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SHORT COMMUNICATIONS

ROLE OF 2-CARBOXYL SUBSTITUENT IN THE TAUTOMERIZATION BETWEEN TWO EQUIVALENT ENOL FORMS OF 3-HYDROXYPHENALENONE

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The interconversion between two equivalent enol forms of 3-hydroxyphenalenone took place predominantly through a diketo form with a free energy of activation of *ca* 14 kcal mol^{-1} in DMSO solution determined by 125·8 MHz ^{13}C NMR measurement. On the other hand, the corresponding interconversion in 2-carboxy-3-hydroxyphenalenone was not frozen on the time scale of ^{13}C NMR spectroscopy down to −60 °C. This acceleration in the interconversion rate of the latter may be interpreted by a double proton switching between the hydrogen-bonded 2-carboxyl and 3-hydroxyenone moieties.

Dynamic aspects of proton transfer in hydrogen-bonded organic molecules in the gas phase have recently been elucidated in great detail by laser-induced fluorescence spectroscopy.[1] Proton transfer in organic crystals has also attracted considerable attention from the viewpoint of developing devices for molecular switches and photo-images.[2] A novel aspect of proton transfer should be observed if the tautomerization is coupled by the π-bond switching of a unique π-conjugated system. In this respect we have chosen 3-hydroxyphenalenone (**1**), because its characteristic electronic structure as an odd-alternant hydrocarbon is well documented.[3] Here we report a mechanistic study on the tautomerization of 3-hydroxyphenalenone and the detection of the degenerated tautomerization in the 2-carboxyl derivative.

The ^{1}H NMR spectrum of **1** in the aromatic region (Figure 1) shows only three kinds of protons ($\delta = 7{\cdot}84$ ppm, t, $J = 8$ Hz; 8·34 ppm, d, $J = 8$ Hz; 8·40 ppm, d, $J = 8$ Hz; DMSO-d_6 at 80 °C), which can be interpreted by **1** having C_{2v} symmetry in solution at this temperature owing to the rapid interconversion between two equivalent enol forms (**1a** and **1b**) and by the concentration of the diketo form being negligibly small (the keto–enol equilibrium of the system was studied by UV spectroscopy[4]). The enolic proton appears at 11·8 ppm, suggesting a strong hydrogen bond to the DMSO molecule. The averaging process may be accounted for by the following mechanisms. First, the interconversion may take place through a proton or hydrogen transfer from the enolic to the carbonyl oxygen. Second, it proceeds through the diketo form with which the the enol forms are in equilibrium. If the proton transfer prevails in the former case, it may occur with the aid of DMSO or another molecule of **1**. For instance, if the two enol molecules form a head-to-head dimer through two hydrogen bonds, double proton transfer coupled with tautomerization may take place efficiently within the dimer [the C=O stretching frequency of a hydrogen-bonded head-to-head dimer of 5,5-dimethylcyclohexa-1,3-dione (dimedone) is observed at 1607 cm^{-1} in chloroform solution, and that of **1** in DMSO at 1662 and 1634 cm^{-1}. The observed frequencies of **1** in DMSO may exclude a significant contribution of the

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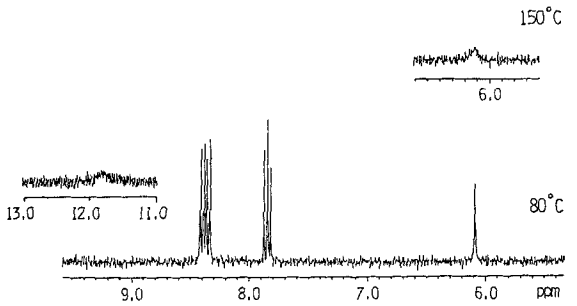
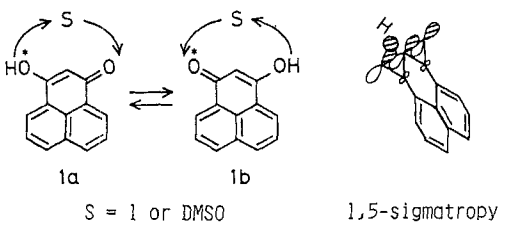


Figure 1. ^{1}H NMR spectrum of **1** in DMSO-d_6 at 80 °C. Inset: signal of the vinylic proton at 150 °C



head-to-head dimer of **1**]. Otherwise, two enol forms may interconvert through a 1,5-sigmatropic shift.

In the second case, the enolic proton migrates to the C-2 carbon to give rise to the diketo form reversibly, where the vinylic proton is assumed to be exchanged with the methylene protons or with the enolic proton during the interconversion [Figure 2(a)]. When the spectra were recorded at elevated temperatures the vinylic proton signal ($\delta = 6{\cdot}04$ ppm) became broadened, accompanied by a slight downfield shift (see inset in Figure 1). This tendency may be best interpreted by the rate of interconversion between the vinylic and the hydroxyl protons becoming rapid enough to affect their line shapes in spite of the large chemical shift of 5·8 ppm. When D_2O was added to the DMSO-d_6 solution of **1**, the vinylic signal disappeared instantaneously. This can be explained by the enolic proton being replaced by a deuteron, and the latter being exchanged with methylene protons during the tautomerization process (The enol–keto interconversion rate at room temperature is calculated to be 250 s^{-1} by using the activation free energy of 14 kcal mol^{-1}).

Judging from these behaviours of the vinylic signal, the interconversion through the diketo form seems most likely to occur in the present case. The ^{13}C NMR spectrum of **1**, on the other hand, showed a distinct temperature dependence [Figure 3(a) and (b)]. The aromatic carbons afforded broad signals at room temperature, but the signals became sharpened at higher temperatures in accordance with the increasing rate of the interconversion, while the signals of the carbon atoms on the C_{2v} axis remained unchanged. The different behaviours of aromatic signals in the averaging process may be understood by considering the chemical shift differences of the aromatic carbons in the *O*-methyl ether **2**, which loses C_{2v} symmetry owing to its fixed enol structure [Figure 3(c)]. Since the significant broadening of the vinylic carbon signal is accompanied by an averaging process of aromatic signals, the observed process in ^{13}C NMR also seems to correspond to interconversion through the diketo form. The rate of interconversion between **1a** and **1b** was estimated to be $1{\cdot}1 \times 10^3$ s^{-1} at 45 °C with an activation free energy of $\Delta G^{\neq} = 14$ kcal mol^{-1} based on the coalescent behaviour of the aromatic carbon signals. (The interconversion rate was found to be slightly dependent on the initial concentration of **1**. This suggests that **1** itself behaves as the catalyst of

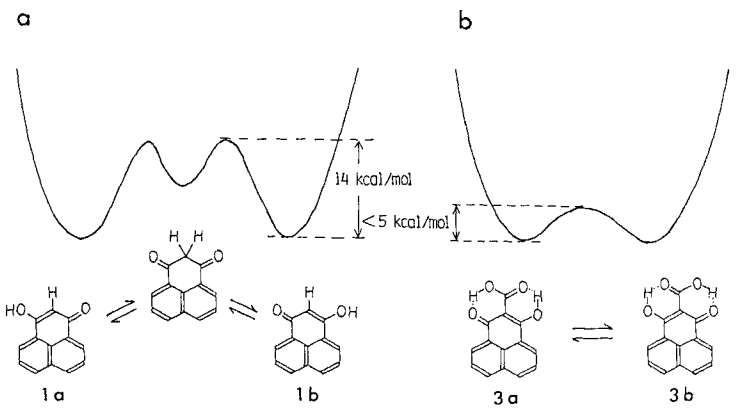


Figure 2. (a) Tautomerization between two equivalent 3-hydroxyphenalenones (**1a** and **1b**) via a 1,3-phenalenedione structure. (b) Degenerated tautomerization between 2-carboxy-3-hydroxyphenalenones (**3a** and **3b**) through the double proton transfer

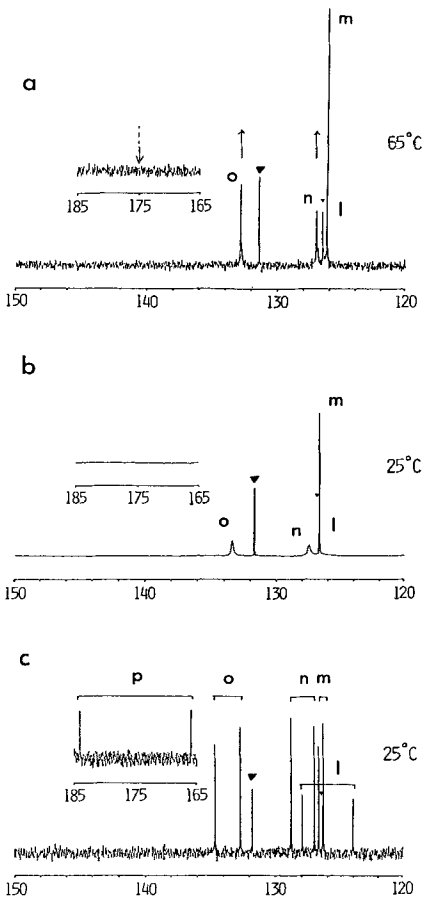


Figure 3. (a) ^{13}C NMR spectrum of **1** in DMSO-d_6 at 65 °C. ▼; Signals of carbon atoms on the C_{2v} axis. (b) Spectrum of **1** recorded at 25 °C. (c) Spectrum of **2** at 25 °C. The letters l–p denote the pair of carbon signals which are assumed to be averaged in **1** by the interconversion

the interconversion. The rate was determined at a concentration of 0·17 mol^{-1}.)

The tautomerization between the two equivalent enol forms may be accelerated by introducing a carboxyl group at the 2-position of **1**, since the two tautomers (**3a** and **3b**) can be switched by the double proton transfer among hydrogen-bonded oxygen atoms [Figure 2(b)]. 2-Carboxy-3-hydroxyphenalenone (**3**) was prepared by condensation of 1,8-naphthalic anhydride with diethyl malonate in the presence of zinc chloride at 170 °C. The crude reaction mixture was extracted with chloroform using a Soxhlet apparatus to give **3** as orange needles [m.p. 220 °C (decomp.)] in 62% (by modifying the procedures for work-up and isolation as described by Gudrinietse *et al.*,[5] one can obtain **3** as the major product together with **1**).

The 500 MHz ^1H NMR spectrum of **3** in $CDCl_3$ displayed three aromatic protons at $\delta = 7{\cdot}84$, 8·34 and 8·74 ppm together with a sharp singlet at $\delta = 15{\cdot}6$ ppm assignable to two hydroxyl protons. The observed spectrum indicates that **3** undergoes a rapid averaging process between the two enol forms. The significant low-field shift of the hydroxyl proton signal suggests that these protons participate in the strong hydrogen bonds and that the two hydroxylic protons are not distinguishable. The spectrum did not show any temperature dependence when the sample was cooled to −60 °C.

The time-averaged spectrum of **3** was also recorded by 125·8 MHz ^{13}C NMR spectroscopy. An averaged chemical shift of C-1 and C-3 was observed at 181·6 ppm, showing a low-field shift by 6·5 ppm compared with the corresponding value of 175·1 ppm in **1**. This is further evidence for the formation of strong hydrogen bonds. The spectrum at −60 °C did not show any significant difference (Figure 4), which strongly suggests that the averaging process in **3** is much faster than that in **1**. Although the intrinsic chemical shifts of C-1 and C-3 are not available, the chemical shift of C-1 in **3** is estimated to be 189 ppm, provided that the chemical shift of C-3 is 173 ppm (since the substitution of a carboxyl group at the *ortho* position of phenol causes a low-field shift of 7 ppm for the carbon attached to the hydroxyl group, the chemical shift of C-3 in **3** was estimated to be 173 ppm with reference to the chemical shift of C-3 (166 ppm) in **2**[6]).

The activation energy of the tautomerization is estimated to be lower than 5 kcal mol^{-1}, its rate being much faster than 4×10^3 s^{-1} at −60 °C. This is in sharp contrast to the spectral features of **1** as described above. The large acceleration of the tautomerization rate observed in **3** can be ascribed to the presence of the 2-carboxylic substituent, i.e. the 2-carboxyl group in **3a** acts as a proton donor to the carbonyl oxygen of the 3-hydroxyphenalenone moiety. The hydroxyl group at the 3-position, in turn, delivers a proton back to the carbonyl oxygen in the carboxyl group, giving rise to **3b** (and vice versa from **3b** to **3a**). In other words, a proton is relayed from the enolic OH to the carbonyl oxygen in the 1-position mediated by the carboxyl substituent. Hence the carboxyl group can be considered to play a key role in the degenerated tautomerization of **3**.

In conclusion, the degenerated tautomerization in **3** is extremely rapid in solution compared with that of the parent compound **1** (a LIF spectroscopic study of **3** in an ultrasonic jet stream may reveal the potential energy surface concerning this unique proton transfer system in detail). This may be achieved by the mediation of the carboxyl substituent at the 2-position. When the intramolecular proton-relay model described here is extended to the intermolecular case, it may manifest a novel transportation phenomenon of great potential interest.

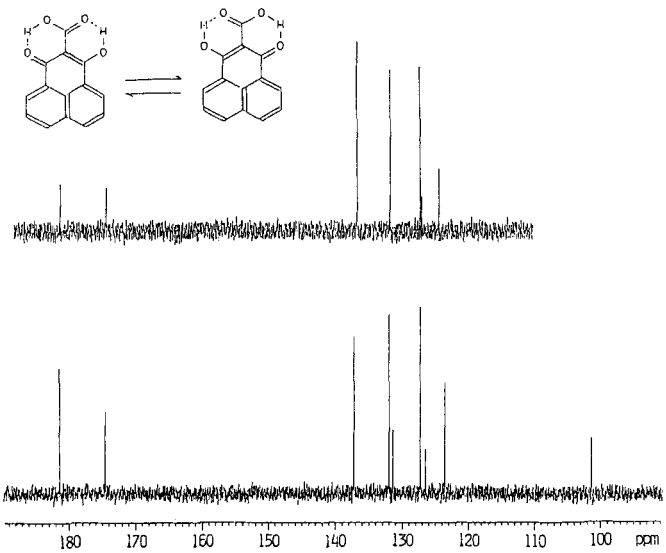


Figure 4. ^{13}C NMR spectra of **3** in $CDCl_3$ at room temperature (above) and at $-60\,^{\circ}C$ (below)

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