

THE STRUCTURE OF 2-HYDROXYCYCLOHEXANONE IN WATER AND IN DIMETHYLSULFOXIDE

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Structure of 2-hydroxycyclohexanone in water and in dimethylsulfoxide was investigated by absorption spectroscopy. Inspection of IR and UV spectra led to a conclusion that in water 2-hydroxycyclohexanone exists in the monomeric structure, while in dimethylsulfoxide it exists mainly in the dimeric or polymeric form contaminating with the monomeric one. The NMR spectra also supported these assignments.

From the data of electric moment, Svrbely and Lander¹⁾ suggested that 2-hydroxycyclohexanone existed in benzene mainly in the enolic form (Fig. 1b). Sheehan, O'Neill and White²⁾ claimed that 2-hydroxycyclohexanone existed as a dimer hemi-ketal form (Fig. 1c) in solid state according to the IR spectrum and the molecular weight determination. During the investigation of the catalytic hydrogenation of 5-keto-D-gluconate³⁻⁵⁾ and 2-hydroxycyclohexanone, we were interested in the molecular form(s) of 2-hydroxycyclohexanone in water and in dimethylsulfoxide (DMSO).

In the present paper, the molecular forms of 2-hydroxycyclohexanone in water and in DMSO were investigated by IR, UV and NMR spectroscopy.

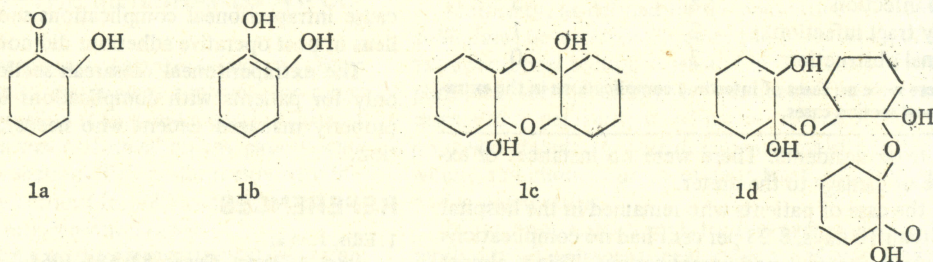


Fig. 1. Structures of 2-hydroxycyclohexanone
(a) monomeric structure.
(b) enolic structure.
(c) dimer hemi-ketal form.
(d) polymeric form.

Results and Discussion

The IR spectra of 2-hydroxycyclohexanone in KBr disc and solutions together with the pure solvents are shown in Fig. 2. It should be noticed that the $>C=O$ absorption

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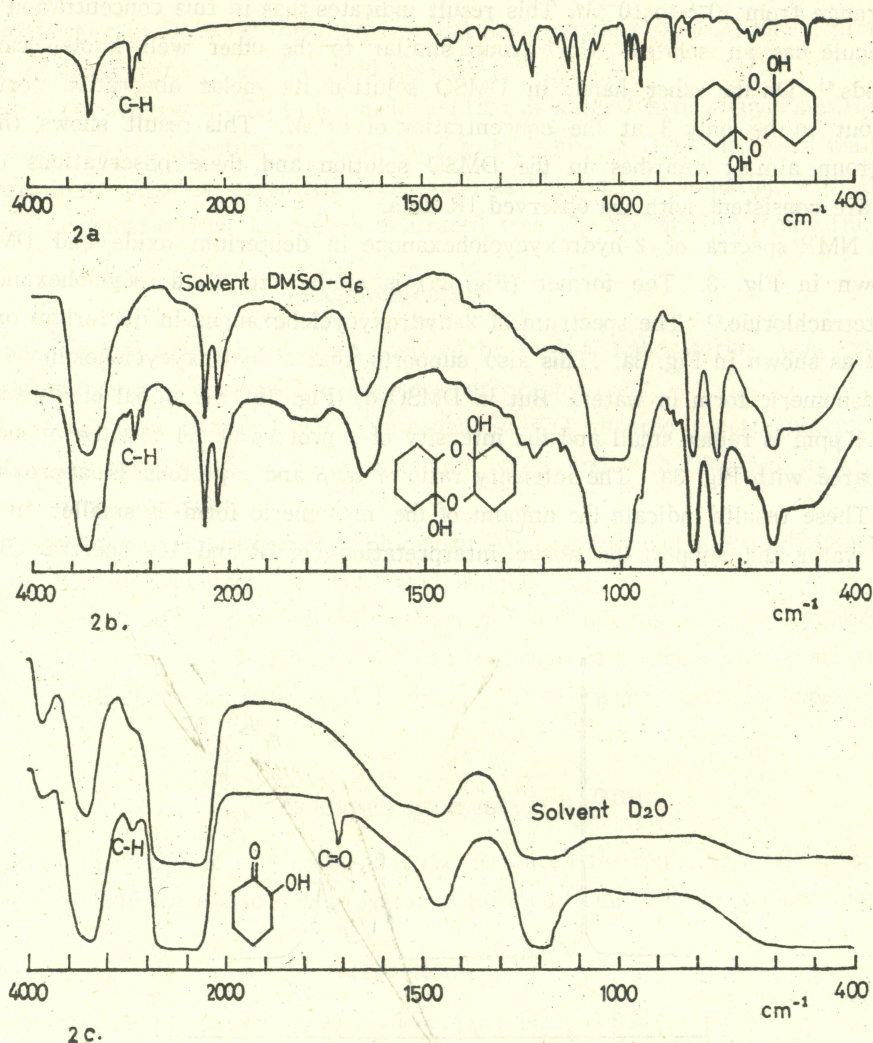


Fig. 2. IR spectra of 2-hydroxycyclohexanone.

- (a) in KBr disc.
- (b) solution in DMSO-d₆ and solvent DMSO-d₆.
- (c) solution in deuterium oxide.

near 1720 cm⁻¹ is negligible in both the KBr disc (Fig. 2a) and in DMSO-d₆ (Fig. 2b) in comparison with the C-H absorption at 2825 to 3000 cm⁻¹, while the ν C=O absorption is apparent in deuterium oxide solution (Fig. 2c). These results suggest that 2-hydroxycyclohexanone exists mainly in dimeric (Fig. 1c) or polymeric (Fig. 1d) in DMSO but a monomeric form (Fig. 1a) in water.

The UV spectra of 2-hydroxycyclohexanone were also investigated in water and in DMSO solutions. Both solutions of the compound gave a maximum absorption around 275 m μ . The molar absorption coefficient ϵ in water was found to be 23 in the concen-

tration range from 10^{-1} to $10^{-3}M$. This result indicates that in this concentration range the molecule has an isolated $>C=O$ group similar to the other well known carbonyl compounds.⁶⁾ On the other hand, in DMSO solution its molar absorption coefficient turned out to be only 3 at the concentration of $10^{-2}M$. This result shows that the $>C=O$ group almost vanishes in the DMSO solution and these observations of UV spectra are consistent with the observed IR data.

The NMR spectra of 2-hydroxycyclohexanone in deuterium oxide and DMSO- d_6 are shown in Fig. 3. The former (Fig. 3a) is similar to 2-chlorocyclohexanone in carbon tetrachloride.⁷⁾ The spectrum of 2-hydroxycyclohexanone in deuterium oxide is assigned as shown in Fig. 3a. This also supports that 2-hydroxycyclohexanone exists in the monomeric form in water. But in DMSO- d_6 (Fig. 3b), the signal of β protons at 2.2 to 2.4 ppm is rather small and the intensity of γ protons at 1.4 to 2.0 ppm increases as compared with Fig. 3a. The intensity ratio of α , β and γ protons is approximately 1:2:6. These results indicate the amount of the monomeric form is smaller in DMSO than in water and support the above interpretations of IR and UV spectra. Both in

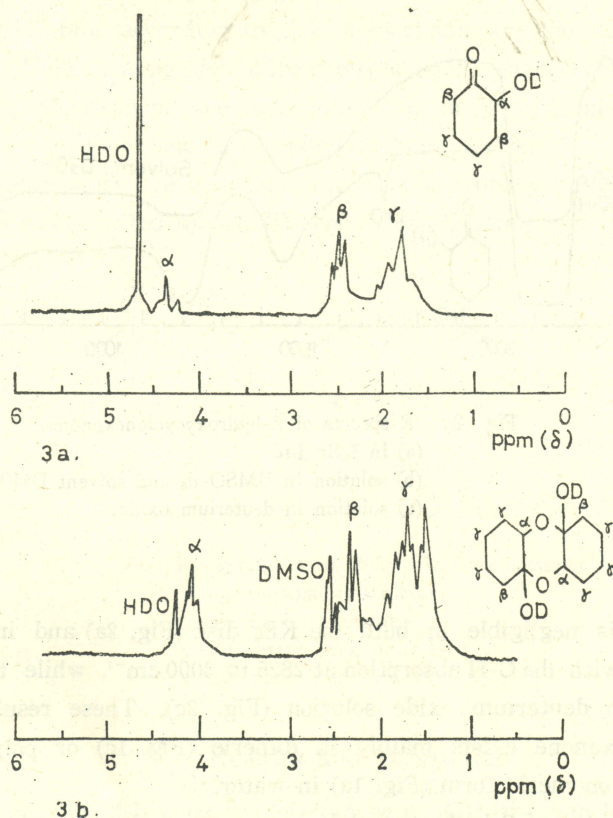


Fig. 3. NMR spectra of 2-hydroxycyclohexanone in
(a) deuterium oxide.
(b) DMSO- d_6 .

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deuterium oxide and in DMSO- d_6 , one can not find the resonance peak of enolic proton of 2-hydroxycyclohexanone in the low-field region.⁸⁾

Inspection of above spectra led to a conclusion that in water 2-hydroxycyclohexanone exists in the monomeric structure as shown in Fig. 1a, while in DMSO it exists mainly in the dimeric (Fig. 1c) or a polymeric form such as Fig. 1d contaminating with 10% to 20% of the monomeric (Fig. 1a) one as estimated from the UV and NMR spectra.

Experimental

A sample of 2-hydroxycyclohexanone supplied by K & K Laboratories, was shown to be pure by elementary analysis and gas chromatography.

The IR spectra were recorded with shimadzu IR-27G infrared spectrophotometer. Sample was measured by mixing with deuterium oxide and with DMSO- d_6 as a thin liquid film at room temperature.

The UV spectra were investigated by Shimadzu QV-50 ultraviolet spectrophotometer. Sample solutions were prepared with water and DMSO.

The NMR spectra were recorded with a Varian T-60 high-resolution spectrometer. Chemical shifts were measured using DSS as an internal reference. Sample solutions were prepared with deuterium oxide and DMSO- d_6 . The measurement was undertaken at 40°.

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