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A novel nine-membered intramolecular hydrogen bonding in methyl naphthoate bearing phenol moiety

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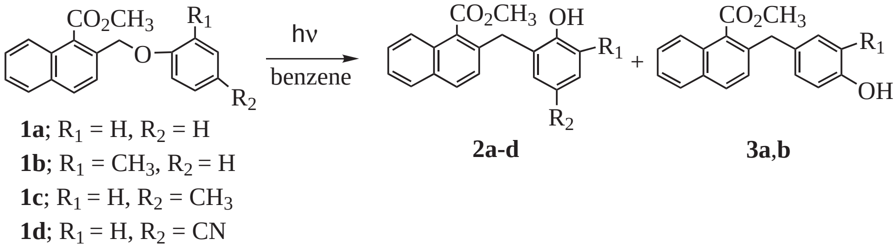
Abstract—A novel nine-membered intramolecular hydrogen bonding between ester carbonyl and phenolic hydroxyl groups was investigated based on X-ray crystallography and variable-temperature ^{1}H NMR spectroscopy. The ^{1}H NMR studies in $CDCl_3$ indicated that a significant downfield shift of the phenolic proton as the temperature is lowered. © 2001 Elsevier Science Ltd. All rights reserved.

Inter- and intra-molecular hydrogen bonding of organic molecules has been well investigated from a variety of fields in organic chemistry.[1] Recent advances in X-ray crystallographic analyses for the crystalline structures having hydrogen bonding have been precisely discussed as regards their chemical and physical properties. However, intramolecular hydrogen bonding of phenol derivatives is less discussed except the chemical and physical behavior of salicylic ester and its related compounds which form the typical six-membered hydrogen bonding.[2] We now report a novel nine-membered intramolecular hydrogen bonding between ester carbonyl and phenolic hydroxyl groups in solid state and in $CDCl_3$ solution.[3]

Compounds **2a**–**d** and **3a**–**b** were prepared by the photo-Claisen type rearrangement of 2-(phenoxymethyl)-1-methoxycarbonylnaphthalene derivatives **1a**–**d** (Scheme 1).[4] The FT-IR spectrum of **2b** (KBr) showed an absorption of the ester carbonyl group at 1698 cm^{-1} which was shifted to a lower wavenumber than that of **1b** and **3b** at 1719 cm^{-1}. It also showed an O–H stretching as a very broad absorption at 3353 cm^{-1}, which was a lower wavenumber than that of **3b** at 3422 cm^{-1}. These spectral data clearly suggested the formation of nine-membered intramolecular hydrogen bonding in solid state. The X-ray crystallographic analysis of **2b** also showed the possibility of intramolecular hydrogen bonding (Fig. 1).[5]

^{1}H NMR studies of **2a**–**d** in $CDCl_3$ at 20°C (5 mM) indicated a significant downfield shift of phenolic hydrogen (7.25, 7.36, 6.93, 8.91 ppm) compared to those of the reference compounds, such as phenol (5 mM, 4.70 ppm), *o*-methylphenol (5 mM, 4.63 ppm), *p*-methylphenol (5 mM, 4.52 ppm), and *p*-cyanophenol (5 mM, 5.52 ppm). ^{1}H NMR chemical shifts of **2a**–**d** at 20°C were independent of those concentrations (1–50



1a; $R_1 = H$, $R_2 = H$
1b; $R_1 = CH_3$, $R_2 = H$
1c; $R_1 = H$, $R_2 = CH_3$
1d; $R_1 = H$, $R_2 = CN$

2a-d

3a,**b**

Scheme 1.

Keywords: nine-membered hydrogen bonding; phenolic hydroxyl group; variable-temperature ^{1}H NMR spectroscopy.

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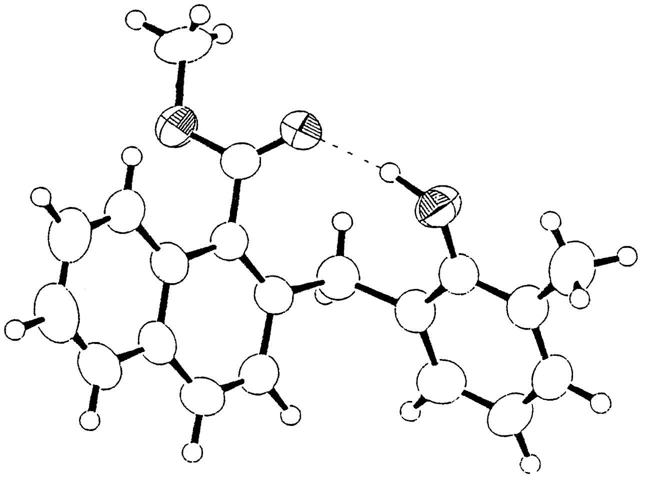
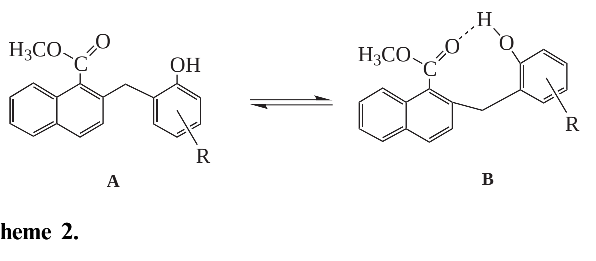


Figure 1. ORTEP drawing of **2b**.

mM). These results clearly show that **2a–d** form the intramolecular hydrogen bonding in $CDCl_3$ solution. In addition, the FT-IR spectrum of **2b** in $CHCl_3$ (5 mM) at room temperature showed two carbonyl absorptions at 1721 (weak) and 1702 (strong) cm^{-1}. The former absorption indicated the existence of free ester carbonyl group, and the latter one was assigned to the hydrogen bonded ester carbonyl group. There is equilibrium between the non-hydrogen bonding state **A** and the fully hydrogen bonding state **B** (Scheme 2).

Fig. 2 shows the temperature dependence of phenolic proton chemical shifts of **2a–d** in $CDCl_3$. They linearly moved downfield with a lowered temperature, and were shifted upfield with a raised temperature. Interestingly, the methylene protons were shifted upfield, but the methyl protons of ester moved downfield with a lowered temperature. The non-hydrogen bonding state **A** and the fully hydrogen bonding state **B** is at fast equilibrium in the NMR time scale, and the observed chemical shifts are weight-averages of those in the two states. The downfield chemical shift of phenolic proton indicates more proportions of the intramolecular hydrogen bonding state in $CDCl_3$. The equilibrium of **2a–d** lies to the intramolecular hydrogen bonding state with a lowered temperature. The substituent effect showed that the hydrogen bonding of **2d**, having an electron-withdrawing group was much stronger than that of **2c** having an electron-donating group. This means that the intramolecular hydrogen bonding depends on the acidity of the phenol.[6]

In conclusion, we have found that **2a–d** formed a novel nine-membered intramolecular hydrogen bonding between ester carbonyl and phenolic hydroxyl groups in $CDCl_3$, and this intramolecular hydrogen bonding is dependent on the acidity of phenol. To the best of our knowledge, this is a rare example of medium ring size hydrogen bonding between aromatic ester carbonyl and phenolic hydroxyl groups. Investigations into the scope, limitation and application of this type of hydrogen bonding are currently in progress.



Scheme 2.

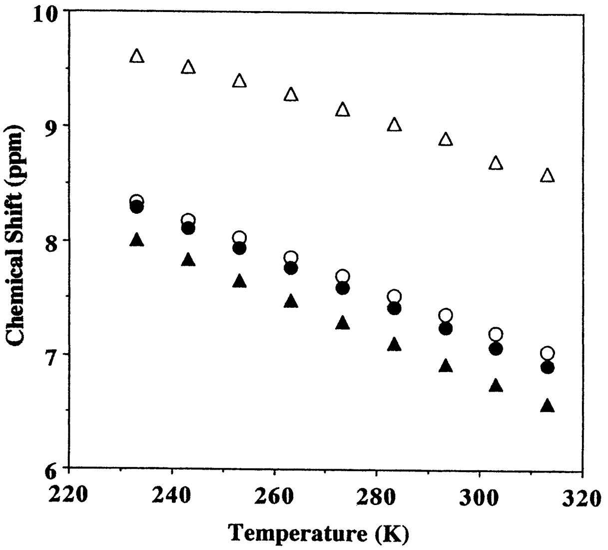


Figure 2. Phenolic proton NMR chemical shifts of **2a–d** ([**2a–d**] = 5 mM) in $CDCl_3$ versus temperature; **2a** (●), **2b** (○), **2c** (▲), **2d** (△).

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3. Very few examples of nine-membered hydrogen bonding structures have been reported, but hydrogen bonding is not discussed in detail: (a) Abell, A. D.; Morris, K. D.; McKee, V. *Aust. J. Chem.* **1990**, *43*, 765–771. (b) Anjaneyulu, A. S. R.; Venugopal, M. J. R. V.; Sarada, P.; Clardy, J.; Lobkovsky, E. *Tetrahedron Lett.* **1998**, *39*, 139–142.
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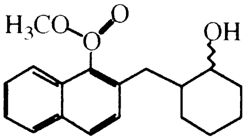
5. Crystal data for **2b**: $C_{20}H_{18}O_3$, $M=306.36$, monoclinic, space group $P2_1/n$ (#14), $a=11.783(2)$, $b=7.231(2)$, $c=19.373(2)$ Å, $\beta=103.83(1)°$, $V=1602.7(6)$ Å^3, $Z=4$, $D_c=1.270$ g cm^{-3}, $T=296$ K, $\mu=0.84$ cm^{-1}, $F(000)=648$, crystal size = 0.60×0.40×0.08 mm by Rigaku AFC5R diffractometer. Final $R1$ value was 0.052 for 1119 reflections (R; $R_w=0.148$; 0.156 for 3561 reflections). The position of hydrogen of OH group was determined from Fourier map. (The distance of O–O; 2.76 (3) Å. The angle of O–H–O; 158°).
6. The temperature dependence of the alcoholic proton in the ^{1}H NMR chemical shift of **4** showed the existence of weak nine-membered intramolecular hydrogen bonding. However, it is much weaker than that of **2a**–**d**. This result indicates that the phenolic hydroxyl group plays an important role in the nine-membered intramolecular hydrogen bonding.



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