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Tautomerizaton of 2-Carboxy-1,3-dibenzo[a,c]tropolone in the Solid State. Possibility of a Symmetrical Structure of the Enol Form

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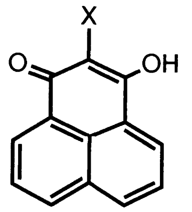
Crystal structure of 2-Carboxy-1,3-dibenzo[a,c]tropolone (**4**) is characterized by intramolecular hydrogen bonds with d(O···O) of 2.400(5) Å, which is one of the shortest distances reported for 3-hydroxyenones. An averaged structure of **4** suggested by solid state ^{13}C (CP/MAS) NMR may be attributed to a genuine symmetry rather than a dynamically averaged one. Namely, the tautomer may have a symmetric structure resulting from the extremely short O···O distance.

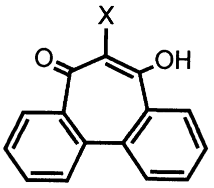
Keto-enol equilibria of 1,3-diketo compounds, such as malonaldehyde, acetylacetone, are often shifted to enol forms in solution based on the stabilization of enol forms by intramolecular hydrogen bonds.[1] In the solid state, they exist almost exclusively in the cis-enol form characterized by strong hydrogen bonds.[2] The potential curve for such hydrogen bonds has been discussed from both experimental and theoretical points of view. Hydrogen bonds shorter than 2.45 Å is considered to have a single well potential, whereas a hydrogen bond potential is usually of an asymmetric double well.[3 - 6] In addition, dynamic behavior in the tautomerization observed in naphthazarin, etc. in the solid state has been a recent topic in the solid state chemistry.[7]

Our current exploration on the hydrogen bonds in 3-hydroxyenones aims at developping physical properties derived from dynamic hydrogen bonds. Recently we found that the tautomerization of 3-hydroxyphenalenone (**1**)



1 : X = H

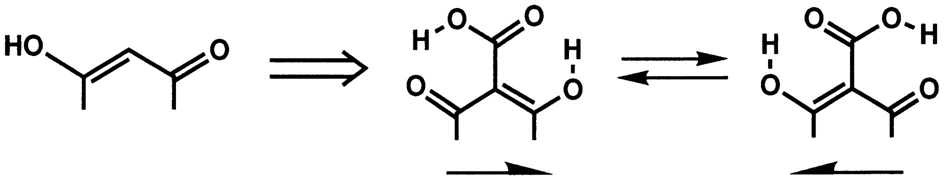
2 : X = COOH



3 : X = H

4 : X = COOH

is extremely facilitated by introducing a carboxyl substituent at the 2-position (Scheme 1).[8] The role of carboxyl group can be considered as a mediation of proton transfer in tautomerization of **2**, and the tautomerization process in the solid state leads to dynamic dielectric properties.[9] With regard to the strong intramolecular hydrogen bond in tropolone,[10] we are now intrigued by the tautomerization of 2-carboxy-1,3-dibenzo[a,c]tropolone (**4**),[11] and revealed that the tautomer of **4** may be considered to exist as an almost symmetric form due to extremely short O···O distances along hydrogen bonds.



Scheme 1. Tautomerization of 3-hydroxyenone mediated by the carboxyl group at the 2-position. The thick arrows stand for the transverse component of the dipole moment of the fragment, which is convertible coupled with the tautomerization.

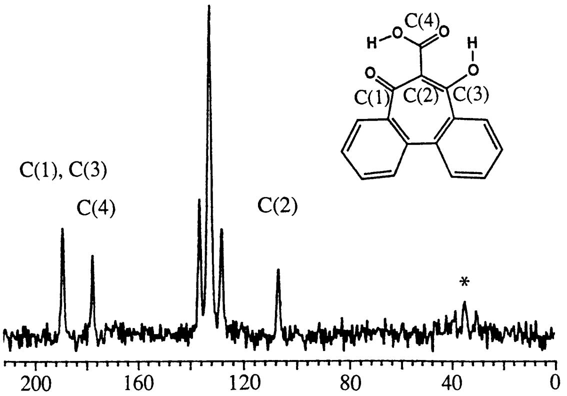
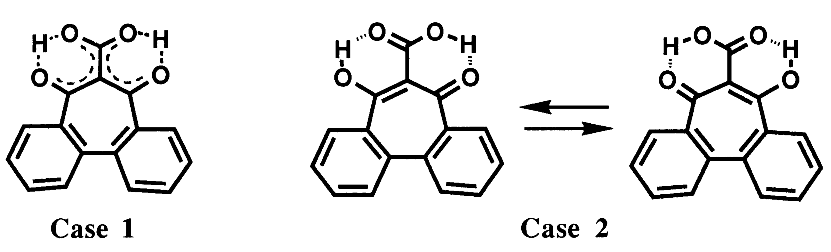


Fig. 1. Solid state ^{13}C (CP/MAS) NMR spectrum of **4**. (* spinning side band)

In order to obtain information on the dynamic structure of 2-carboxyl-1,3-dibenzo[a,c]tropolone **4** in the solid state, solid state ^{13}C NMR (CP/MAS) measurements were performed on a polycrystalline sample. The signals for C(1) and C(3) carbons of **4** appear at an averaged position of 189 ppm as shown in Fig. 1. This is contrasting with the result of 1,3-dibenzo[a,c] tropolone (**3**) in which carbonyl and enolic carbons are observed separately at 193 and 167 ppm, respectively.



Scheme 2. Possibilities of observing the symmetric enol form of **4**.

Case 1: a genuine symmetric structure of **4** with single well potentials for the hydrogen bonds.

Case 2: a time-averaged symmetric structure based on a rapid tautomerization between asymmetric tautomers with double well potentials for the hydrogen bonds.

Even the carbonyl and enolic carbons of dibenzoylmethane give two separate peaks, although strong hydrogen bond is formed in its cis-enol form in the solid state.[12)] The spectral feature of **4** may be interpreted either by a symmetric structure (molecular symmetry : C_2) or by a dynamic disorder between two enol forms (Scheme 2).

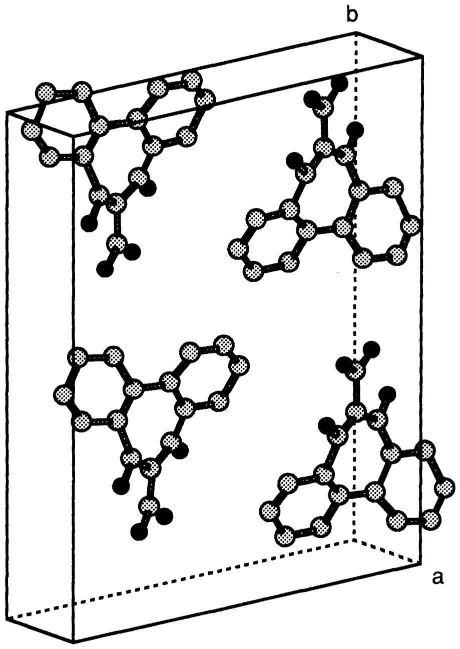


Fig. 2. Crystal structure of **4**.

The crystal structure of **4** determined by X-ray crystallography is demonstrated in Fig. 2.[13)] The molecule **4** has helicity in the biphenyl moiety due to the repulsion between hydrogen atoms at the ortho-positions. The torsional angle between the phenyl rings is 34 degrees. The d,l optical antipodes, derived from the helicity, are stacked separately in columns along the *a* axis, resulting in a meso crystal as a whole. The carboxyl and enolic groups form intramolelular hydrogen bonds of 2.400(5) Å. This O···O distance is extremely short even for cis forms of 3-hydroxyenones : regular O···O distances in such systems are in the range of 2.45 - 2.62 Å.[2,5)] The short O···O distance in **4** is ascribable mainly to the steric effect of the tropolone ring, i.e., the angle between C(1)-C(2)-C(3) is larger than those for 3-hydroxycyclohexanones, leading to the shorter contact between the oxygen atoms along hydrogen bonds. It may be natural to suspect that the eletronic effect of the tropolone ring is also responsible for the strong hydrogen bonds, because protonation on tropolones results in a stable tropylium ions, which can be considered as a canonical structure of hydrogen bonded species. Judging from the extremely short O···O distances, hydroxyl protons may be located almost in the middle of the oxygen atoms.

Dielectric response of a single crystal of **4** was measured to examine the polarity inversion in **4** coupled with tautomerization. The dielectric response, however, was not observed in the temperature range of 300 -10 K. The result shows a sharp contrast to the case of **2**, in which a paraelectric behavior is found at room temperature under ambient pressure.[9)] This tendency may be explained by the fact that the invertible dipole moment of **4** is almost zero due to the symmetric structure of the enol form.

In summary, we found a unique 3-hydroxyenone derivative in which the enol form may exist as an almost symmetrical structure with a single minimum in the potential surface along the tautomerization path, although an experimental discrimination is still difficult between the real symmetrical structure and the time-averaged one which is achieved through a rapid equilibrium with a small barrier to interconversion.

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13) [$C_{16}H_{10}O_4$] : Monoclinic, space group $C2/c$, $a = 3.791(1)$, $b = 19.298(6)$, $c = 16.049(5)$ Å, $\beta = 90.65(4)°$, $V = 1174.1(6)$ Å^3, $Z = 4$, All atoms except hydroxyl hydrogens were located and refined. The non-H atoms were refined anisotropically. $R = 8.6\%$; 99 parameters, 1010 independent reflections.

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