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Laser Excited Fluorescence Spectrum and X-Ray Diffraction Study of Intramolecular and Intermolecular Hydrogen Bonds of 5-Isopropyltropolone

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Electronic spectra have been measured to investigate intra and intermolecular hydrogen bonds for jet-cooled 5-isopropyltropolone and the hydrogen bonded complex between 5-isopropyltropolone and water in the S_1-S_0 region. No transition due to a 5-isopropyltropolone dimer has been detected in the laser fluorescence excitation spectrum, although formation of a dimer in crystalline 5-isopropyltropolone has been suggested from the X-ray diffraction study. This implies that the formation of the dimer is prevented in the gas phase owing to very fast intramolecular proton transfer.

1. Introduction

The intramolecular hydrogen bonds of tropolone and its derivatives have been studied extensively by measuring UV absorption[1,2], laser fluorescence excitation,[3-8] and IR spectra.[9,10] In contrast with numerous data concerning the intramolecular hydrogen bonds of tropolone and its derivatives, little is known on the intermolecular hydrogen bonds. Shimanouchi and Sasada[11] studied the crystal structure of tropolone. It was suggested that the hydroxyl group of tropolone forms a dimer. Okubo et al.[12] measured UV absorption spectrum of tropolone in a mixed solvent of methylcyclohexane and isopentane (1 : 1) at room temperature and 77K. At room temperature the band origin for the S_1-S_0 electronic transition was identified at 373.4 nm, while the origin band shifted to 369.0 nm. They concluded that the absorption spectrum at 77K was due to the formation of a dimer on the basis of calculation of the electronic energy levels.

In this work, the electronic spectra of 5-isopropyltropolone and the hydrogen-bonded complex between 5-isopropyltropolone and water have been studied. We have attempted to detect the electronic transition of a 5-isopropyltropolone dimer in a ultracold gas phase by using a supersonic free expansion. Although the crystal strucure of 5-isopropyltropolone was studied by Berg *et al.*,[13] we reinvestigated the ctystal structure of 5-isopropyltropolone by noting intra- and intermolecular hydrogen bonds and the torsional angles of the methyl groups in relation to the electronic spectrum.

2. Experimental

The experimental apparatus for the laser fluorescence excitation spectrum was essen-

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tially the same as that described previously. [7,8] Briefly, the sample gas mixed with He carrier gas was expanded by using a pulsed with an orifice (300 − 400 μm diam.), which was operated at 5 Hz. The S_1-S_0 transition of 5-isopropyltropolone was excited by using a nitrogen laser pumped dye laser source (Molectron UV22 and DL14). The resulting total fluorescence was collected by a f = 5 cm lens, and detected with a photomultiplier (Hamamatsu R955) and averaged with a boxcar integrator (NF BX-531). The dispersed fluorescence spectrum was measured by using a Spex 1702 monochromator.

Crystalline 5-isopropyltropolone was a gift from Dr. Haruki Tsuruta in Takasago Research Institute. A crystal of dimensions ca. 0.15×0.20×0.12 nm was sealed in a thin walled Lindemann-glass tube to minimize loss by sublimation. An Enraf-Nonius CAD-4 diffractometer equipped with graphite monochromatized Mo Kα radiation were used for the measurement. The lattice parameters were obtained from settings of 18 reflections with $7.32 < \theta < 11.73°$. The $\omega - 2\theta$ scan technique was used to collect intensities of 2858 independent reflections with $1 < \theta < 30°$ ($-10 < h < 10$, $0 < k < 25$, $0 < l < 9$), 813 of which were considered as observed [$I < 3\sigma(I)$]. The low yield of the observed intensities was owing to employing the Lindemann-glass tube. Three standard reflections were monitored every 3600s, and there was no significant variation in intensity during data collection; intensities were not corrected for absorption. Structure were solved by a direct method (*MULTAN 11/82*) ; H positions were determined by difference Fourier synthesis. Refinement was carried out by full matrix least squares using F. The C and O atoms were assumed anisotropic, while the H atom was isotropic and fixed at 4.0Å^2. Final conventional parameters are $R=0.048$, $R_W=0.062$, and $W=4F_0^2/[\sigma(F_0)^2]^2$; $(\triangle/\sigma)_{max}$ in final least squares cycle 0.69; final difference Fourier height maximum (absolute valus) 0.27 eA^{-3}; refined secondary extinction value was $g=1.36\times10^{-6}$. Atomic scattering factors were cited from *International Tables for X-ray Crystallography*.[14] Computation was carried out on PDP11/23 computer by using *Enraf-Nonius SDP-Plus* and *ORTEP* programs.[15]

3. Results and Discssion

3.1 Laser fluorescence excitation spectra of 5-isopropyltropolone and the hydrogen-bonded complex between water

A typical laser fluorescence excitation spectra of 5-isopropyltropolone (−OH) and its −OD compound are shown in **Figs. 1a** and 1*b*, respectively. The origin bands for the electronic transitions of 5-isopropyltropolone (− OH) and 5-isopropyltropolone (− OD) were identified at 26888 cm^{-1} and 26937 cm^{-1}, respectively. Numerous low frequency bands have been detected in the region $\triangle\tilde{\nu}$ ($\tilde{\nu} - 0_0^0$) = 0 − 150 cm^{-1}. These bands are considered to be due to torsional modes of the methyl groups and out-of-plane bending modes. The vibronic pattern was too complicated to assign these bands definitely.

The $0 - {}^+_+$ and 0^-_- transitions are allowed in a symmetrical potential energy function along the proton transfer coordinate. We extensively searched for the 0^-_- transition. If the 0^-_- transition is detected in **Fig. 1a**, the corresponding transition will be remarkably red shifted in **Fig. 1b** by analogy with the excitation spectrum of tropolone.[1-8] However, the 0^-_- transition has not been identified in **Fig. 1**. The nonobsevation of the 0^-_- transition implies that the height of the barrier to tunneling is increased considerably in S_0 and/or S_1.

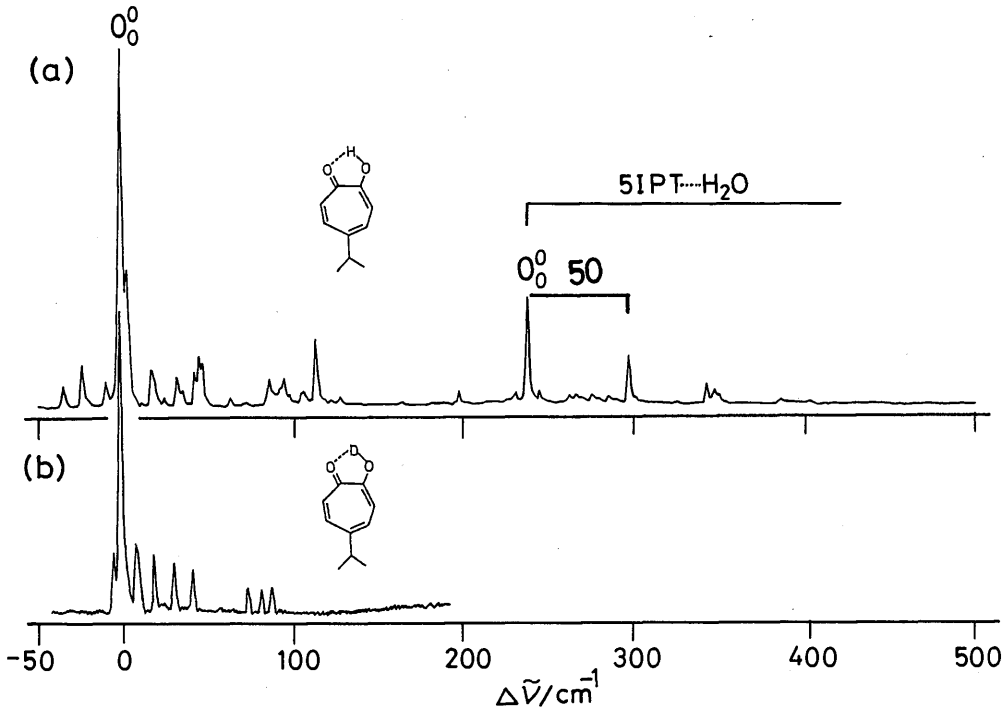

Fig. 1 Laser fluorescence excitation spectra of 5-isopropyltropolone (−OH) and the hydrogen bonded complex between 5-isopropyltropolonr and water (*a*), and 5-isopropyltropolone (−OD)[b]. The stagnation pressure of He was 0.4 atm.

Since the vibronic structre in S_1 of 5-isopropyltrpolone is very different from that of tropolone, the height of barrier may be significatly increased in S_1.

The fluorescence excitation spectrum of 5-isopropyltropolone is very similar to that of 4-isopropyltropolone.[7] The frequency and intensity distribution of low-frequency bands in the excitation spectrum of 4-isopropyltropolone were essentially the same as those in the laser fluorescence excitation spectrum of 5-isopropyltropolone. This implies that the geometry of the isopropyl group of 5-isopropyltropolone is very similar to that of 4-isopropyltropolone both in S_1 and S_0, which is consistent with the geometry of the isopropyl groups of crystalline 4-isopropyltropolone[16] and 5-isopropyltropolone for which the torsional angles are listed in a table 1 in the following section.

The bands at 27126 and 27176 cm^{-1} are assigned as the transitions due to the hydrogen-bonded complex between 5-isopropyltropolone and water, since the intensities of these bands increased when water was added in the nozzle housing. The band at 27126 cm^{-1} could be assigned as the band origin, while the band at 27176 cm^{-1} is considered to be the intermolecular vibration between 5-isopropyltropolone and water. The origin band of the hydrogen-bonded complex between 5-isopropyltropolone and water is shifted 238 cm^{-1} from the origin band of the monomer, suggesting that the carbonyl oxygen atom of 5-isopropyltropolone acts as a proton acceptor.

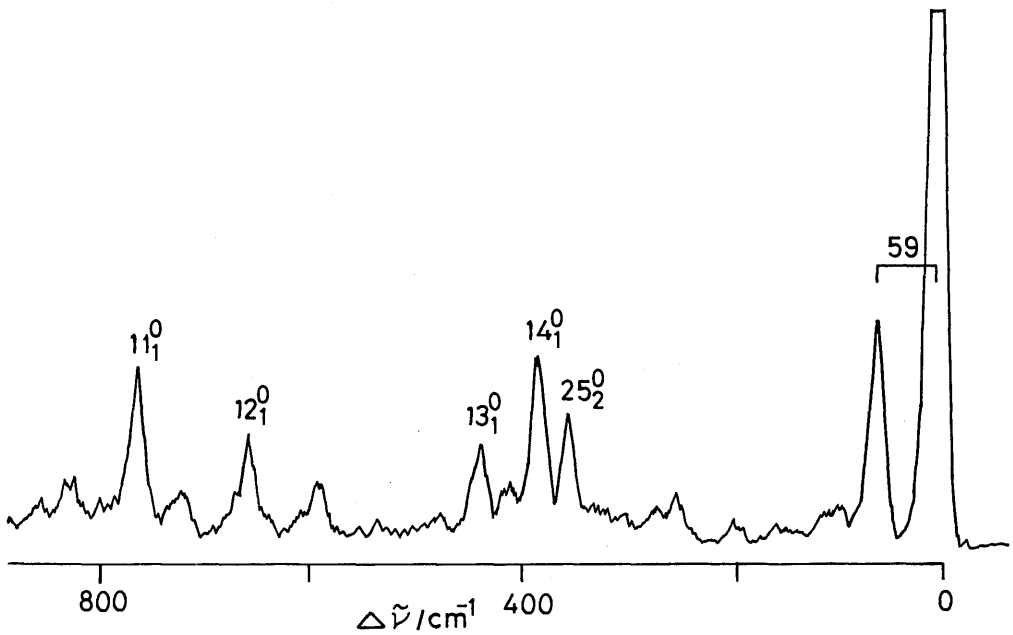

Fig. 2 Dispersed fluorescence spectrum obtained by exciting the band origin of the hydrogen-bonded complex between 5-isopropyltropolone and water.

The laser fluorescence excitation spectrum of a hydrogen-bonded complex between tropolone and water has been measured by Tomioka *et al.*[6] We reexamined the laser fluorescence excitation spectrum of the hydrogen-bonded complex between tropolone and water. The shift of the band origin of the complex from the tropolone monomer was 289 cm^{-1}, which is much larger than 238 cm^{-1} measured for 5-isopopyltropolone. **Figure 2** shows a dispersed fluorescence spectrum obtained by excitation of the origin band. The frequency for the fundamental of the intermolecular vibration in S_0 has been measured to be 59 cm^{-1} which is much larger than the corresponding frequency of 50 cm^{-1} is S_1. This suggests that the force constant is larger in S_0 than S_1.

A tropolone dimer was detected in the absorption spectrum of solution at 77K. The band origin of the dimer was about 5 nm blue shifted from the monomer band.[12] If 5-isopropyltropolone froms a dimer in the ultracold expansion, the origin band of the dimer is expected to be blue shifted. We extensively searched for bands due to the dimer by varying the stagnation pressure of He and nozzle temperature to increase the vapor pressure. However, no vibronic bands other than the monomer bands has been detected. We also attempted to detect transitions of a tropolone dimer, but they could not be detected in the laser fluorescence excitation spectrum. The nonobservation of 5-isopropyltropolone and tropolone dimers will be due to very fast proton tunneling.[3-6,8] The delocalization of the hydroxylic proton may prevent the formation of dimer in the gas phase.

3.2 Crystal structure of 5-isopropyltropolone

Figure 3 shows the molecule and numbering of the atoms. The final atomic coordinates and isotropic temperature factors are given in **Table 1**. The crystal structure of 5-isopropyltropolone is summarized as follows; monoclinic, $P2/n$, $a=7.5487(6)$, $b=18.2733(6)$, $c=6.6166(6)$ Å, $\beta=104.97(3)$, $V=881.7(2)$ Å^3, $Z=4$, $D_X=1.237$g cm^{-3}, λ (Mo $K\alpha$) $=0.71073$Å, μ (Mo $K\alpha$) $=0.079$ mm^{-1}, $F(000)=352$, $K=293$K, $R=0.048$ for 813 reflections with $I>3\sigma(I)$. These data are consistent with the previous work of Berg *et al.*[13] within the experimental error.

Bond length and angles, and some relevant torsional angles are shown in **Table 2**. The formal double bonds in the ring C(6)-C(5), C(1)-C(7), and C(4)-C(3) are longer than the pure double bond length of 1.337Å. On the other hand, the formal single bonds C(6)-C(7) and C(4)-C(5) are slightly larger than the typical aromatic value of 1.395 Å,[17] while the C(1)-C(2) and C(1)-C(7) bond lengths are significantly longer than the other bond lengths, which suggests that partial cyclic π electron delocalization is small. The seven-membered ring deviates slightly from planarity, the maximum deviation being 0.042 Å. The two carbon atoms C(9) and C(10) in the isopropyl group lie on opposite sides of the mean plane through the ring at distances of 1.429 and 0.209 Å. The relevant torsional angles listed in Table 2 are very close to those of 4-isopropyltropolone.[16]

The crystal packing shown in **Fig. 4** is significantly different from that of 4-isopropyl-

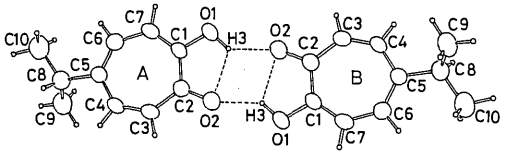

Fig. 3 Structure of a dimer with atomic labeling except for Hatoms. Hydrogen bonds are indicated by broken lines.

Table 1 Final atomic coordinates and equivalent isotropic thermal parameters (Å^2) with e.s.d.'s in parentheses

	X	Y	Z	B_{eq}*
O(1)	0.9868(3)	0.0506(2)	0.7018(4)	5.54(6)
O(2)	0.7931(3)	0.0218(2)	0.9602(4)	5.95(7)
C(1)	0.8095(4)	0.0700(2)	0.6438(5)	3.72(7)
C(2)	0.7078(4)	0.0508(2)	0.7925(5)	3.84(7)
C(3)	0.5134(4)	0.0620(2)	0.7494(5)	4.06(7)
C(4)	0.3933(4)	0.0946(2)	0.5884(5)	3.80(7)
C(5)	0.4136(4)	0.1293(2)	0.4069(5)	3.64(7)
C(6)	0.5760(5)	0.1312(2)	0.3519(5)	4.23(8)
C(7)	0.7505(4)	0.1035(2)	0.4560(5)	4.32(8)
C(8)	0.2406(5)	0.1643(2)	0.2721(5)	4.87(9)
C(9)	0.1833(5)	0.2284(2)	0.0527(6)	6.1(1)
C(10)	0.2421(6)	0.1830(3)	0.0527(6)	7.0(1)

*$B_{eq}=4/3\,(\beta_{11}a^2+\beta_{22}b^2+\beta_{33}c^2+\beta_{12}ab\cos\gamma+\beta_{13}ac\cos\beta+\beta_{23}bc\cos\alpha)$.

Table 2 Bond lengths (Å), bond angles (°) with e.s.d.'s in parentheses and selected torsional angles (°)

O(2)-C(2)	1.246(4)	C(1)-C(7)	1.353(4)	O(2)-C(2)-C(1)	117.9(3)
O(1)-C(1)	1.342(4)	C(4)-C(3)	1.346(4)	O(2)-C(2)-C(3)	120.4(3)
C(2)-C(3)	1.435(4)	C(4)-C(5)	1.401(5)	C(1)-C(2)-C(3)	121.7(3)
C(2)-C(1)	1.442(5)	C(8)-C(10)	1.494(6)	C(7)-C(6)-C(5)	130.4(3)
C(6)-C(7)	1.413(4)	C(8)-C(9)	1.519(6)	O(1)-C(1)-C(2)	114.1(3)
C(6)-C(5)	1.366(5)	C(8)-C(5)	1.520(4)	O(1)-C(1)-C(7)	116.7(3)
				C(2)-C(1)-C(7)	129.2(3)
				C(3)-C(4)-C(5)	132.7(3)
C(5)-C(8)-C(10)	116.4(3)	C(10)-C(8)-C(5)-C(6)	15.8		
C(5)-C(8)-C(9)	110.1(3)	C(10)-C(8)-C(5)-C(4)	−163.4		
C(10)-C(8)-C(9)	112.6(3)	C(9)-C(8)-C(5)-C(6)	−113.9		
C(6)-C(7)-C(1)	130.8(3)	C(9)-C(8)-C(5)-C(4)	66.8		
C(6)-C(5)-C(4)	123.0(3)				
C(6)-C(5)-C(8)	121.8(3)				
C(4)-C(5)-C(8)	115.2(3)				

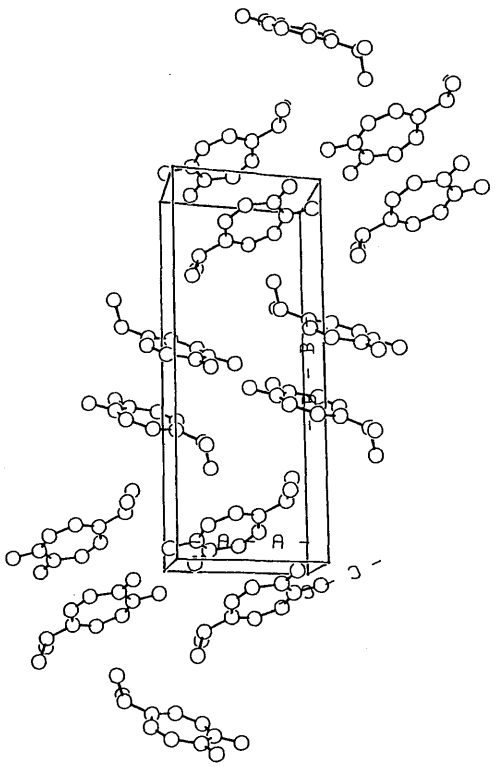

Fig. 4 Crystal packing of 5-isopropyltropolone.

ltropolone; the space group for the 4-isopropyltropolone crystal is $I2/c$ with $Z=8$.[16] The hydroxyl group forms a bifurcated hydrogen bonds as shown in Fig. 3. The intermolecular hydrogen bonds between 5-isopropyltropolones forms a dimer and the two molecules are coplanar as is the case for tropolone.[11] The distances O(1)(A)-O(2)(B) and O(2)-H(3)(B) are 2.755 and 1.980 Å, respectively. These values are in excellent agreement with corresponding values of 2.754 and 1.98Å for the tropolone dimer. The agreement of distances O(1)(A)-O(2)(B) and O(2)(A)-H(3)(B) between 5-isopropyltropolone and tropolone will not be accidental. A characteristic diamond-shape arrangement of O(1)(A), O(2)(A), O(1)(B), and O(2)(B) shown in **Fig. 1** seems to be favorable to the bifurcated hydrogen bond. This suggests that the hydrogen bonding force prevails in the molecular packing.

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