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# Studies of the $\pi \rightarrow \pi^*$ Absorption Bands of α-Santonin

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**Synopsis.** The $\pi \rightarrow \pi^*$ S–S absorption spectra of α-santonin in solutions up to the vacuum UV region were obtained. Based on the results of the MO calculations, the observed four $\pi \rightarrow \pi^*$ bands of α-santonin could be favorably assigned.

Heretofore, the electronic spectrum of α-santonin in the wavelength region shorter than 220 nm has never been reported.[1] We have measured the spectra of α-santonin in solutions up to the vacuum UV region. We have also carried out MO calculations on the π-electronic system of α-santonin, which is similar to that of 1,4-cyclohexadiene-3-one, in order to assign the observed $\pi \rightarrow \pi^*$ bands.

The electronic spectra were measured in the same manner as in the previous works.[2] The solvents—*n*-heptane, 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), and ethanol—were the same as those used in the previous works. α-Santonin of the Japan pharmacopaeia was used without further purification (mp 171.5—172.5 °C).

In the P-P-P method calculations, the electronic integral values which were used in the calculations on *p*-benzoquinone, *etc.* in one[2a] of the previous works were used. All the singly-excited configurations were included. In this work, according to the results of the X-ray analysis of 2-bromo-α-santonin,[3] the π-electronic system of α-santonin was assumed to be planar and to be of the $C_{2v}$ symmetry. The atomic distances of the conventional C=O, C–C, and C=C bonds were assumed to be 1.22, 1.47, and 1.35 Å respectively.[3,4] In the calculations, the intramolecular environmental effect on the π-electronic system of α-santonin was ignored.

The longest-wavelength singlet absorption band of α-santonin is the $n \rightarrow \pi^*$ band near 340 nm.[5] In Fig. 1, four $\pi \rightarrow \pi^*$ bands can be observed in an *n*-heptane solution near 255, 230, 200, and 180 nm. These $\pi \rightarrow \pi^*$ bands are denoted as Bands A, B, C, and D (Table 1).

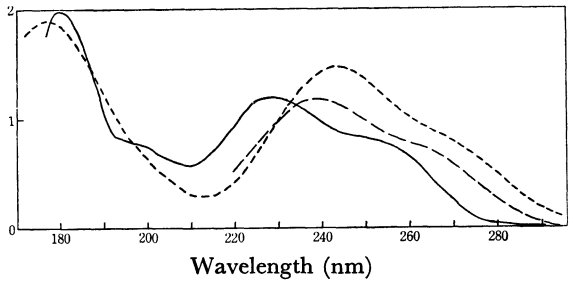


Fig. 1. Absorption spectra of α-santonin in various solvents. ——: *n*-heptane, — — : ethanol, ----: 1,1,1,3,3,3-hexafluoroisopropanol.
(In an *n*-heptane solution the scale of the ordinate is arbitrary.)

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TABLE 1. WAVELENGTHS AND MOLAR ABSORPTION COEFFICIENTS OF THE ABSORPTION MAXIMA (the values in parentheses are the latter)

| *n*-Heptane (nm) | Ethanol | HFIP | Band name |
|---|---|---|---|
| ~255 | ~265 (7060) | ~270 (7950) | A |
| 229.5 | 238.5 (11900) | 243.5 (14700) | B |
| ~200 | | | C |
| 180 | | 177 (19000) | D |

TABLE 2. CALCULATED EXCITATION ENERGIES, OSCILLATOR STRENGTHS, AND SYMMETRY SPECIES OF THE SINGLET $\pi,\pi^*$ EXCITED STATES AND THE CORRESPONDING $\pi \rightarrow \pi^*$ BANDS IN AN *n*-HEPTANE SOLUTION

| | Calcd | | | Obsd | |
|---|---|---|---|---|---|
| No. | Symmetry | *E*(eV) | *f* | Band name | *E*(eV) |
| 1 | $B_2$ | 5.139 | 0.042 | A | ~4.9 |
| 2 | $A_1$ | 5.343 | 0.577 | B | 5.4 |
| 3 | $B_2$ | 6.058 | 0.041 | C | ~6.2 |
| 4 | $A_1$ | 7.156 | 0.033 | | |
| 5 | $A_1$ | 7.367 | 1.036 | D | 6.9 |

Bands A and C can be observed as shoulders. As for the solvent effects on the $\pi \rightarrow \pi^*$ bands in Fig. 1, Band D in a HFIP solution is far broader than that in an *n*-heptane solution. Furthermore, in a HFIP solution, Bands A and B shifts greatly toward longer wavelengths, while Band D shifts a little toward shorter wavelengths, in comparison with those in an *n*-heptane solution. In a HFIP solution, Band C can hardly be observed because of its blue-shift in comparison with that in an *n*-heptane solution. These solvent effects may be due to the strong hydrogen-bond formation between α-santonin and HFIP.[2b] Based on the calculated results, these four $\pi \rightarrow \pi^*$ bands can be reasonably assigned, as is shown in Table 2. The first column of this table denotes the numbering of the magnitude of the calculated excitation energies. In this table, the data on the higher excited states with small *f*-values have been omitted. Since the energy difference between the Nos. 4 and 5 states is small, the $\pi \rightarrow \pi^*$ band corresponding to the No. 4 state may be hidden by Band D. Based on the calculated results, it may be concluded that Bands B and D and Bands A and C are polarized parallel to, and perpendicular to, the C–O bond axis respectively. It is interesting that, according to the calculated results, the excited state of Band D is largely localized in two vinyl groups (*ca.* 66%). The above-mentioned fact that the excitation energies of Band D in an *n*-heptane and a HFIP solutions are relatively close to each other can be reasonably ex-

plained by this calculated result regarding Band D. The broadness of Band D in a HFIP solution may be due to an intensification of the $\pi \rightarrow \pi^*$ band corresponding to the No. 4 state, in addition to the above-mentioned blue-shift of Band C, comparison with those in an *n*-heptane solution.

The quinols have a $\pi$-electronic system similar to that of $\alpha$-santonin. In the $\pi \rightarrow \pi^*$ absorption spectrum of 6-acetoxy-3-oxo-bicyclo-0,3,4-nonadiene-(1,4), which is classified as one of the quinols, in an ethanol solution, as reported by Wessely *et al.*,[6] two $\pi \rightarrow \pi^*$ bands, corresponding to Bands A and B, can be observed. On the other hand, in the absorption spectrum of spiro-5,5-undeca-1,4-dien-3-one, which also has a $\pi$-electronic system similar to that of $\alpha$-santonin, in an *n*-hexane solution, up to the vaccum UV region, as reported by Boschi *et al.*,[7] $\pi \rightarrow \pi^*$ bands corresponding to Bands A and C can hardly be observed. The assignment of its two $\pi \rightarrow \pi^*$ bands, corresponding to Bands B and D, by Boschi *et al.*,[7] based on the P-P-P method calculation, agrees with that in Table 2.

We have also carried out similar MO calculations on other various planar conjugated dienones. According to the calculated results, in all the cross-conjugated dienones, among the singlet excited states and the lowest state does not have the largest *f*-value, unlike as in the cases of the linearly-conjugated dienones.

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