

Solvent effects on ^{13}C and ^1H NMR shielding of cyclic ketones: An experimental and theoretical study

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Abstract

^1H and ^{13}C NMR chemical shifts of various cyclic ketones from four to seven-membered rings have been measured and compared with calculated data in 17 different solvents. The solvent effects on NMR spectra were simulated with the polarizable continuum model (PCM). Magnetic shielding tensors were performed using the DFT coupled gauge-included atomic orbital calculations. A multi-linear-regression analysis has been carried out using the Kamlet–Abboud–Taft (KAT) solvatochromic parameters in order to elucidate and quantify the solvent effects on the ^1H and ^{13}C chemical shifts of the select compounds. It has been found that there is a good correlation between the solvent induced chemical shifts of ^{13}C and π^* scale of solvent polarity. ^1H chemical shifts are affected mainly by polarity–polarizability and basicity of the solvent. The agreement between the calculated and the experimental data is good in all instances.

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1. Introduction

The importance of the carbonyl functional group, particularly the cyclic functionality, is demonstrated by the fact that this functional group is present in some antibiotics [1]. Because of the important of the carbonyl group in organic chemistry, it has been the object of continuously increasing interest and consequently, it is very difficult to cite all corresponding studies. However, we can mention, for instance, a several investigations concerning the electric field effect of the carbonyl group in cyclic ketones [2] and others which considered only aliphatic ketones [3]. Concerning solvent effects on ^1H and/or ^{13}C chemical shift of carbonyl group, except a very earlier contributions [4], there is almost complete lack of information including observed and calculated NMR chemical shifts for cyclic ketones. We have also been involved for some time in the study of the basicity of the carbonyl group, both in gas

phase and in solution [5]. We are now extending this study to the effect of the solvent on the ^1H and ^{13}C chemical shifts, from experimental and theoretical points of view as continuation to our studies on carbonyl compounds. There is no doubt that NMR spectroscopy is an essential tool for all branches of chemistry due to the richness of information that can be obtained.

More than two centuries have elapsed since Thomson and Nernst studies on the connection between the dielectric constant of a solvent and its dissociating power [6,7]. Ever since, several approaches using the dielectric constant as a parameter in describing any solvent system were developed [8–13]. However, it was often difficult to calculate and/or experimentally separate these contributions. For this reason, other approaches have been developed to understand and predict solvent effects. They can be grouped into empirical correlations, based on some experimental bulk solvent parameter, and computational approaches, based on quantum chemistry and model theory. Several techniques have been developed to study this concept, in particular NMR spectroscopy. From both experimental and

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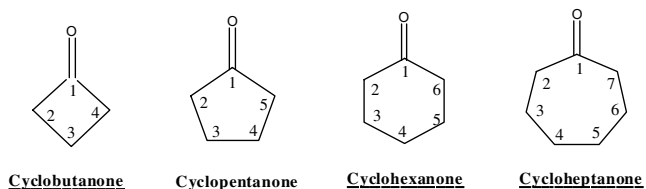
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theoretical points of view, solvent effect has been a steady increase of interest on NMR properties [14]. Comprehensive works on solvent effects on chemical shifts [15–17] and coupling constants [16–20] date back to the mid of 1970 and the beginning of 1980. As consequence, linear functions with few parameters for description of the solvent effect are proposed [21–25]. One of the most interesting and the most extensively applied method is that proposed by Kamlet, Abboud and Taft (KAT) using linear solvation relationships [26–30].

From theoretical point of view, the polarizable continuum model (PCM) proposed by Tomasi et al. [31] has been demonstrated in any occasions to be useful in describing the influence of the solvent on some properties of molecules in solution [32].

In this paper we have examined the solvent effect on the ^1H and ^{13}C chemical shifts of some cyclic ketones from both experimental and theoretical point of view. These data will allow to more detailed analysis of the influence of the solvent polarity–polarizability on the chemical shifts as well as the nature of the solute–solvent interactions. Furthermore, it will be shown, via a comparative treatment, that the PCM model is capable to predict the chemical shifts with a very satisfactory precision.

Thus, the following compounds were investigated in 17 different solvents:



According to the KAT model, the observed chemical shift of compound X at dilute solution in solvent Y , $\delta(X, Y)$, is decomposed into five contributions [30].

$$\delta(X, Y) = \delta(X, CH) + s^X(\pi_Y^* + d^X\eta_Y) + a^X\alpha_Y + b^X\beta_Y \quad (1)$$

consider a solute X (ion or neutral species) in a solvent Y , in all case, the charge distribution of X will interact with that of Y assuming that Y is a continuous dielectric, its polarization follows. The field created by the polarized dielectric interacts with the charge distribution of the solute and leads to its modification. Other important but more specific solvent–solute interactions able to perturb the electronic distribution of the solute are hydrogen bonding and charge transfer. Of course, the concept of Y being a continuous dielectric is only an approximation. A number of empirical scales of solvent polarity–polarizability have been developed over the years. They are based on the experimental effect of solvent on physical and reactivity properties of some reference solutes considered as molecular probes [33,34].

Table 1
Solvent parameters π^* , α , β and η taken from reference [26]

Solvent	π^*	β	α	η
Cyclohexane	0.00	0.00	0.00	0.00
Diethyl ether	0.27	0.47	0.00	0.00
Carbon tetrachloride	0.28	0.00	0.00	0.50
Tetrahydrofuran	0.58	0.55	0.00	0.00
Butyronitrile	0.71	0.00	0.00	0.00
Acetone	0.71	0.48	0.08	0.00
1,2-Dichloroethane	0.81	0.00	0.00	0.50
Propylene carbonate	0.83	0.40	0.00	0.00
Dimethylformamide	0.88	0.69	0.00	0.00
Dimethylsulfoxide	1.00	0.76	0.00	0.00
Toluene	0.54	0.11	0.00	1.00
Benzene	0.59	0.10	0.00	1.00
Fluorobenzene	0.62	0.07	0.00	1.00
Anisole	0.73	0.22	0.00	1.00
Acetophenone	0.90	0.49	0.00	1.00
Benzonitrile	0.90	0.41	0.00	1.00
Nitrobenzene	1.01	0.39	0.00	1.00

The systematic quantitative study of the influence of the medium on NMR chemical shifts and the use of these effects for the construction of empirical “medium polarity scales” date back to 1963. So the empirical π^* scale corresponds to the solvent polarity–polarizability scale [27,30]. $\delta(X, CH)$ is the chemical shift of X measured in cyclohexane as reference. This reference solvent does not form a hydrogen bond ($\alpha_Y = \beta_Y = 0$). The η_Y parameter is a polarizability correction term for polychlorinated ($\eta_Y = 0.5$) and aromatic ($\eta_Y = 1.0$) solvents. In fact, there is evidence indicating that this term actually accounts for interactions (probably charge-transfer) between the aromatic ring of the solvents and the solvatochromic indicators used to construct the π^* scale. The α_Y scale of solvent acidity describes the ability of the solvent to donate a proton in an hydrogen bond solvent–solute interaction. The β_Y scale of solvent basicity describes the ability of the solvent to accept a proton in a hydrogen bond solvent–solute interaction. The coefficients s^X , a^X and b^X denote the sensitivity of $\delta(X, Y)$ to such solvent effect (polarity–polarizability, acidity and basicity respectively). The $s^X d^X$ coefficient defines the sensitivity of $\delta(X, Y)$ to the polarizability adjustment term. Table 1 lists the solvent parameters used in this work [26].

2. Computational details

Quantum chemical calculations were performed with the use of the Gaussian 03 set of programs [35]. All structures were fully optimized with the density functional theory (DFT) using Becke’s three parameter hybrid method [36] and correlation functional of Lee–Yang–Parr (B3LYP) [37–39] in conjunction with the 6-311+G* [40] basis set. Chemical shifts of the considered compounds were calculated at the same level using the Gauge-Included Atomic Orbital (GIAO) approach [41,42]. Absolute isotropic magnetic shieldings were transformed into chemical shifts by referencing to the shieldings of a standard compound (TMS)

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