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Electronic Absorption and Phosphorescence Spectra of 2-Acetylfuran. Conformations in the Ground and Excited Triplet States

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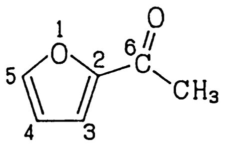
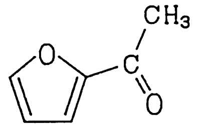
The electronic absorption and phosphorescence spectra of 2-acetylfuran were measured in various media at room and low temperatures. It was found that 2-acetylfuran exists as an equilibrium mixture of the O–O *s-cis* and O–O *s-trans* conformers in polyethylene (PE) film. Here, the O–O *s-trans* conformer was considered to be a major species, and the O–O *s-cis* conformer a minor species in a nonpolar medium such as PE. On the other hand, in a polar medium such as poly(vinyl alcohol), 2-acetylfuran existed almost completely as the *s-cis* conformer. The 0–0 phosphorescence bands of the O–O trans- and *cis*-species were at 447 and 427 nm in PE, respectively. The S_1 states for both conformers are $n\pi^*$ in character, while the T_1 states are $\pi\pi^*$.

2-Acetylfuran changes conformations, O–O *s-cis* and O–O *s-trans*, with changes in circumstances.[1–5)]



O–O s-cis



O–O s-trans

IR spectra have shown that the O–O *s-cis* and O–O *s-trans* forms have vibrational bands at 1294 and 1281 cm^{-1} respectively, in carbon tetrachloride.[3)] These bands are ascribed to the C(2)–C(6) stretching vibrational modes. 2-Acetylfuran exists as an equilibrium mixture of *s-cis* and *s-trans* forms in polar solvents such as acetonitrile and in a neat liquid, while mainly as the *s-trans* form in the gas phase and in a nonpolar solvent.[3)] The UV absorption spectrum of 2-acetylfuran consists of three band systems whose band maxima are at 307, 267, and 219 nm in methanol.[5)] The 307 nm band was assigned to an $n\pi^*$ transition, and the latter two bands to $\pi\pi^*$ transitions.

In this investigation, the electronic absorption and phosphorescence spectra of 2-acetylfuran were measured under various conditions. From the spectral results together with MO calculations, the conformations and electronic structures in the ground and excited triplet states and the nature of the electronic transitions are discussed for the two conformers.

Experimental and MO Calculations

Commercially available 2-acetylfuran (Wako Pure Chemical Ind.) was purified by distillation in vacuo. Cyclohexane (Wako) was distilled after removal of a trace amount of benzene by passage through a silica-gel column. The preparations of PVA (poly(vinyl alcohol)) and PE (polyethylene) films were described elsewhere.[6–8)] The absorption spectra were recorded on a Shimadzu UV-360 spectrophotometer equipped with an N_2-cryostat.[9)] Phosphorescence spectra were measured with a Shimadzu RF-502 fluorimeter with a rotating sector. Phosphorescence decay curves were stored in a Kawasaki Electronica transient memory (TMR-120), a Xe-flash lamp being used as an exciting light source. The phosphorescence light was analyzed with a Narumi grating spectrophotometer, and the monochromatic light was detected by a Hamamatsu Photonics R-928 photomultiplier.

A modified PPP method was adopted for the MO calculations, which could take σ-type nonbonding electron pairs into account.[8)] Semiempirical parameters used were as follows,

$$I_p(\text{-C=})=11.22\ \text{eV} \qquad E_a(\text{-C=})=0.62\ \text{eV}$$
$$I_p(\text{=O})=17.32\ \text{eV} \qquad E_a(\text{=O})=2.65\ \text{eV}$$
$$I_p(\text{O:})=33.00\ \text{eV} \qquad E_a(\text{O:})=11.47\ \text{eV}$$

Here, $I_p(r)$ and $E_a(r)$ mean a valence state ionization potential and an electron affinity, respectively, of an atom r, and -C= represents an sp^2-type carbon atom, =O a carbonyl oxygen with a π electron, and O: an oxygen atom with π or σ-type lone electron pairs. Resonance integrals were obtained by the variable β method of Nishimoto and Forster.[10)] In CI calculations, all one-electron excited configurations were considered.

Results and Discussion

Absorption spectra. Figure 1 shows the absorption spectra of 2-acetylfuran in PE and PVA films, and ME (a 1 : 1 mixture of methanol and ethanol) at 101 K, and in cyclohexane and ethanol at room temperature. This compound has two electronic bands at 311.5 and 263.0 nm in cyclohexane, whose 0–0 transitions are at 356 and

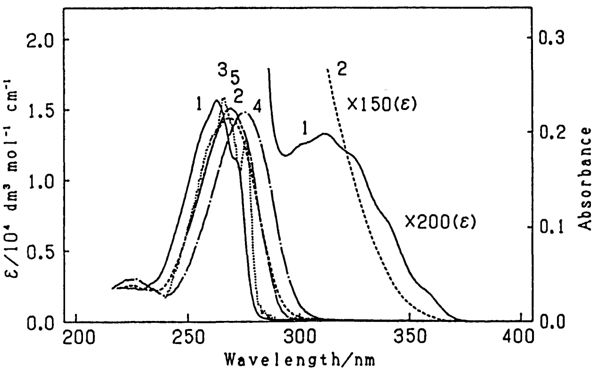


Fig. 1. The electronic absorption spectra of 2-acetylfuran in cyclohexane(1, ——) and ethanol (2, ------) at room temperature, and in PE(3, ······), PVA(4, —·—) and ME(5, —··—) rigid matrices at 101K. For 1 and 2, the ordinate unit is in ε, and for 3, 4 and 5, in absorbance.

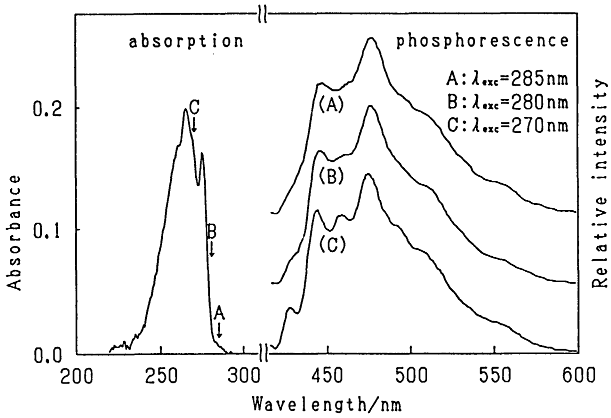


Fig. 2. The phosphorescence spectra of 2-acetylfuran excited at various wavelengths in PE film at 101 K. The phosphorescence spectra (A), (B), and (C) were obtained by excitation at the A, B and C positions, respectively.

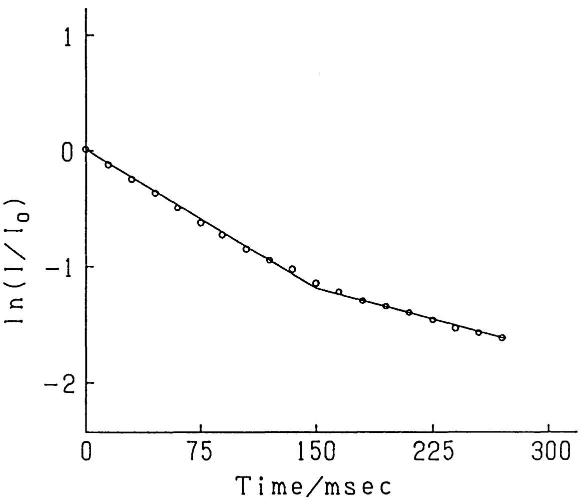


Fig. 3. The plots of $\ln(I/I_0)$ against time. I_0 and I are phosphorescence intensities at initial and arbitrary times, respectively. The monitored wavelength: 459 nm.

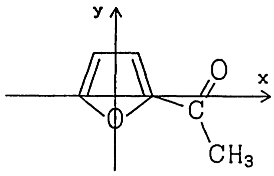
272 nm, respectively. In addition, a weak band is seen around 225 nm. The 311.5 and 263.0 nm bands have been assigned to $n\pi^*$ and $\pi\pi^*$ transitions, respectively.[5] The 263.0 nm band is red-shifted in ethanol, and appears at 269.0 nm, while the structured $n\pi^*$ band at 311.5 nm is blue-shifted and buried under the tail of the strong 269.0 nm $\pi\pi^*$ band. 2-Acetylfuran shows an absorption band maximum at 275.5 nm in PVA film, at 270 nm in ME glass, and at 266.0 nm in PE film at low temperature. Furthermore, in PE, the 0–0 band is clearly found at 276.5 nm. Detailed discussions concerning the above spectral data will be presented in connection with emission spectral data.

Phosphorescence Spectra. Phosphorescence spectra of 2-acetylfuran in PE film are dependent on excitation wavelengths as seen in Fig. 2. The phosphorescence spectra A, B, and C were obtained by excitation at 285(A), 280(B), and 270(C) nm, respectively. Spectrum A has peaks at 447 and 478 nm, and shoulders around 427, 460, 496, and 509 nm. With decreasing excitation wavelengths, the 427 and 460 nm bands are intensified, and in spectrum C the two bands appear as clear peaks. This indicates that 2-acetylfuran exhibits two kinds of phosphorescence bands. The two kinds of bands may be due to two chemical species. The O–O *s-cis* and O–O *s-trans* forms were considered to be these two species. In fact, IR spectroscopic studies have shown that 2-acetylfuran exists mainly as the O–O *s-trans* form in nonpolar solvents such as $\mathrm{CCl_4}$, in which the O–O *s-cis* form is also contained as a minor component.[3] To confirm the above considerations, the decay of phosphorescence intensity was monitored at 459.0 nm and $\ln(I/I_0)$ was plotted against time as shown in Fig. 3. Here, I_0 and I are initial and arbitrary time phosphorescence intensities, respectively, From this figure, it is also apparent that two phosphorescent species exist in PE film, i.e., the phosphorescence intensity shows dual exponential decay. On the other hand, monitoring at 475 and 420 nm corresponding to the band positions of the *s-trans* and *s-cis* conformer phosphorescences, respectively, we can get two differently-declined straight lines, from which one can obtain two different lifetimes, 84 ms and 170 ms, respectively. The short- and long-lived triplet species may be ascribed to the O–O *s-trans* and *s-cis* isomers, respectively. As described above, the S_1 states of the two conformers are of $n\pi^*$. However, the observed triplet lifetimes are too long to be assigned as T_1 states of $n\pi^*$, i.e., the T_1 states are considered to be $\pi\pi^*$. The strong 447 and 478 nm phosphorescence bands in Fig. 2 may be due to the major species, the O–O *s-trans* conformer, and the relatively weak 427 and 460 nm bands to the minor species, the O–O *s-cis* conformer. The 427 and 447 nm bands are considered to be 0–0 transitions of the *s-cis* and *s-trans* conformers,

Table 1. The Calculated Transition Energies and Intensities of O–O *s-cis* and O–O *s-trans* Conformers Compared with the Observed Values for 2-Acetylfuran

	Calcd						Obsd		
	cis-Conformer			*trans*-Conformer			PE	Cyc.	PVA
	ΔE[a]	f[b]	P_o[c]	ΔE	f	P_o	ΔE	$\Delta E(I)$[e]	$\Delta E(I)$[e]
S_1 ($n\pi^*$)	377.5	Forb.[d]	—	377.3	Forb.	—	—	356 (0.001)	—
S_2 ($\pi\pi^*$)	263.2	0.4869	−34.7	268.9	0.4005	−14.9	276.5	272 (1.000)	275.5 (1.000)
S_3 ($\pi\pi^*$)	218.1	0.0157	−87.6	222.2	0.0068	59.5	—	ca. 225 (0.152)	228 (0.174)
S_4 ($\pi\pi^*$)	199.9	0.3145	64.4	201.9	0.2148	58.5	—	—	—
T_1 (cis)=585.4 nm (2.12 eV, $\pi\pi^*$)								T_1(cis)=427 nm (2.90 eV)[f]	
T_1 (trans)=592.4 nm (2.09 eV, $\pi\pi^*$)								T_1(trans)=447 nm (2.78 eV)[f]	

a) Transition energy/nm.
b) Oscillator strength.
c) Polarization direction with respect to the X axis.
d) Forbidden.
e) Relative intensity.
f) Measured in PE film.



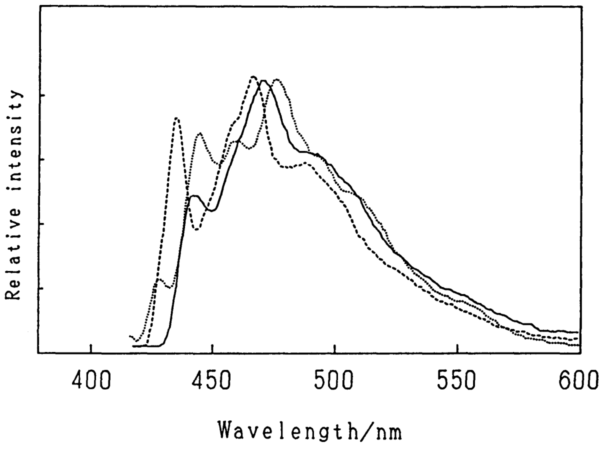


Fig. 4. The phosphorescence spectra of 2-acetylfuran in PVA (——) and ME (------). In this figure, the phosphorescence spectrum in Fig. 2(C)(······) is also shown for comparison.

respectively.

Figure 4 shows the phosphorescence spectra of 2-acetylfuran in polar the matrices ME and PVA at 101 K. In this figure, the phosphorescence spectra measured in PE film at 101 K is also shown for comparison, being regarded as due to the *trans* conformer. The phosphorescence spectrum of this compound in ME matrices consists of peaks at 435, 465, and 486 nm and shoulders around 457 and 504 nm; in PVA, the peaks are at 442 and 469 nm and the shoulders are around 460, 490, and 507 nm. In the polar matrices, no excitation wavelength dependency has been observed in the phosphorescence spectra, indicating that there exists only one kind of phosphorescent species. This species is considered to be the O–O *s-cis* conformer, because the *s-cis* conformer is more polar than the *s-trans* ones.[3] It was found that the 0–0 phosphorescence band of the *s-cis* conformer is red-shifted with an increase in the solvent polarity, i.e., the 0–0 phosphorescence band of the *s-cis* conformer is at 427 nm in PE, at 435 nm in ME, and at 442 nm in PVA. This also indicated that the T_1 state is of a $\pi\,\pi^*$character.

MO Calculation. In order to obtain more detailed information on the electronic nature of 2-acetylfuran, we performed MO calculations, and summarized the results in Table 1. The first band (band maximum=311.5 nm, 0–0 band position=356 nm) is assigned to the calculated $S_0 \rightarrow S_1$ ($n\pi^*$) transition, and the second one (band maximum=263.0 nm, 0–0 band position=272 nm) to the $S_0 \rightarrow S_2$ ($\pi\,\pi^*$) transition. The very weak band around 225 nm may be assigned to the $S_0 \rightarrow S_3$ ($\pi\,\pi^*$) transition. According to these MO calculations, the T_1 state energy of the O–O *s-cis* conformer was computed to be 2.12 eV (585.4 nm), and that of the O–O *s-trans* conformer to be 2.09 eV (592.4 nm). These results explain well the above observation, i.e., the former calculated T_1 state energy is greater than that of the latter. The S_2 state energy (263.2 nm, 4.71 eV), corresponding to the excitation wavelengths used here, of the O–O *s-cis* conformer was also computed to be higher than that of the S_2 energy (268.9 nm, 4.61 eV) of the O–O *s-trans* conformer, in accordance with the present observation. That is, the observed S_2 state energy of the O–O *s-cis* conformer is positioned at the higher energy side of the O–O *s-trans* conformer.

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