajan, T. Rangarajan, M. Uma, K. S. Meena, and V. Sundaramurthy, *Indian J. Chem., Sect. B*, **27B**, 26 (1988).

24) K. Pandiarajan, J. Christophor Newton Benny, and T. N. Jagdish, unpublished results.

25) K. Ramalingam, K. D. Berilin, N. Satyamurthy, and R. Sivakumar, *J. Org. Chem.*, **44**, 471 (1979).