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Solvent effects on relative stabilities and ^{14}N NMR shielding of cytosine tautomers: continuous set of gauge transformation calculation using polarizable continuum model

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Abstract

The structure and relative energies of the tautomers of cytosine in gas phase and in different solvents are predicted using MP2 and density functional theory methods. The order of stability for these tautomers is C3 > C1 > C2 > C4 > C5 > C6, calculated by MP2 and C1 > C3 > C2 > C4 > C5 > C6, calculated by B3LYP method.

In wide range of solvent dielectrics, relative energy calculation is performed and in all solvents the oxo-amino form C1 is predicted as the most stable tautomer. An empirical equation also calculated for dependence of the relative energy of transition state between C1 and C3 to dielectric of solvents that have no hydrogen bonded to oxygen.

Solvent induced effect on nitrogen NMR shielding of two dominant tautomers is calculated using density functional theory combined with polarizable continuum model and using the continuous set gauge transformation. Direct and indirect solvent effects on shielding are also calculated.

Keywords: Cytosine; NMR shielding; Solvent effect; Ab initio

1. Introduction

The relative stability of tautomers of the pyrimidine base cytosine is of fundamental importance to the structure of DNA. The occurrence of rare tautomers has been put forward as a possible mechanism of spontaneous mutation [1,2].

Heterocyclic tautomeric equilibria are highly sensitive to environmental effects such as solvent polarity or transition to the gas phase (Fig. 1). For example, the equilibrium constant for the pyridone/hydroxy pyridine equilibrium has been shown to change by a factor 1000 on going from a polar to a non polar solvent [3]. It is very likely that the interpretation of data obtained in solution in terms of the relative stability of the tautomers in the gas phase will be erroneous unless the effect of the solvation and association of environmental effects a knowledge of the relative gas phase tautomeric stabilities is an essential prerequisite. The six tautomers of cytosine, considered in this paper are in Scheme 1.

Experimentally, both the hydroxy-amino (C3) and oxo-amino (C1 and C4) forms have been identified in matrix isolation infrared studies [4,5], with the C3 found in higher concentration. There is also some evidence for the presence of a small amount of the oxo-imino form (C2). Microwave spectroscopy has

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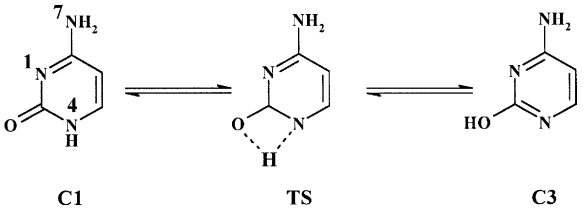
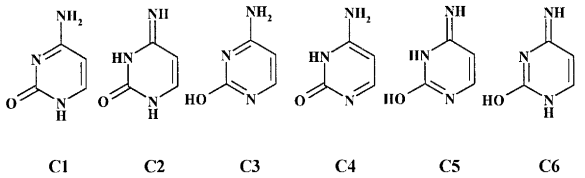


Fig. 1. Transition structure between C1 and C3.



Scheme 1.

yielded rotational constants for some tautomers that correspond to these structures [6].

On the theoretical side, many calculations have been carried out on the relative stabilities of the cytosine tautomers [7–13]. The energy differences between them are small and extremely sensitive to the approach used, giving rise to various results. Fogarasi [7] calculated single point coupled cluster single and double (CCSD) energies at MP2-optimized geometries for the five lowest isomeric forms of cytosine with a double-zeta basis. Kobayashi [13] also has performed a high quality calculation on those tautomers.

The final order of stability Fogarasi arrived at was: hydroxy-amino < oxo-imino < oxo-amino and for Kobayashi: hydroxy-amino < oxo-amino < oxo-imino.

The solvent dependence of tautomeric equilibria has also been the subject of many experimental studies [14–16]. The tautomeric equilibria of hydroxypyridines have also been studied theoretically owing to their relevance to the oxo-amino ⇔ hydroxy-amino tautomerism of nucleic acids [17–19].

It has been well established that solvents with large dielectric constants favor the more polar tautomers. For the tautomerism of hydroxypyridine system, this means that the equilibria will shift towards the pyridone in more polar solvents because the oxo form tautomer is usually the more polar species. Earlier, theoretical studies of tautomeric reactions were essentially concerned with those that happen in the gas phase. It is almost that efforts have been made to stimulate tautomeric process in solvents since 1989 [20–23]. Hobza and Sponer [24] have published a review about structure, energetics and dynamics of the nucleic acid base pairs. Ab initio calculation of nuclear magnetic shielding has become an indispensable aid in the investigation of molecular structure and accurate assignment of NMR spectra of compounds. Because most of the systems studied experimentally are in solution, the formulation of satisfactory theoretical models for solvated systems has been the object of continuously increasing interest [25–27].

Evaluation of the dependability of such models requires its rigorous application to various types of molecular systems and comparison of compound results with experimental data. The data from the experimental studies constitute a database of experimental nitrogen shielding that can be utilized to evaluate the reliability of NMR calculations for systems in solution. The solvation effect is taken into account via the Self-Consistent Reaction Field (SCRF) method. This method is based on Onsager reaction field theory of electrostatic solvation. In this model, the solvent is considered as a uniform dielectric with a given dielectric constant ε. The solute is placed into a cavity within the solvent. SCRF approaches differ in

Table 1
Relative stabilities of cytosine tautomers in gas phase (kcal/mol)

	MP2/6-31 + G(d,p)//MP2/6-31 + G(d,p)	MP2/6-311 + G(d,p)//MP2/6-31 + G(d,p)	B3LYP/6-311 + G(2d,p)//MP2/6-31 + G(d,p)
C1	0.651103	1.547563	0.0
C2	2.414782	3.070466	1.796057
C3	0.0	0.0	0.533006
C4	8.036639	8.710459	6.981106
C5	13.589345	13.428326	13.465036
C6	21.725006	21.398199	21.787255

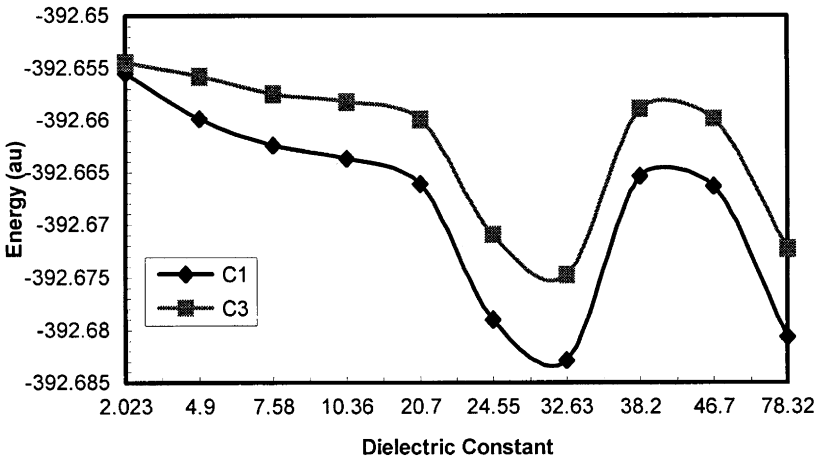


Fig. 2. Variation of energy (au) with ε for C1 and C3.

how they define the cavity and the reaction field. Tomasi's Polarized Continuum Model (PCM) [29,30] defines the cavity as a union of a series of interlocking atomic spheres. The effect of polarization of the solvent continuum is represented numerically.

Manalo et al. [28] using PCM and continuous set gauge transformation (CSGT) [31] method calculate nitrogen NMR shielding of tetrazine and isomeric tetrazoles in a wide range of solvents encompassing a broad spectrum of dielectric constant ε. PCM has proved useful in describing the effects of the solvent on some characteristics of the molecule in solution [32]. Recent theoretical studies using PCM include calculation of dipole polarizability and hyperpolarizabilities, magnetic susceptibility and nuclear magnetic shielding [33,34] and of course solvent effect on NMR shielding of solutes [35].

In 1997, a new PCM method called the integral equation formulation [36,37], was introduced. In this method, diverse types of dielectrics (standard isotropic liquids, intrinsically anisotropic media like liquid crystals and solid matrices and ionic solutions) are treated in a single common approach. All PCM calculations in this report have been performed using this formalism as implemented in GAUSSIAN 98 [38].

2. Computational details

The ab initio molecular orbital calculations were

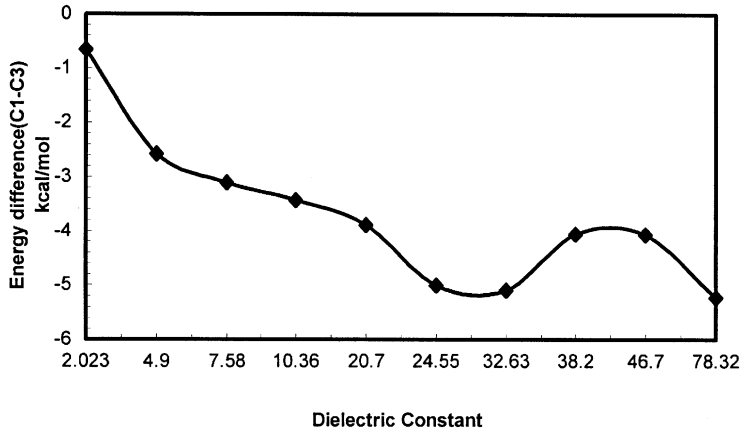


Fig. 3. Variation of energy difference between C1 and C3 with ε.

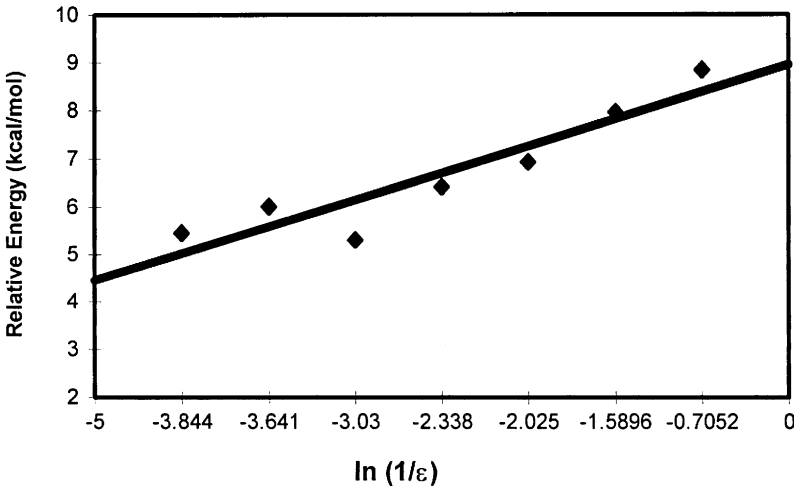


Fig. 4. Linear dependence of relative to $\ln(1/\varepsilon)$ for solvents that do not have the –OH group.

carried out with the GAUSSIAN 98 program. Geometry optimizations in the gas phase for all six tautomers were performed at the Hartree–Fock (HF) and second order Møller–Plesset (MP2) levels with 6-31G(d) and 6-31 + G(d,p) basic sets. For two dominant tautomers C1 and C3, geometry optimization also performed with 6-311++G(d,p) basis at MP2 level.

The unavailability of PCM-gauge invariant atomic orbital [33,34] in GAUSSIAN 98 has restricted us to exploit PCM–CSGT [33] in nuclear shielding calculations. Direct and indirect contributions to the total solvation effect are examined. Direct effects involve perturbation of solvent on the electronic wave function of the solute held at fixed geometry; indirect effect are due to the relaxation of the solute geometry under the influence of the solvent [33,34]. The same convention adopted by Witanowski et al. [39] is used to describe trends in shielding data; thus, a positive solvent effect indicates an increase in nuclear shielding.

The PCM cavity is defined by using Pauling [38] radius for each solute atom. The model chemistry used for shielding calculations is B3LYP/6-311++G(2d,2p). This corresponds to the approximation method that makes use of Becke-Style 3-parameter density functional theory [40] with the Lee–Yang–Paar correlation functional [41]. The triple-ζ basis set adds three sizes of s and p functions on heavy atoms and hydrogens, respectively, as well as diffuse functions on both.

Relative solvent effects are calculated using the corresponding nuclear shielding in cyclohexane as

Table 2
Relative stabilities of cytosine tautomers in different solvents (kcal/mol)

Solvent C6	Level/basis set	C1	C2	C3	C4	C5	C6
Water	MP2/6-311++G(d,p)//MP2/6-31 + G(d,p)	0.0	6.2208	3.5178	4.7472	17.8559	21.1592
	B3LYP/6-311 + G(2d,p)//MP2/6-31 + G(d,p)	0.0	7.5996	6.8630	6.1712	23.3901	27.084
Methanol	MP2/6-311++G(d,p)//MP2/6-31 + G(d,p)	0.0	6.0410	3.4202	4.8641	17.7122	21.1581
	B3LYP/6-311 + G(2d,p)//MP2/6-31 + G(d,p)	0.0	7.3791	6.7322	6.2125	23.1271	26.9550
DMSO	MP2/6-31 + G(d,p)//MP2/6-31 + G(d,p)	0.0	4.8368	2.8411	5.4997	17.4159	21.1847
	B3LYP/6-311 + G(2d,p)//MP2/6-31 + G(d,p)	0.0	5.5099	5.1727	5.5413	19.5245	23.9374
Ethanol	MP2/6-31 + G(d,p)//MP2/6-31 + G(d,p)	0.0	5.1441	3.4932	5.1348	17.3164	20.3024
	B3LYP/6-311 + G(2d,p)//MP2/6-31 + G(d,p)	0.0	7.2397	6.6503	6.2228	22.9434	26.8721

Table 3
Variation of relative stability of transition state between C1–C3 with ε (MP2/6-31 + G(d,p) with PCM model of solvation)

ε	$E_{relative}$ (kcal/mol)
78.32	0.0
46.7	5.4449
38.2	6.0045
24.55	− 1.6965
32.63	0.6134
20.7	5.2996
10.36	6.4255
7.58	6.9418
4.9	7.9657
2.023	8.8494

reference. Direct ($\Delta\sigma_{dir}$) and indirect ($\Delta\sigma_{ind}$) solvent effects are obtained with a slight modification of the method used by Cammi et al. [34]. Instead of deriving $\Delta\sigma_{dir}$ from the difference of the PCM-optimized shielding and the PCM shielding of the molecule held at the geometry optimized in vacuo, it is obtained from the shielding calculated in vacuo for a molecule that is geometry optimized in the solution. Thus

$$\Delta\sigma_{dir} = \sigma_{sol}(R_v) - \sigma_{cyc}(R_v) \quad (1)$$

$$\Delta\sigma_{ind} = \sigma_{vac}(R_s) - \sigma_{vac}(R_{cyc}) \quad (2)$$

where $\sigma_{sol}(R_v)$ is the value of the nuclear shielding computed in solution but with the solute in the geometry optimized in vacuo, and $\sigma_{vac}(R_v)$ and $\sigma_{vac}(R_{cyc})$ are the corresponding parameters for the calculation with cyclohexane.

Table 4
PCM–CSGT nitrogen NMR shielding (ppm) for C1

Solvent	ε	N(1)	N(4)	N(7)
Water	78.32	20.7318	89.2079	164.0336
DMSO	46.7	11.2301	93.0906	162.3470
Nitromethane	38.2	11.1221	93.1108	162.3660
Ethanol	24.55	19.5839	89.5668	164.0700
Methanol	32.63	19.9903	89.4398	164.0557
Acetone	20.7	10.6315	93.2017	162.4538
Dichloroethane	10.36	9.6190	93.3861	162.6380
THF	7.58	8.9203	93.5117	162.7665
Chloroform	4.9	7.5993	93.7434	163.0153
Cyclohexane	2.023	3.3320	94.4434	163.8613

Table 5
PCM–CSGT nitrogen NMR shielding (ppm) for C3

Solvent	ε	N(1)	N(4)	N(7)
Water	78.32	30.6593	5.1748	171.5490
DMSO	46.7	22.2065	7.4266	168.9552
Nitromethane	38.2	22.1423	7.4042	168.9635
Ethanol	24.55	29.8018	5.2551	171.4799
Methanol	32.63	30.1068	5.2276	171.5095
Acetone	20.7	21.8507	7.3004	169.0012
Dichloroethane	10.36	21.2535	7.0757	169.0813
THF	7.58	20.8439	6.9142	169.1381
Chloroform	4.9	20.0773	6.5925	169.2484
Cyclohexane	2.023	17.6721	5.4234	169.3627

3. Results and discussions

3.1. Gas phase

The relative stabilities of the cytosine structures are given in Table 1. They reproduce those found by Kobayashi, including the unexpectedly different orderings between MP2 (C3 > C1) and DFT (C1 > C3). The relative stabilities obtained at the DFT level found the oxo-amino form to be the lowest in energy (Fig. 2). DFT (especially B3LYP) calculations is probably too sensitive and thus unreliable for such calculations.

3.2. Solvent effects on structure

Oxo-amino form (C1) is predicted as the most stable form by both MP2 and DFT methods in all solvents. Our calculations found that the hydroxy-amino (C3) form was considerably destabilized by solvation as shown in Figs. 3 and 4. The standard approach of the PCM (without any explicit solvent molecules), as is used here, appears to be a good first step in the theoretical investigation of the effect of solvent on nuclear magnetic shielding (Table 2). In the first instance, irregular variations were observed concerning relative energy versus dielectric constant, where the energy variations are concluded as the result of two levels of regular changes:

(a) Energy variations with solvents that have no hydrogen bonded to oxygen.
(b) Energy variations with solvents that have hydrogen bonded to oxygen (Table 3).

It is well observed that energy values increase

Table 6
Value of $\Delta\sigma_{dir}$ and $\Delta\sigma_{ind}$ calculated for C1

ε	$\Delta\sigma_{dir}$			$\Delta\sigma_{ind}$		
	N(1)	N(4)	N(7)	N(1)	N(4)	N(7)
78.32	17.3998	− 5.2355	0.1723	− 2.386	0.5178	− 1.2747
46.7	7.8981	− 1.3528	− 1.5143	− 1.3361	0.7857	− 0.0552
38.2	7.7901	− 1.3326	− 1.4953	− 1.3799	0.7694	− 0.0775
24.55	16.2519	− 4.8766	− 0.2087	− 2.4441	0.412	− 1.2775
32.63	16.6583	− 5.0036	− 0.1964	− 2.3483	0.3529	− 1.3005
20.7	7.2995	− 1.2417	− 1.4075	− 1.3671	0.6196	− 0.1410
10.36	6.2870	− 1.0573	− 1.2233	− 1.1176	0.6036	− 0.0958
7.58	5.5883	− 0.9317	− 1.0948	− 0.9961	0.5932	− 0.0415
4.9	4.2673	− 0.7000	− 0.8460	− 0.8311	0.3621	− 0.1525
2.023	0.0	0.0	0.0	0.0	0.0	0.0

nonlinearly with decrease in dielectric constants in the former case while future investigations are required to explain the latter. By plotting the relative energy versus $\ln(1/\varepsilon)$, the following equation is derived (Fig. 4):

$$E_{rel} = 1.11438 \ln(1/\varepsilon) + 9.216; \quad \text{Correlation Coeff.} = 0.9597. \tag{3}$$

As shown in Fig. 4, some points do not match on the line and such deviations might be due to factors such as polarizability and dipole moment. Results that are more accurate might be obtained if successive values of dielectric constants in a narrower range are chosen (Tables 4 and 5).

It is clear that an increase in the dielectric constants increases the stability of TS, implying that the TS is a polar species.

3.3. Solvent effects on NMR spectra

Solvation effect on NMR spectra consists of two parts: $\Delta\sigma_{dir}$ and $\Delta\sigma_{ind}$. Tables 6 and 7 report the values of nitrogen NMR shielding of the compounds studied. It might be suggested that optimization of solute molecule in solvent followed by shielding calculations is similar to shielding calculations of solvent–solute as an isolated system. However, if the molecule is first optimized in gas phase and then NMR shielding calculations is performed in the solvent, the solvent–solute interactions are taken into consideration for NMR shielding calculation.

Therefore, in solvent effect studies, it is more

Table 7
Value of $\Delta\sigma_{dir}$ and $\Delta\sigma_{ind}$ calculated for C3

ε	$\Delta\sigma_{dir}$			$\Delta\sigma_{ind}$		
	N(1)	N(4)	N(7)	N(1)	N(4)	N(7)
78.32	12.9872	− 0.2486	1.9163	− 2.2766	0.0761	− 1.5238
46.7	4.5344	2.0032	− 0.6775	− 0.6156	0.6654	− 0.0401
38.2	4.4702	1.9808	− 0.6692	− 0.6482	0.6108	− 0.0560
24.55	12.1297	− 0.1683	1.8472	− 2.1988	0.0036	− 1.4968
32.63	12.4347	− 0.1958	1.8768	− 2.1880	− 0.0678	− 1.5017
20.7	4.1786	1.877	− 0.6315	− 0.6506	0.5095	− 0.0635
10.36	3.5814	1.6523	− 0.5514	− 0.4787	0.5027	− 0.0515
7.58	3.1718	1.4908	− 0.4946	− 0.4109	0.4561	− 0.0020
4.9	2.4052	1.1691	− 0.3843	− 0.3528	0.3053	− 0.0784
2.023	0.0	0.0	0.0	0.0	0.0	0.0

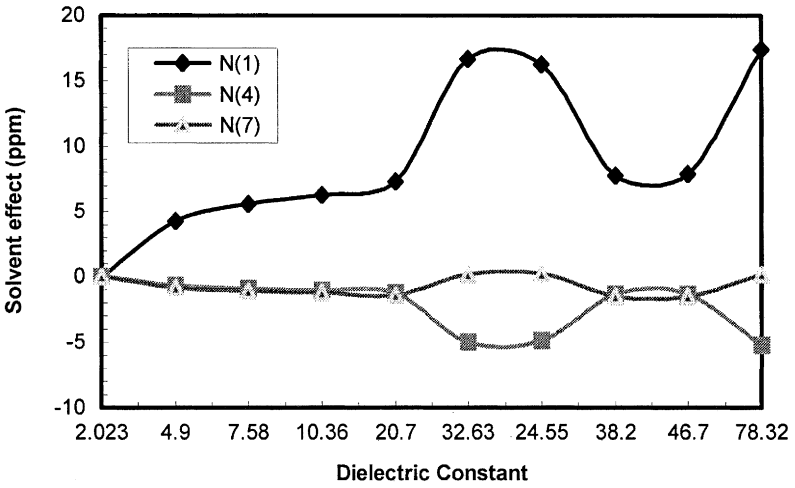


Fig. 5. Dependence of calculated solvent effect on the nuclear magnetic shielding of ^{14}N in C1.

advisable to carry out shielding calculations in solution even with a fixed (gas-phase optimized) solute geometry, than to perform shielding computations in vacuo for a solute where the geometry is optimized in solution. As the dielectric constant of the solvent increases, N1 and N4 are more shielded and deshielded, respectively and presented in Figs. 5 and 6. These changes take place gradually, except where protic solvents, water, ethanol and methanol are used. In such a case, the N4 deshielding as well as the N1 shielding increases suddenly and the amounts of variations are greater for N1. Such changes are greater in the case of C1 as compared to C3.

It is apparent that for a more accurate prediction of solvent effects on shielding and relative stabilities, it is necessary to consider specific solute–solvent interactions by introducing one or several solvent molecules in the calculations.

4. Conclusion

This work presents a self consistent reaction field

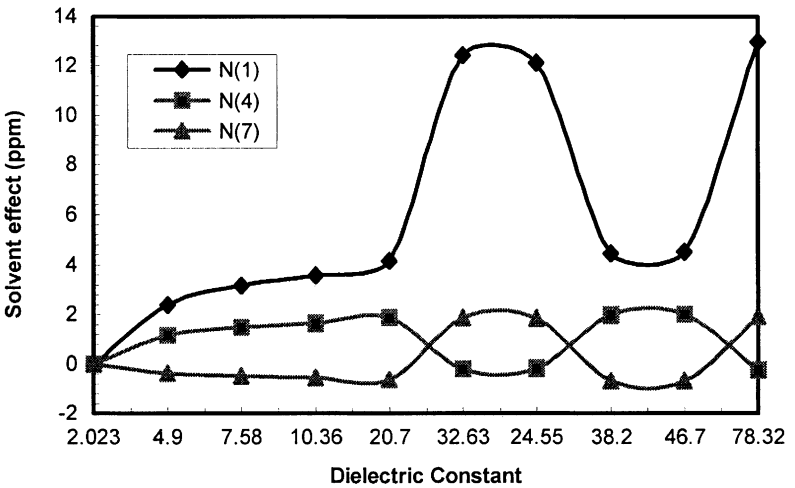


Fig. 6. Dependence of calculated solvent effect on the nuclear magnetic shielding of ^{14}N in C3.

study of relative stability and NMR nitrogen shielding calculations for two dominant tautomers of cytosine; oxo-amino and hydroxy-amino forms. MP2 level of theory combined with 6-31 + G(d,p) basis predicted the energy difference of C1–C3 about 0.65 kcal/mol and MP2/6-31 + G(d,p) optimized geometry followed by MP2/6-311++G(d,p) single point energy calculation predicted this difference about 1.55 kcal/mol in gas phase.

In the liquid phase, both MP2 and density functional levels of theory with 6-31 + G(d,p) and MP2/6-311++G(d,p), respectively, show the oxo-amino C1 tautomer as the most stable form.

This work also presented the application of PCM for calculation of nitrogen NMR shielding constants. For C1 and C3l, N(1) has the maximum and N(7) has the minimum range of variations in a wide range of dielectrics, respectively. Of course, to achieve better results, it is necessary to consider hydrogen bonding by introducing one or more solvent molecules in the calculations.

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