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THE IMPACT OF SOLVENT POLARITY ON THE STABILITY, ELECTRONIC PROPERTIES, AND ^{1}H NMR CHEMICAL SHIFT OF THE CONFORMERS OF 2-CHLORO-3-METHYLCYCLOHEXAN-1-ONE OXIME: A CONCEPTUAL DFT APPROACH [**]

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In this article, the stability of the conformers of 2-chloro-3-methylcyclohexan-1-one oxime was investigated at the wB97XD/6-311G(d,p) level of theory. Using the self-consistent reaction field theory (SCRF) based on the Polarizable Continuum Model (PCM), the solvent impacts were examined. Solvent influence on the total energy, relative energy, dipole moment, the energies of frontier orbitals, and proton chemical shift of these molecules was investigated. The associations between these parameters and solvent polarity functions including both the dielectric constant (ε) and refractive index (n_D) of the liquid medium were found. Moreover, NBO analysis was used to illustrate the hyperconjugative anomeric effect on the conformers.

Keywords: *2-chloro-3-methylcyclohexan-1-one oxime, vinylogous hyperconjugative anomeric effect, natural bond orbital analysis (NBO), solvent effect, Kirkwood–Bauer–Magat equation (KBM).*

ВЛИЯНИЕ ПОЛЯРНОСТИ РАСТВОРИТЕЛЯ НА СТАБИЛЬНОСТЬ, ЭЛЕКТРОННЫЕ СВОЙСТВА И ХИМИЧЕСКИЙ СДВИГ В ^{1}Н ЯМР СПЕКТРАХ КОНФОРМЕРОВ 2-ХЛОР-3-МЕТИЛЦИКЛОГЕКСАН-1-ОН ОКСИМА: КОНЦЕПТУАЛЬНЫЙ ПОДХОД, ОСНОВАННЫЙ НА ТЕОРИИ ФУНКЦИОНАЛА ПЛОТНОСТИ

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Стабильность конформеров 2-хлор-3-метилциклогексан-1-он оксима исследована в рамках wB97XD/6-311G(d,p) уровня теории. Влияние растворителя изучено с использованием самосогласованной теории реакционного поля, основанной на модели поляризуемого континуума. Исследовано влияние растворителя на общую энергию, относительную энергию, дипольный момент, энергии пограничных орбиталей, протонный химический сдвиг этих молекул. Установлены связи между этими параметрами и функциями полярности растворителя, включающими в себя диэлектрическую постоянную (ε) и показатель преломления (n_D) жидкой среды. Анализ естественных связывающих орбиталей использован для иллюстрации гиперконъюгативного аномерного эффекта на конформерах.

Ключевые слова: *2-хлор-3-метилциклогексан-1-он оксим, винилогусный гиперконъюгативный аномерный эффект, анализ естественных связывающих орбиталей, влияние растворителя, уравнение Кирквуда–Бауэра–Магата.*

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Introduction. In general, the anomeric effect is explained as the preference of an electronegative substituent at Cl (the anomeric carbon) of a pyranosides ring for the axial rather than equatorial orientation, in contrast to the predictions based solely on steric grounds [1–4]. The "generalized anomeric effect" is defined as the preference for the gauche conformer over the anti-conformer in an R–Y–CH_2–X fragment, where Y is an element possessing lone pairs (e.g., O, S), and X is an electronegative atom (e.g., O, N, halogen) [5, 6]. The other type of this stereoelectronic interaction is named the vinylogous anomeric effect, extending over four bonds [7]. To understand the origin of the anomeric effect, two rationalizations are the electrostatic [8, 9] and the hyperconjugation [10, 11] models, which are normally accepted. Many theoretical and experimental studies have been reported about the anomeric effect in various organic cycle systems [12–24].

Synthesis of the series of trans-3-alkyl-2-chlorocyclohexanones, 2 (methyl, ethyl, isopropyl, and tert-butyl), was reported and indicated to exist primarily in the diequatorial chair conformation except for the tert-butyl derivative, which favors a twist-boat. Formation of the oximes and various oxime derivatives (methyloxime, silyloxime) leads to a significant conformational inversion for the methyl, ethyl, and isopropyl systems. It is supposed that these compounds exist mainly in the diaxial chair conformation. A strong hyperconjugative stabilization of the axial conformation is recommended as the origin of this preference, which is called the vinylogous anomeric impact [25].

The solvent effect is one of the simple topics of chemistry and leads to the extensive alterations in the molecular behaviors via promoting some changes to the interactions between solute and solvent molecules [26–28]. To consider the solvent effect in quantum mechanical (QM) calculations of electronic structure, several methods were developed [29, 30]. The solvent effect on the structural and spectroscopic properties of various chemical systems was studied [31–56]. Also, the solvent effect on the barrier height has been explored in various systems [57–62].

In this work, we studied the solvent impact on the stability and electronic and structural properties of the conformers of 2-chloro-3-methylcyclohexan-1-one oxime at the wB97XD/6-311G(d,p) level of theory. The stability of the conformers was explored with the natural bond orbital (NBO) analysis.

Computational methods. All calculations were conducted via the Gaussian 09 software package [63]. The standard 6-311G(d,p) basis set [64–66] was utilized in the calculations. Geometry optimization was performed utilizing the wB97XD method. The wB97XD functional uses a version of Grimme's D2 dispersion model, which is the latest functional from Head-Gordon and coworkers and includes empirical dispersion [67]. After finding the stationary points, their identities, as energy minima structures, were confirmed through vibrational analysis. A vibrational analysis was conducted at each stationary point found, confirming its identity as an energy minimum. The population analysis has also been conducted by the natural bond orbital method [68] at the wB97XD/6-311G(d,p) level of theory using the NBO 6.0 program [69] through the Gaussian 09 software. For the solvation impacts assessment, we utilized a self-consistent reaction field (SCRF) method, particularly utilizing the polarizable continuum model (PCM) [70]. Chemical shift values are calculated using the gauge independent atomic orbital (GIAO) method and basis sets of optimization [71].

Results and discussion. *Energetic aspects.* Figure 1 represents conformers and abbreviations of the 2-chloro-3-methylcyclohexan-1-one oxime molecule. The absolute energy and relative energy values of conformers in the gas phase and various solvent are shown in Table 1. As is observed, the **I**-conformer is more stable than the **II**-conformer in the solution and gas phases. Also, the relative energy values decrease in the solution phase compared to the gas phase. The relative energy values decrease in more polar solvents.

As is seen, the studied molecules are more stable in the solution phase, and its stability increases with increasing dielectric constant of the solvents. Consequently, existing in the solvent, the molecules are stabilized energetically by electrostatic interaction with the solvent.

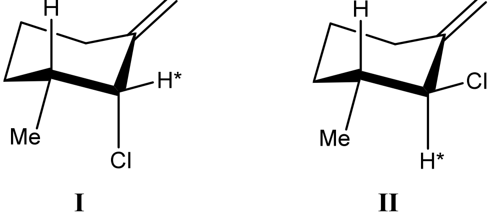

Fig. 1. The structures of the two selected conformers of 2-chloro-3-methylcyclohexan-1-one oxime.

TABLE 1. Absolute Energy (E, Hartree), Relative Energy (ΔE, Kcal/Mol) and Solvation Energy (E_{solv}, Kcal/Mol) Values of Conformers of 2-Chloro-3-Methylcyclohexan-1-One Oxime in Gas and Solution Phases at the wb97xd/6-311G(d,p) Level of Theory

Solvent	ε	n_D [80]	E		ΔE		E_{solv}	
			I	**II**	**I**	**II**	**I**	**II**
Gas	–		–864.0984	–864.0924	0.00	3.78	–	–
Chloroform	4.71	1.45	–864.1032	–864.0984	0.00	3.01	–3.02	–3.78
Chlorobenzene	5.70	1.52	–864.1036	–864.0989	0.00	2.95	–3.23	–4.05
THF	7.43	1.41	–864.1040	–864.0994	0.00	2.87	–3.48	–4.38
Dimethyldisulfide	9.60	1.52	–864.1043	–864.0998	0.00	2.81	–3.67	–4.63
Dichloroethane	10.13	1.44	–864.1043	–864.0999	0.00	2.80	–3.70	–4.68
Cyclohexanone	15.62	1.45	–864.1047	–864.1004	0.00	2.73	–3.94	–4.99
o-Nitrotoluene	25.67	1.55	–864.1050	–864.1007	0.00	2.67	–4.11	–5.22
Propanonitrile	29.32	1.37	–864.1051	–864.1008	0.00	2.66	–4.15	–5.27
N,N-Dimethylformamide	37.22	1.43	–864.1051	–864.1009	0.00	2.64	–4.20	–5.34

Note. ε and n_D are dielectric constants and refractive index of the solvent, respectively.

Table 1 provides solvation energy values of the complex. A solvation energy values are computed using the following equation:

$$E_{\text{solv}} = E_{\text{solv}} - E_{\text{gas}}.$$

Table 1 shows that by increasing the dielectric constant of solvents, these values decrease. As can be observed, the stability of the **II**-conformer in the solution phase is greater than the **I**-conformer. The observed relations of the solvation energy vs. dielectric constant of solvent are fitted by quadratic formulas. The corresponding fitting equations are:

$$E_{\text{solv}}(\mathbf{I}) = 0.0018\,\varepsilon^2 - 0.1024\,\varepsilon - 2.7407, \qquad R^2 = 0.9422,$$

$$E_{\text{solv}}(\mathbf{II}) = 0.0023\,\varepsilon^2 - 0.1345\,\varepsilon - 3.4147, \qquad R^2 = 0.9435.$$

Greater stability of the **I**-conformation is attributed to the hyperconjugative anomeric effect (Fig. 2). Figure 2 presents the canonical (resonance) structure depicting the proposed vinylogous hyperconjugative interaction. The following section illustrates this effect.

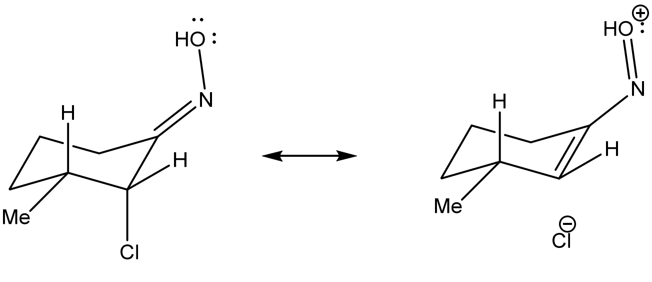

Fig. 2. Vinylogous hyperconjugative anomeric effect (by π-σ* hyperconjugation) in the **I**-conformer of 2-chloro-3-methylcyclohexan-1-one oxime.

NBO analysis. In the present study using the concept of natural bond orbital (NBO) analysis, the partitioning of the total electronic energy E(tot) into Lewis E(L) (orbital population ni = 2.0) and non-Lewis E(NL) parts (see Table 2) is performed. The localized Lewis component E(L) is associated with more than 99.5% of the full electron density and incorporates a good estimate of all steric and classic electrostatic impacts. The non-Lewis E(NL) part explains all types of conjugation. Table 2 indicates that the **I**-conformer would be more desirable if only effects of conjugations are considered.

TABLE 2. Results of the NBO Analysis and Energy Decomposition of Total Electronic Energy *E*(total) into Lewis *E*(L), non-Lewis *E*(Nl), Total Steric *E*(steric) and Electrostatic *E*(NCE) Energies (in kcal/mol) of Conformers of 2-chloro-3-methylcyclohexan-1-one Oxime at the wB97XD/6-311G(d,p) Level of Theory

Conformer	*E*(steric)	Δ*E*(steric)	*E*(NCE)	Δ*E*(NCE)	*E*(L)	Δ*E*(L)	*E*(NL)	Δ*E*(NL)
I	615.90	9.78	–326.45	0.00	–863.55	0.00	–346.35	0.00
II	606.12	0.00	–322.29	4.16	–863.54	1.60	–344.18	2.17

The total steric energy *E*(ST) from the NBO analysis was calculated, indicating that steric interactions in the **II**-conformer are more pronounced than in the **I**-conformer.

The Natural Coulomb Electrostatic energies *E*(NCE) total and its Lewis components were calculated in [72]. Table 2 further shows that on the basis of NCE values, the **I**-conformer conformation would be more preferable.

Therefore, according to Table 4, the **I**-conformer is an example of stabilization of a form that is preferred by electrostatic and conjugation impacts and is not preferred mainly by steric effects.

Dipole moment. Because a greater dipole moment may increase the overall energy of a conformation, the population of a conformation with a greater dipole moment may be decreased compared to the conformation with the smaller dipole moment [73]. A greater dipole moment is associated with the greater charge distribution (polarization). Therefore, conformations with smaller dipole moments can be harder than those with larger dipole moments.

The results indicate that the dipole moments for the more stable conformation **I** of the studied compound are smaller than its corresponding **II**-conformation (Table 1).

The observed relations of the dipole moment values with dielectric constant of solvent are fitted by quadratic formulas. The corresponding fitting equations are:

$$\mu(\mathbf{I}) = -0.0004\varepsilon^2 + 0.0237\varepsilon + 2.8727, \qquad R^2 = 0.9502,$$

$$\mu(\mathbf{II}) = -0.0005\varepsilon^2 + 0.0297\varepsilon + 3.3781, \qquad R^2 = 0.9463.$$

The linear correlations between ground state dipole moment of this complex and solvent polarity functions, which frequently include both the refractive index and dielectric constant of the liquid medium, are explored. In this work, we use the Lippert–Mataga polarity function (called orientation polarizability of the solvent) [74, 75] and the Bakhshiev polarity function [76–79]. The equations of these functions include:

Lippert–Mataga polarity function:

$$F(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}.$$

Bakhshiev polarity function:

$$F_1(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2}\left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right).$$

The linear correlations between μ and these solvent polarity functions include:

$$\mu(\mathbf{I}) = 1.8172\, F(\varepsilon,n) + 2.7083, \qquad R^2 = 0.8711,$$

$$\mu(\mathbf{II}) = 2.2603\, F(\varepsilon,n) + 3.1751, \qquad R^2 = 0.8704,$$

$$\mu(\mathbf{I}) = 0.5623\, F_1(\varepsilon,n) + 2.75, \qquad R^2 = 0.982,$$

$$\mu(\mathbf{II}) = 0.6993\, F_1(\varepsilon,n) + 3.227, \qquad R^2 = 0.9809.$$

It can be observed that there is a better association between ground state dipole moment and Bakhshiev polarity function in the studied molecules (Fig. 3).

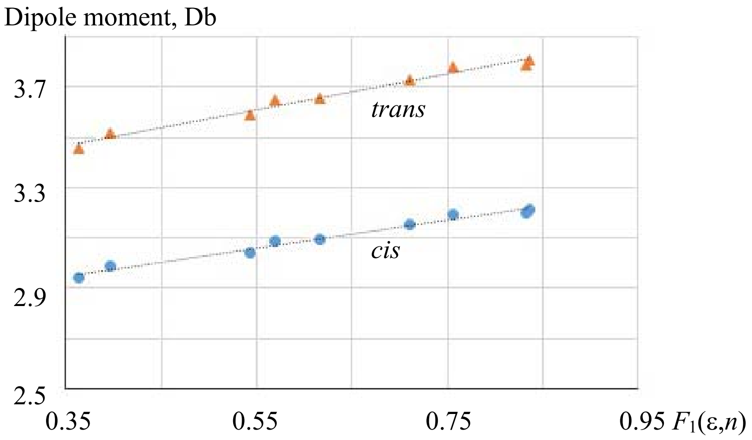

Fig. 3. Correlations between ground state dipole moment and Bakhshiev polarity function in the two conformers of 2-chloro-3-methylcyclohexan-1-one oxime.

Molecular orbital analysis. Table 3 represents the energies of the frontier orbitals (HOMO, LUMO) and the corresponding HOMO–LUMO energy gap values of the investigated molecules.

Based on the calculation results, frontier orbitals have greater stability in various solvents compared to the vacuum phase. Therefore, the title complex in the solvent is harder to decrease and easier to oxidize. This trend is, maybe, associated with the intermolecular interactions between the studied molecules and solvent. The stability of frontier orbitals increases with increase in solvent polarity.

HOMO–LUMO gap values of the cis conformer show smaller values in the solvent phase rather than in the gas phase. In more polar solvents, this gap is smaller. In the **II**-conformer, these values are larger in the solvent phase rather than in the gas phase. In more polar solvents, this gap is higher. Usually, an increase in HOMO–LUMO gap represents high excitation energy and is related to a low chemical reactivity. Thus, this complex in the solvent is more stable compared to the gas phase.

It can be seen that a change of solvent exerts merely a small effect on the HOMO and LUMO level and hence only influences somewhat the HOMO-LUMO gaps.

TABLE 3. Dipole Moment (μ, Debye), Frontier Orbital Energy (a.u) and HOMO-LUMO Gap (eV) Values of Conformers of 2-chloro-3-methylcyclohexan-1-one Oxime in Gas and Solution Phases at the wB97XD/6-311G(d,p) Level of Theory

Solvent	μ		**I**			**II**		
	I	**II**	*E*(HOMO)	*E*(LUMO)	gap	*E*(HOMO)	*E*(LUMO)	gap
Gas	2.38	2.70	–0.3390	0.0520	10.637	–0.3357	0.0694	11.025
Chloroform	2.94	3.46	–0.3418	0.0467	10.571	–0.3388	0.0677	11.061
Chlorobenzene	2.99	3.52	–0.3420	0.0463	10.566	–0.3391	0.0675	11.063
THF	3.04	3.59	–0.3423	0.0457	10.559	–0.3394	0.0673	11.066
Dimethyldisulfide	3.09	3.65	–0.3426	0.0453	10.555	–0.3397	0.0671	11.068
Dichloroethane	3.09	3.66	–0.3426	0.0452	10.553	–0.3397	0.0670	11.068
Cyclohexanone	3.15	3.73	–0.3429	0.0447	10.547	–0.3401	0.0668	11.071
o-Nitrotoluene	3.19	3.78	–0.3431	0.0443	10.543	–0.3403	0.0666	11.073
Propanonitrile	3.20	3.79	–0.3432	0.0443	10.542	–0.3404	0.0666	11.073
N,N-Dimethylformamide	3.22	3.81	–0.3432	0.0441	10.540	–0.3405	0.0665	11.074

^{1}H NMR spectra. The ^{1}H NMR spectra data for the studied molecules are shown in Table 4. These values exhibit signals of the H* atom at 4.02 and 3.41 ppm in the gas phase, for **I** and **II** conformations, respectively. In various solvents, the chemical shift value of H* is increased. These values are increased via the solvent polarity increment. The resulting solvent-induced chemical changes indicate that the shielding constant of a nucleus in a particular molecule is related to the electronic.

TABLE 4. C-H* Bond Distance (Å) and Chemical Shift Values of H* Atom in the Conformers of 2-chloro-3-methylcyclohexan-1-one Oxime in Gas and Solution Phases at the wB97XD/6-311G(d,p) Level of Theory

Solvent	R(C-H)		δ(H*)	
	I	**II**	**I**	**II**
Gas	1.088	1.095	4.022	3.410
Chloroform	1.088	1.094	4.145	3.657
Chlorobenzene	1.088	1.094	4.154	3.678
THF	1.088	1.094	4.166	3.702
Dimethyldisulfide	1.088	1.094	4.175	3.722
Dichloroethane	1.088	1.094	4.177	3.726
Cyclohexanone	1.088	1.094	4.189	3.750
o-Nitrotoluene	1.088	1.094	4.198	3.769
Propanonitrile	1.088	1.094	4.199	3.773
N,N-Dimethylformamide	1.088	1.094	4.202	3.779

The dependence of values of chemical shifts on the dielectric constant of solvents has been investigated, and the observed relations of the chemical shift values with the dielectric constant of the solvent are fitted by quadratic formulas. The corresponding fitting equations are:

$$\delta({}^1\mathrm{H}, \mathbf{I}) = -8 \times 10^{-5}\,\varepsilon^2 + 0.0049\,\varepsilon + 4.1307, \qquad R^2 = 0.9493,$$

$$\delta({}^1\mathrm{H}, \mathbf{II}) = -0.0002\,\varepsilon^2 + 0.0104\,\varepsilon + 3.6283, \qquad R^2 = 0.9497.$$

The first theoretical treatment of the solvent-induced chemical shift changes was determined by the Kirkwood–Bauer–Magat equation (KBM) via the following equation:

$$\frac{\delta_{\mathrm{gas}} - \delta_{\mathrm{sol}}}{\delta_{\mathrm{gas}}} = \frac{\Delta\delta}{\delta_{\mathrm{gas}}} = \frac{C(\varepsilon - 1)}{2\varepsilon + 1},$$

where δ_{gas} is the vibrational frequency of the solute in the gas phase, δ_{sol} is the frequency of the solute in the solvent, ε is the dielectric constant of the solvent, and C is a constant relying on the dimensions and electrical properties of the vibrating solute dipole.

The dependence of the chemical shift values of the H atom in the studied molecules versus (ε – 1)/(2ε + 1) of the KBM equation exhibits a linear association. These equations are as follows:

$$\mathbf{I}:\ \frac{\Delta\delta}{\delta_{\mathrm{gas}}} = \frac{0.116(\varepsilon - 1)}{2\varepsilon + 1} + 0.01;\ R^2 = 0.9989,$$

$$\mathbf{II}:\ \frac{\Delta\delta}{\delta_{\mathrm{gas}}} = \frac{0.289(\varepsilon - 1)}{2\varepsilon + 1} + 0.03;\ R^2 = 0.9988.$$

The regression coefficients using the data for the investigated solvent systems are shown for the ^{1}H NMR chemical shift values of the complex in the following equation:

$$\mathbf{I}:\ \frac{\Delta\delta}{\delta_{\mathrm{gas}}} = -0.011 + 0.116\frac{\varepsilon - 1}{2\varepsilon + 1} + 0.002\frac{n^2 - 1}{2n^2 + 1};\ R^2 = 0.989,$$

$$\mathbf{II}:\ \frac{\Delta\delta}{\delta_{\mathrm{gas}}} = -0.031 + 0.288\frac{\varepsilon - 1}{2\varepsilon + 1} + 0.005\frac{n^2 - 1}{2n^2 + 1};\ R^2 = 0.989.$$

Therefore, the solvent-induced chemical shift changes indicate a good linear association with the modified-KBM equation.

C-H spin-spin coupling constants. Table 5 shows the total nuclear spin-spin coupling (J), the Fermi contact (FC) and spin-dipolar (SD) terms, the diamagnetic spin orbital (DSO), and the paramagnetic spin orbital (PSO) terms of the studied molecules for the C–H* bond. According to Table 5, the Fermi contact (FC) gives the greatest contribution to the ^{1}J(C-H) constant of the molecules. It can be seen, that the ^1J(C-H) values for the **I**-conformer are larger compared to the **II**-conformer. Our findings indicate an inverse relationship between ^1J(C-H) and the C-H distance, i.e., larger ^1J(C-H) values are associated with shorter C-H distances.

TABLE 5. Total Nuclear Spin-Spin Coupling (J), the Fermi Contact (FC) and Spin–Dipolar (SD) Terms, and the Diamagnetic Spin Orbital (DSO) and Paramagnetic Spin Orbital (PSO) Terms of C-H* in the Conformers of 2-Chloro-3-Methylcyclohexan-1-One Oxime in Gas and Solution Phases at the Wb97xd/6-311G(D,P) Level of Theory

Solvent	**I**					**II**				
	FC	SD	PSO	DSO	TOTAL	FC	SD	PSO	DSO	TOTAL
Gas	140.20	0.32	–0.46	1.39	141.46	130.28	0.22	–0.20	1.44	131.74
Chloroform	141.28	0.33	–0.51	1.38	142.49	133.14	0.25	–0.28	1.42	134.53
Chlorobenzene	141.36	0.34	–0.51	1.38	142.57	133.38	0.25	–0.29	1.42	134.76
THF	141.47	0.34	–0.52	1.38	142.67	133.67	0.25	–0.30	1.42	135.04
Dimethyldisulfide	141.55	0.34	–0.52	1.38	142.74	133.90	0.26	–0.30	1.42	135.27
Dichloroethane	141.56	0.34	–0.52	1.38	142.76	133.94	0.26	–0.30	1.42	135.31
Cyclohexanone	141.67	0.34	–0.53	1.38	142.86	134.23	0.26	–0.31	1.41	135.59
o-Nitrotoluene	141.74	0.34	–0.53	1.38	142.93	134.45	0.26	–0.32	1.41	135.81
Propanonitrile	141.76	0.34	–0.53	1.38	142.95	134.50	0.26	–0.32	1.41	135.86
N,N-Dimethylformamide	141.78	0.34	–0.53	1.38	142.97	134.57	0.26	–0.32	1.41	135.92

As seen in Table 5, ^{1}J(C-H) constants are larger in the solution phase in compared to the gas. The ^{1}J(Pt–C) values increase through an increment in polarity of the solvents.

Conclusion. In this study, a theoretical study was reported on the conformers of 2-chloro-3-methylcyclohexan-1-one oxime at the wB97XD/6-311G(d,p) level of theory in the gas and solution phases. Our results illustrated, that the **I**-conformation has greater stability than the **II**-conformation in the gas and solution phases. The greater stability of the **I**-conformation was favored by electrostatic and conjugation effects and was not favored predominantly by steric effects. The stability of title molecules increased in more polar solvents. The ground state dipole moment values showed good linear relationships with the Bakhshiev polarity function. A good relationship was found between the δ(H) and KBM solvent parameters. The Fermi contact (FC) gives the greatest contribution to the ^{1}J(C-H) constant of the molecules.

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