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# $^{13}$C NMR spectroscopic studies of the behaviors of carbonyl compounds in various solutions

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ABSTRACT

$^{13}$C NMR spectroscopic studies were performed for carbonyl compounds having a hydroxyl group, a carboalkoxy group, an acetoxy group, or a carboxyl group in various solvents with different polarities for observation of their behaviors of $^{13}$C NMR chemical shifts of carbonyl carbons in solutions. It was found that the chemical shifts of the carbonyl carbons in $^{13}$C NMR have good correlation with the empirical parameter for solvent polarities, $E_T^N$, depending on the structures. Inter- or intramolecular hydrogen bonding and dipolar-dipolar interactions appear to play a key role in this observation.

## Introduction

NMR spectroscopy is a useful tool for studying not only structures of molecules but also their internal and external chemical environments. With the use of NMR spectroscopy, a fair number of studies have been reported for investigation of inter- or intramolecular interactions of organic molecules through various forces such as hydrogen-bonding, dipole-dipole forces, metal coordination, van der Waals interaction, and anisotropic effects. For example, quantitative assessment of intramolecular hydrogen bonding is reported for flavones having OH or NH groups based on the $^{1}$H NMR chemical shifts for the hydroxy protons in chloroform-*d* and in DMSO $d_6$.[1] A criterion for a non-covalent intermolecular attractive interaction of halogenated solvents was proposed by $^{31}$P NMR chemical shifts of triethylphosphine oxide in correlation with calculated parameters.[2] Many other NMR spectroscopic studies have also been reported that provide insights into solvent effects derived by interaction between organic molecules and solvent molecules.[3]

Carbonyl compounds are known to form aggregates by intermolecular forces, such as hydrogen bonding and dipole-dipole interaction in a solution. Their behaviors have been under close scrutiny with the use of NMR spectroscopy for several decades. For example, during the investigation of Marangoni flow around a camphor disk on water, a good linear correlation was observed between an empirical parameter for solvent polarity ($E_T^N$)[2,4] and the $^{13}$C NMR chemical shifts of the carbonyl (C=O) carbon in camphor in various NMR solvents,[5] as the $^{13}$C chemical shifts of the C=O were shifted downfield with the increase of $E_T^N$. It has been concluded that the downfield shift was caused by the increased polarity surrounding the camphor molecule, leading to decease of the electron densities of the carbonyl carbon. This is a similar observation previously reported for the $^{13}$C NMR chemical shifts for the carbonyl carbon of acetone.[3d] Since $^{13}$C NMR chemical shifts can be a reasonable indicator of electron density, here we extended this study to more polar carbonyl compounds, including esters, carboxylic acids, and carboxylates in order to observe how the polarities of the solvents affect the carbonyl groups. We further studied more polar carbonyl compounds having more than one polar functional group in the same molecule by $^{13}$C NMR spectroscopy in order to observe how the combination of these polar functional groups is influenced by the polarities of the solvents.

## Results and discussion

We first measured the $^{13}$C NMR chemical shifts of the carbonyl groups in acetic acid, ethyl acetate, and sodium acetate in various solvents, and plotted them against the solvent polarity parameter,

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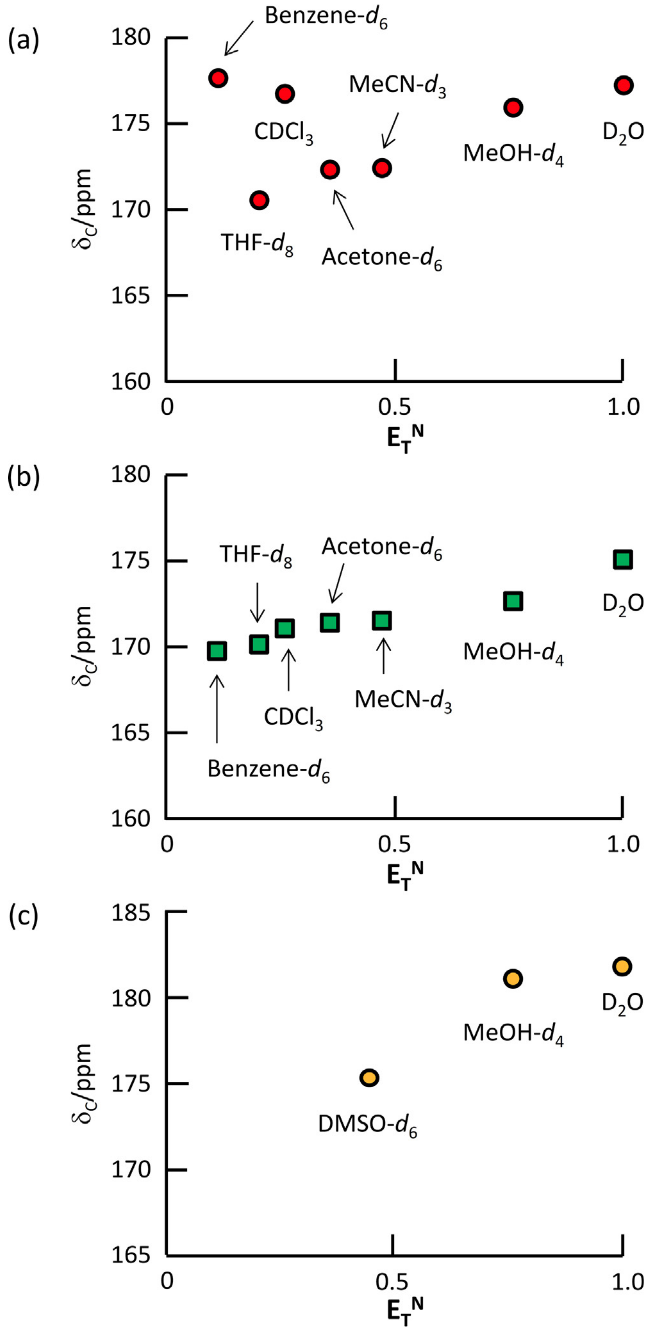
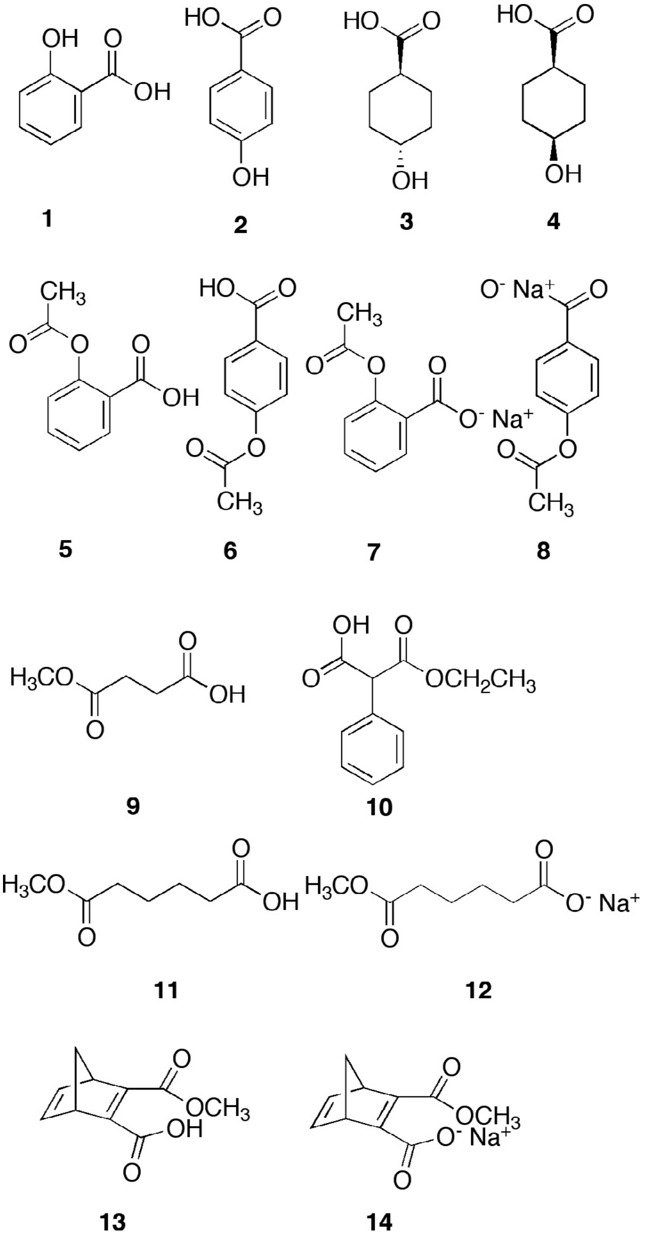


**Fig. 1.** $^{13}$C NMR chemical shifts of carbonyl carbons of (a) acetic acid, (b) ethyl acetate, and (c) sodium acetate.

$E_T^N$, as shown in Fig. 1. The carbonyl group in acetic acid shows irregular changes with no particular correlation with $E_T^N$, while the carbonyl groups in ethyl acetate and in sodium acetate shows downfield shifts with increase of $E_T^N$. We reasoned that intermolecular hydrogen bonding in acetic acid is counteracting the polarity of the solvent, while such influence does not exist in the others and hence show clearer correlation with the $E_T^N$.

Therefore, we continued this investigation for carbonyl compounds, **1**–**14**, having various polar functional groups such as a hydroxyl group, acetoxy group, carboalkoxy group, or carboxyl group, including half-esters in various solvents for observation of their behaviors of $^{13}$C NMR chemical shifts of carbonyl carbons in solutions (Scheme 1), focusing on the correlation between the solvent polarities and influence by the combination of these polar groups.[6]



**Scheme 1.** Carbonyl compounds studied by $^{13}$C NMR spectroscopy.

We next examined the correlation between $^{13}$C NMR chemical shifts for the carbonyl carbons and the solvent polarity parameter $E_T^N$ for 2-hydroxybenzoic acid (**1**), 4-hydroxybenzoic acid (**2**), and *trans*- and *cis*-4-hydroxycyclohexane carboxylic acids (**3** and **4**). However, as shown in Fig. 2, no particular correlation was observed between the chemical shifts of the carbonyl carbons in the COOH groups of **1**–**4** and the solvent polarity parameter $E_T^N$. We reasoned that in **1**, the intramolecular hydrogen bonding keeps the chemical shift near-constant. In **2**, **3**, and **4**, intermolecular hydrogen bonding of the carboxyl groups and hydroxyl groups as well as dipolar interaction with solvent molecules are conceivable, and these forces may be countervailing, making the chemical shifts irregular. It is notable that the carboxyl carbons in **1** and **2** show noticeable upfield shifts compared to those in **3** and **4** in all the solvents because of somewhat increased electron densities through the resonance effect from the benzene rings.