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Molecular dynamics of *cis*-1-(2-hydroxy-5-methylphenyl)ethanone oxime and *N*-(2-hydroxy-4-methylphenyl)acetamide in solution studied by NMR spectroscopy

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The formation of hydrogen bonds and molecular dynamics for the molecules *cis*-1-(2-hydroxy-5-methylphenyl)ethanone oxime (I) and *N*-(2-hydroxy-4-methylphenyl)acetamide (II) have been investigated in solution using NMR. The results confirm the formation of O–H···O, O–H···N and O···H–N type inter- and intramolecular hydrogen bonds. Spin-lattice relaxation times (T_1), activation energy of molecular dynamics and energy of intramolecular hydrogen bonds have been determined.

Keywords: molecular dynamics; spin-lattice relaxation time; hydrogen bond; conformers

Introduction

NMR spectroscopy plays an important role in studying various interactions in solution including hydrogen-bond formation.[1–18] The NMR line shape is sensitive to temperature and chemical exchange processes and can be used successfully to study of fast reversible reactions. Thus, NMR has become an important tool to evaluate the kinetics of reactions at equilibrium over a very large dynamic range; its results have theoretical and practical significance for chemistry and molecular physics.

Experimental

NMR spectra

NMR experiments were performed on a Bruker Fourier transform (FT) NMR spectrometer AVANCE 300 (300 for ^{1}H and 75 MHz for ^{13}C) with a BVT 3200 variable temperature unit in 5 mm sample tubes using Bruker Standard software (TopSpin 3.1). The ^{1}H and ^{13}C chemical shift were referenced to internal TMS; ^{1}H: digital resolution = 0.23 Hz, SW = 7530 Hz, TD = 32 K, SI = 16 K, the 90° pulse length = 10 μs, PL1 = 3 dB; ^{13}C: digital resolution = 0.27 Hz, SW = 17 985 Hz, TD = 64 K, SI = 32 K, the 90° pulse length = 9 μs, PL1 = 1.5 dB. Spin–lattice relaxation times were measured by the inversion–recovery method 180°–τ–90° (error in calculations ±0.1–0.5 s), and NOE factors were calculated from ^{13}C NMR spectra, recorded with and without NOE enhancement (error in calculations ±5%). NMR-grade deuterated dimethylsulfoxide (DMSO-d_6) (99.7%, containing 0.3% H_2O), acetone-d_6 (99.7%) and CCl_4 (100%, several drops of D_2O were added for the lock signal as external standard) were used for the solutions of *cis*-1-(2-hydroxy-5-methylphenyl)ethanone oxime (**I**) and *N*-(2-hydroxy-4-methylphenyl)acetamide (**II**). Dipole–dipole (DD) and spin–rotation (SR) relaxation times were calculated by the known methods[9–11] (Eqn (1)).

$$\begin{aligned} \mathrm{SR} = (2-\eta)/2;\ R_1{}^{\mathrm{SR}} = \mathrm{SR}/T_1;\ T_1{}^{\mathrm{SR}} = 1/R_1{}^{\mathrm{SR}};\ \mathrm{DD} \\ = 100 - \mathrm{SR};\ R_1{}^{\mathrm{DD}} = \mathrm{DD}/T_1;\ T_1{}^{\mathrm{DD}} = 1/R_1{}^{\mathrm{DD}} \end{aligned} \quad (1)$$

where SR is the spin–rotation, η is the NOE factor, T_1 is the spin–lattice relaxation time, and $R_1{}^{\mathrm{SR}}$ and $R_1{}^{\mathrm{DD}}$ are the relaxation rates and ($T_1{}^{\mathrm{SR}}$) and ($T_1{}^{\mathrm{DD}}$) are the relaxation times.

The NMR spectra for the four exchange sites were calculated by the program 'WINDNMR' (version 7.1.13).[2]

Syntheses

Cis-1-(2-hydroxy-5-methylphenyl)ethanone oxime (**I**) was obtained by reaction of 0.25 mol 2-hydroxy-5-methylacetophenone with 0.29 mol hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) in 325 ml ethanol at temperature 78 °C, reaction time 1 h (Scheme 1).[19]

The synthesis of *N*-(2-hydroxy-4-methylphenyl)acetamide (**II**) was performed from 0.1 mol *cis*-1-(2-hydroxy-5-methylphenyl) ethanone oxime in a mixture of 20 ml water and 60 ml 98% H_2SO_4; the reaction was carried out at 120 °C for 2 h (Beckman rearrangement) (Scheme 3).[19]

Purities and structures were confirmed by thin-layer chromatography (Silufol UV-254) and NMR spectroscopy (Tables 3 and 7).

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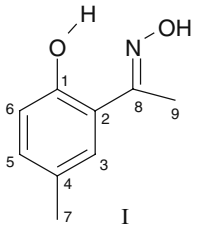
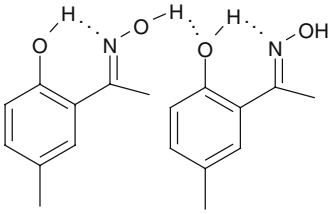


cis-1-(2-hydroxy-5-methylphenyl)ethanone oxime

Scheme 1. Structures and atom numbering of I.



Scheme 2. Formation intramolecular and intermolecular hydrogen bond for the molecule I.

Discussion

Oxime compounds are used as antidotes for nerve agents[20–23]; amides are widespread in nature and used in technology as structural materials. These compounds contain hydroxyl and carbonyl groups, aromatic rings and nitrogen atoms. The behavior of such molecules in solution as well as the presence or absence of molecular association is of considerable theoretical and practical interest. This concerns particularly the formation of hydrogen bonds, inter- and intramolecular interactions in solution for the oxime and the amide derivatives of *p*-cresol.

To study the hydrogen bonding in **I**, NMR investigations were carried out in different solvents (CCl_4, DMSO-d_6, acetone-d_6) at various concentrations and temperatures, and the results are given in Table 1.

It can be seen from the results that in 5% acetone-d_6 solution the hydroxyl proton resonances merge at 22 °C into one peak due to fast proton exchange. In 10% DMSO-d_6 solution, the proton chemical shifts for N–OH and OH decrease continuously with rising temperature from $\delta = 11.34$ at 22 °C to 11.21 ppm at 60 °C for N–OH and from $\delta = 11.49$ to 11.31 ppm for OH until finally one peak at $\delta = 11.21$ ppm is observed for OH. Except in 10% DMSO-d_6 solution, the proton integral intensity decreases only for N–OH continuously in the range of 22–60 °C, with rising temperature from 1 to 0.2 protons as a result of fast proton exchange with residual water. The same holds true for N–OH and water in the CCl_4 solution (several drops of D_2O were added for the lock signal observed at $\delta = 4.69$ ppm).

These results are explained by the intramolecular hydrogen bonds between O–H···N in the molecule and N–OH···O type intermolecular hydrogen bonds between the molecules of **I** (Scheme 2). The energy of intramolecular hydrogen bond at 22 °C and in the 0.1% CCl_4 solution is equal 6.81 ± 0.2 kcal/mol (or 28.53 kJ/mol).

Table 2. Relaxation times (T_1 for ^{13}C in seconds) for different CH_3 and CH groups of **I** at various temperatures and activation energies of intramolecular mobility, recorded in 5% acetone-d_6 solution

Fragments	Number of atom	Nucleus	T_1 at 22 °C (s)	T_1 at 50 °C (s)	E_a (kJ/mol)
CH_3	7	^1H	2.76	3.40	5.89
CH_3	9	^1H	3.46	4.28	6.01
CH_3	7	^{13}C	7.13	8.75	5.79
CH_3	9	^{13}C	10.21	12.66	6.08
CH	6	^{13}C	4.94	–	–
CH	3	^{13}C	4.78	–	–
CH	5	^{13}C	4.69	–	–

For **I** and **II**, the intramolecular hydrogen bond energies were calculated using Schaefer's formula.[24]

$$\Delta\delta = -0.4 \pm 0.2 + E \qquad (2)$$

where $\Delta\delta$ is given in parts per million relative to phenol ($\delta = 4.29$ ppm) and E in kcal/mol.

The calculated relaxation times (T_1, s) of **I** in acetone-d_6 solution (5%) are listed in Table 2 for different methyl groups at 22 and 50 °C and for CH groups only for 22 °C. The proton relaxation times for the two methyl groups (T_1) increase with temperature (Table 2), and the NOE factors for protonated carbons (Table 3) confirm the dipolar relaxation mechanism.

In the temperature interval of 22–50 °C, the activation energies of intramolecular mobility of methyl group were calculated[6] (Table 2) by the following formula with an error in of ±0.1–0.5 kJ/mol.

$$E = 19.13[T^{(1)}T^{(2)}/(T^{(2)} - T^{(1)})]\log(T_1^{(2)}/T_1^{(1)}) \qquad (3)$$

Table 1. Chemical shifts of hydroxyl protons (δ_{OH}) of **I**, in different solvents at various concentrations and temperatures

Solvent	Concentration (%)	Temperature (°C)	δ_{OH} (ppm)
Acetone-d_6	5	22	12.12 (2H, N–OH + OH)
DMSO-d_6	10	22	11.34 (1H, OH) and 11.49 (1H, OH)
–	–	30	11.29 (0.8H, N–OH) and 11.43 (1H, OH)
–	–	40	11.25 (0.6H, N–OH) and 11.37 (1H, OH)
–	–	50	11.23 (0.4H, N–OH) and 11.35 (1H, OH)
–	–	60	11.21 (0.2H, N–OH) and 11.31 (1H, OH)
–	–	70	11.21 (1H, OH)
CCl_4	10	22	4.69 (1H, N–OH) and 11.20 (1H, OH)
–	0.1	22	4.69 (1H, N–OH) and 10.70 (1H, OH)
–	–	70	4.69 (1H, N–OH) and 10.27 (1H, OH)

Table 3. NMR data, NOE factors (^{13}C) and T_1 values for **I**

Fragments	Number of atom	^1H, ^{13}C NMR (DMSO-d_6, δ) (ppm)	NOE factor (η)	T_1 (s)
C	1	155.5	0.8	–
C	2	118.5	0.8	–
CH	3	7.35 (s, 1H, C_6H_3), 127.7	1.8	4.78
C	4	127.3	0.9	–
CH	5	7.05 (d, 1H, C_6H_3, $^3J_{H-H} = 8.43$ Hz), 130.8	1.9	4.69
CH	6	6.75 (d, 1H, C_6H_3, $^3J_{H-H} = 8.43$ Hz), 116.5	2.0	4.94
CH_3	7	2.2 (s, 3H, CH_3), 19.8	1.3	7.13
C	8	158.1	0.7	–
CH_3	9	2.23 (s, 3H, CH_3), 9.9	1.9	10.21
OH	–	11.49	–	–

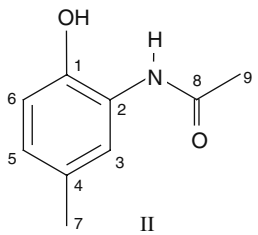
Table 4. SR and DD mechanisms of relaxation (^{13}C) for **I**; R_1^{SR}, T_1^{SR}, R_1^{DD} and T_1^{DD} are respective relaxations rates and times, respectively

Fragments	Number of carbon atom	SR (%)	DD (%)	R_1^{SR} (s^{-1})	T_1^{SR} (s)	R_1^{DD} (s^{-1})	T_1^{DD} (s)
CH	3	10	90	0.0209	47.8	0.2092	4.78
CH	5	5	95	0.0107	93.45	0.2026	4.94
CH	6	0	100	0	4.89	0.0203	49.3
CH_3	7	35	65	0.0491	20.40	0.0912	10.96
CH_3	9	5	95	0.0049	204.1	0.0931	10.7

where $T^{(1)}$ and $T^{(2)}$ are temperatures and $T_1^{(1)}$ and $T_1^{(2)}$ relaxation times.

Furthermore, the contributions of SR and DD mechanisms were taken into account and the corresponding carbon relaxation rates (R_1^{SR}), (R_1^{DD}) and relaxation times (T_1^{SR}) and (T_1^{DD}) were calculated from the spectra recorded in acetone-d_6 solution. The results are given in Table 4. The methyl groups at the unsaturated bond and aromatic fragment are sterically strained, allowing only partial internal rotation (5 and 35%, respectively).

In **I**, two E_a values (5.89 and 5.79; 6.01 and 6.08 kJ/mol) were calculated for the methyl groups from T_1 experiments at ^1H and ^{13}C nuclei. Identical E_a values for different target nuclei suggest isotropic molecular reorientations in the molecule. Except for aromatic carbons attached to one proton, all the carbons show identical relaxation times (Tables 2 and 3). These data also confirm the isotropic character of molecular motions.[1]



II

N-(2-Hydroxy-4-methylphenyl)acetamide

Scheme 3. Structures and atom numbering of II.

Table 5. Chemical shifts for hydroxyl protons (δ_{OH}) of **II** in different solvents at various concentrations and temperatures

Solvent	Concentration (%)	Temperature (°C)	δ_{OH} (ppm)
Acetone-d_6	5	−50	9.37, 9.72, 9.57 and 9.55 (N–OH + OH)
–	–	−40	9.70, 9.68, 9.56 and 9.54 (N–OH + OH)
–	–	−30	9.61, 9.6, 9.53 and 9.51 (N–OH + OH)
–	–	−20	9.55, 9.54, 9.50 and 9.48 (N–OH + OH)
–	–	−5	9.50, 9.48 and 9.44 (N–OH + OH)
–	–	5	9.44, 9.43 and 9.40 (N–OH + OH)
–	–	15	9.38 and 9.37 (N–OH + OH, coalescence)
–	–	22	9.2 and 9.1 (N–OH + OH)
–	–	50	9.15 and 9.09 (N–OH + OH)
DMSO-d_6	10	22	9.48 and 9.2 (N–OH + OH)
–	–	90	9.06 and 8.98 (N–OH + OH)
CCl_4	10	22	9.21 and 9.15 (N–OH + OH)
–	0.1	22	9.04 and 8.99 (N–OH + OH)

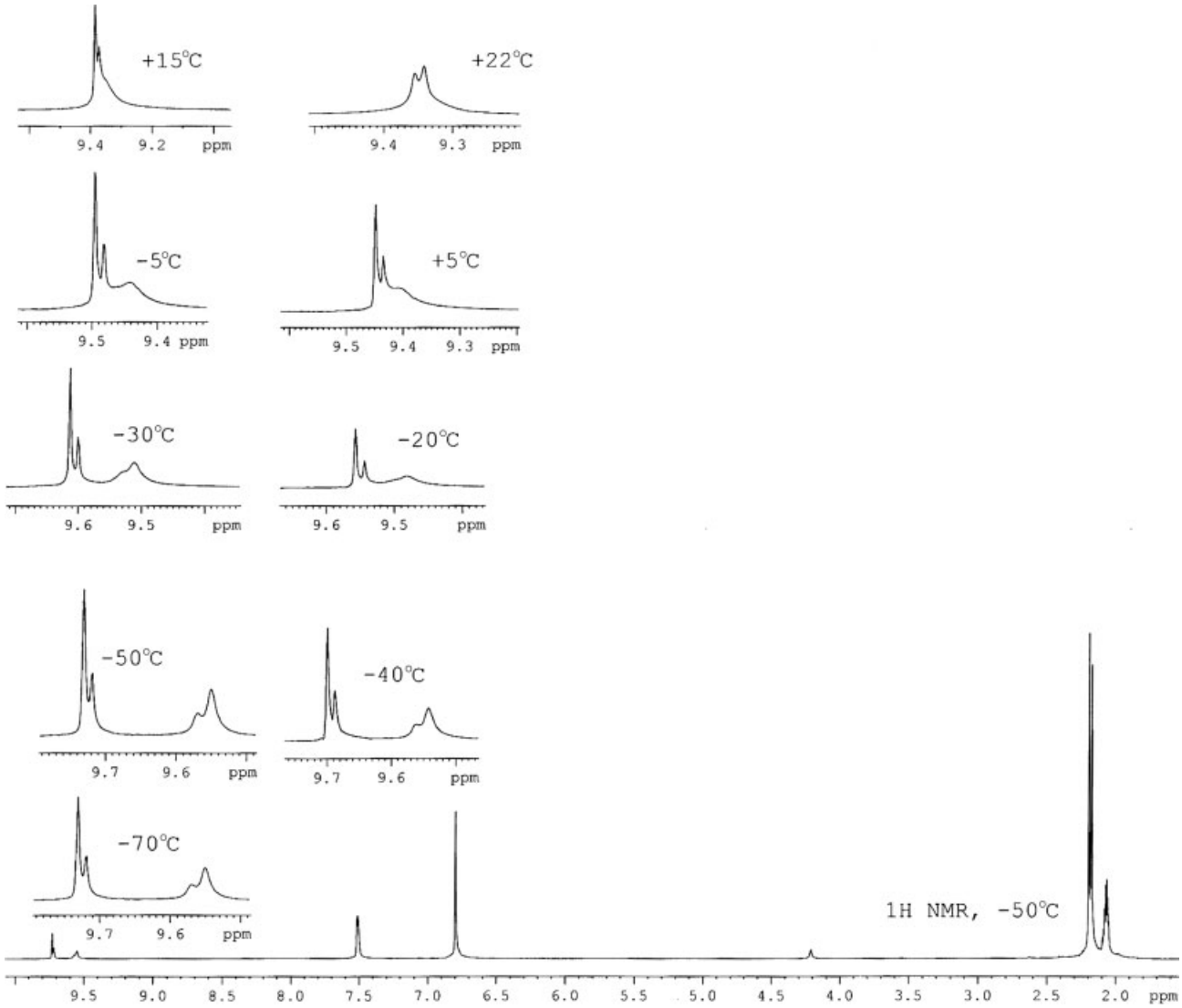


Figure 1. ^{1}H NMR spectral sections of **II** in 5% acetone-d_6 solution at $-70\,^{\circ}$C to $+22\,^{\circ}$C.

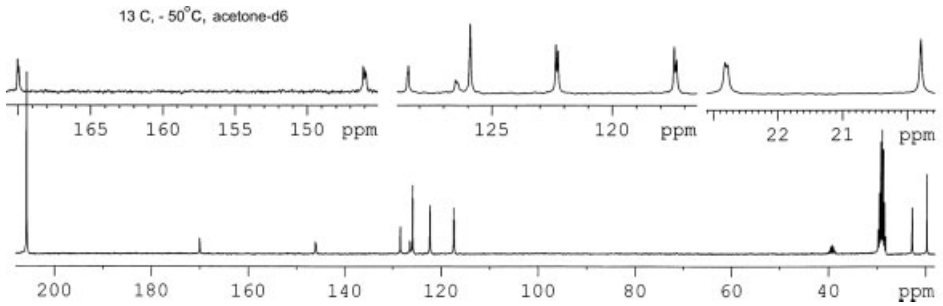


Figure 2. ^{13}C NMR spectral section of **II** in 5% acetone-d_6 solution at $-50\,^{\circ}$C.

Further NMR investigations were carried out on *N*-(2-hydroxy-4-methylphenyl)acetamide (**II**; Scheme 3) and the results are given in Table 5.

Concentrations changes for CCl_4 solutions have only a weak influence on the hydroxyl chemical shift. The temperature dependence in DMSO-d_6 (10%) and acetone-d_6 (5%) show a decrease with rising temperature: for DMSO-d_6 from $\delta = 9.48$ and 9.2 ppm at $22\,^{\circ}$C to $\delta = 9.06$ and 8.98 ppm at $90\,^{\circ}$C; and for acetone (Fig. 1) from $\delta = 9.73$, 9.72, 9.57 and 9.55 ppm at $-50\,^{\circ}$C to $\delta = 9.15$ and 9.09 ppm at $50\,^{\circ}$C with a coalescence point at $15\,^{\circ}$C.

The ^{13}C NMR spectrum at $-50\,^{\circ}$C (Fig. 2) showed, for all carbons, two signals instead of one and in the ^{1}H NMR spectrum the aromatic proton signal (singlet peak) was shifted from $\delta = 7.32$ (at $22\,^{\circ}$C) to $\delta = 7.51$ ppm (at $-50\,^{\circ}$C). This results can be explained by the complicated rotation around the N–Ar bond

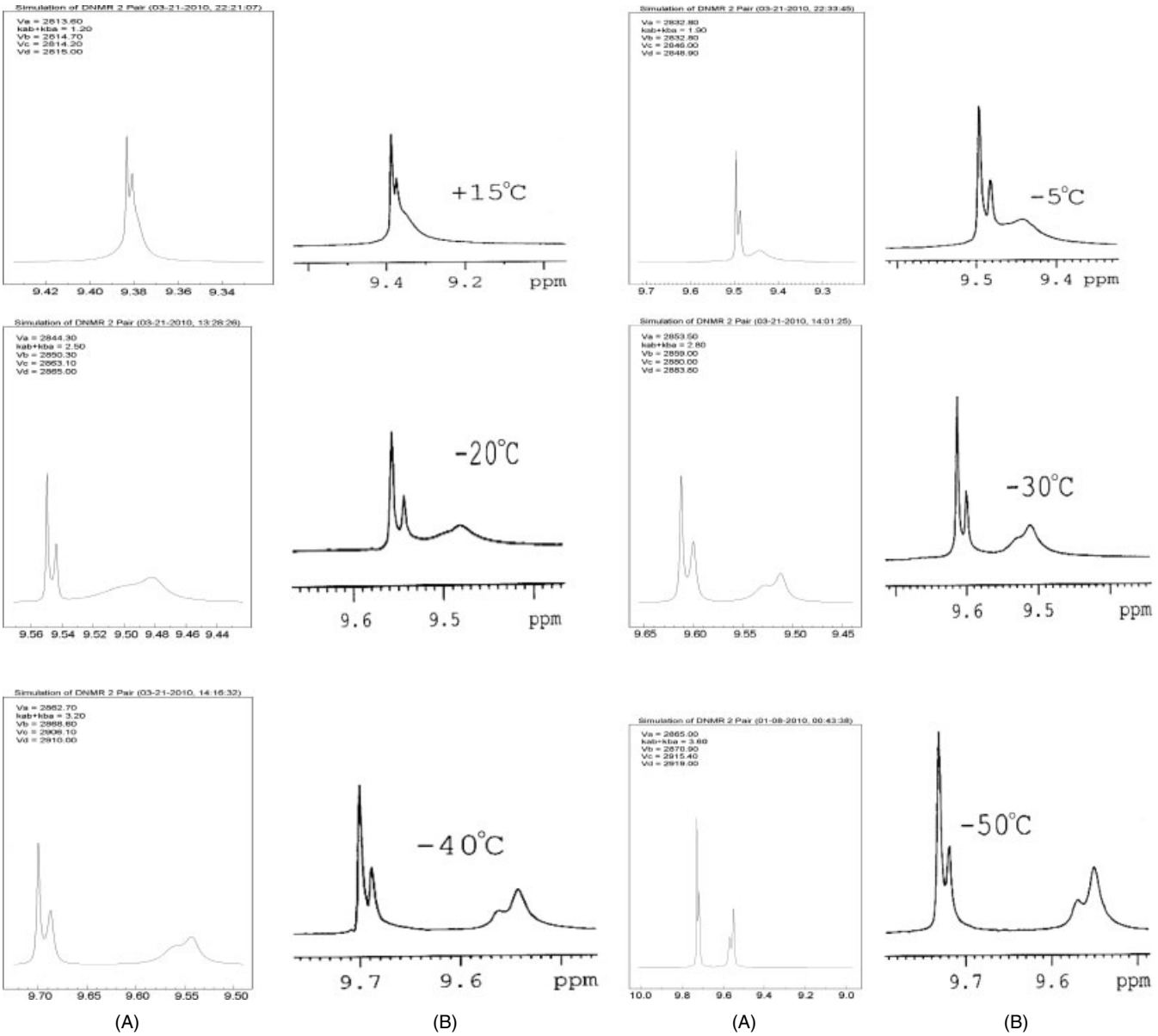


Figure 3. Simulation of DNMR (A) and experimental (B) ^{1}H NMR spectral sections of **II**.

Table 6. Relaxation times (T_1 for ^{13}C in seconds) for different CH_3 and CH groups of **II** at various temperatures and activation energies of intramolecular mobility, recorded in 5% acetone-d_6 solution

Fragments	Number of atom	T_1 at −20 °C (s)	T_1 at 22 °C (s)	T_1 at 50 °C (s)	E_a (kJ/mol)
CH_3	7	4.18	6.50	8.00	18.35
CH_3	9	3.98	5.92	7.83	19.13
CH	6	–	2.78	3.52	6.67
CH	3	–	2.51	3.15	6.42
CH	5	–	2.65	3.36	6.71

Table 7. NMR data, NOE factors (^{13}C) and T_1 values for **II**

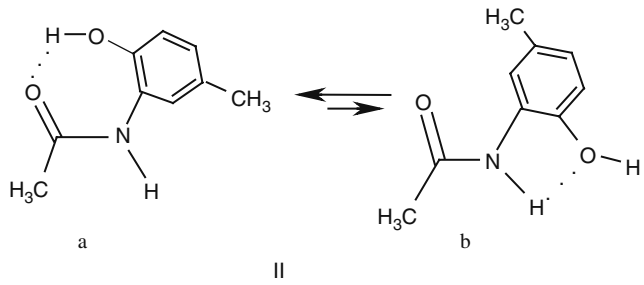
Fragments	Number of atom	^{1}H, ^{13}C NMR (acetone-d_6 δ (ppm)	NOE factor (η)	T_1 (s)
C	1	146.2	–	–
C	2	126.1	–	–
CH	3	7.28 (s, 1H, C_6H_3), 122.1	1.66	2.51
C	4	128.5	–	–
CH	5	6.82 (m, 1H, C_6H_3), 125.6	1.92	2.65
CH	6	6.82 (m, 1H, C_6H_3), 117.1	1.68	2.78
CH_3	7	2.18 (s, 3H, CH_3), 19.6	–	–
C	8	169.8	1.14	6.50
CH_3	9	2.2 (s, 3H, CH_3), 22.5	1.12	5.92
OH, NH	–	9.1 and 9.2 (s, 2H, NH, OH)	–	–

and the possible existence of two conformers (a and b for the *Z* form) for the molecule *N*-(2-hydroxy-4-methylphenyl)acetamide (**II**; Scheme 4).[25,26] Our studies confirmed the formation of two intramolecular hydrogen bonds (of the O···H–O, O···H–N type) in

Table 8. SR and DD mechanisms of relaxation (^{13}C) for **II**

Fragments	Number of carbon atom	SR (%)	DD (%)	R_1^{SR} (s^{-1})	T_1^{SR} (s)	R_1^{DD} (s^{-1})	T_1^{DD} (s)
CH	3	17	83	0.0677	14.77	0.3307	3.02
CH	5	4	96	0.0151	66.23	0.3623	2.76
CH	6	16	84	0.0576	17.36	0.3022	3.31
CH_3	7	43	57	0.0662	15.11	0.0877	11.40
CH_3	9	44	56	0.0743	13.46	0.0946	10.57

R_1^{SR}, T_1^{SR}, R_1^{DD} and T_1^{DD} are respective relaxations rates and times, respectively.



N-(2-Hydroxy-4-methylphenyl)acetamide

Scheme 4. Two conformers in solution for the molecule II.

the conformers (a) and (b). The energy of intramolecular hydrogen bonds at 22 °C and in 0.1% CCl_4 solution is 5.13 ± 0.2 kcal/mol (or 21.5 kJ/mol).

The NMR spectrum of the four exchange sites was calculated by 'WINDNMR' (version 7.1.13), resulting in the rate constants ($k = 3.6\ s^{-1}$ at −50 °C, 3.2 s^{-1} at −40 °C, 2.8 s^{-1} at −30 °C, 2.5 s^{-1} at −20 °C, 1.9 s^{-1} at −5 °C, 1.2 s^{-1} at +15 °C) in acetone-d_6 solution (Fig. 3). The free energy of activation has been calculated by the formula[2]

$$\Delta G_c = 2.3RT_c[10.32 + \log(T_c/k_c)] = 69.91\ \text{kJ/mol} \qquad (4)$$

The calculated relaxation times (T_1 for carbons, s, in 5% acetone-d_6 solution) for different CH_3 and CH groups of **II** at various temperatures are given in Table 6.

The spin–lattice relaxation time increases with rising temperature. This is a typical feature of DD relaxation. The activation energies of intramolecular mobility were calculated in the temperature intervals −20 to +50 °C for the CH_3 groups and 22–50 °C for the CH groups (Table 6).

Further NOE factors, relaxation times (T_1) and the contributions of SR, DD mechanism for **II** were taken into account and the corresponding carbon relaxation rates (R_1^{SR}), (R_1^{DD}) and relaxation times (T_1^{SR}) and (T_1^{DD}) were calculated in acetone-d_6. The results are given in Tables 7 and 8.

Conclusions

Our investigations confirm the formation of intramolecular hydrogen bonds between O–H···N within the molecule and N–OH···O type intermolecular hydrogen bonds between oxime molecules (**I**).

The results can be explained by the existence two conformers (a and b for the *transoid* or *Z* form) for the molecule *N*-(2-hydroxy-4-methylphenyl)acetamide (**II**) for which the formation of two intramolecular hydrogen bonds (O···H–N, O···H–O type) can be confirmed (Scheme 4). For **I** and **II,** the intramolecular hydrogen bond energy, the activation energies of intramolecular mobility, and for **II** the free energy of activation (69.91 kJ/mol) and rate constants were calculated.

NOE factors, relaxation times (T_1), the contributions of SR and DD mechanisms, the corresponding carbon relaxation rates (R_1^{SR}), (R_1^{DD}) and relaxation times (T_1^{SR}), (T_1^{DD}) for **I** and **II** were calculated in acetone-d_6.

The methyl groups at unsaturated bond, the carbonyl and the aromatic fragments are sterically strained allowing only partial internal rotation (Tables 4 and 8).

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