Summary

Compounds having a skeleton of dibenzo-*p*-dioxin (I) show a characteristic color (mostly blue or greenish blue and sometimes violet) in concentrated sulfuric acid with an oxidizing agent such as potassium nitrate. A series of electron spin resonance studies have revealed that the coloring was due to the formation of the cation radicals such as Ia.

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7. Masao Tomita and Shin-ichi Ueda : Studies on the Dibenzo-*p*-dioxin (Diphenylene Dioxide) Derivatives. XXXIX.*1 Electron Spin Resonance Absorption Spectra of Dibenzo-*p*-dioxin Derivatives in Antimony Pentachloride.

(*Faculty of Pharmaceutical Sciences, Kyoto University**2)

In the previous paper*1 the authors reported that the blue colored sulfuric acid solutions of dibenzo-*p*-dioxin (I) derivatives always gave electron spin resonance (ESR) absorption spectra and the coloring was due to the formation of cation radicals such as Ia.

Dibenzo-*p*-dioxin derivatives in antimony pentachloride also gave a blue color and, therefore, the formation of the cation radicals was expected.

In order to confirm the existence of the cation radicals, the electron spin resonance spectra of dibenzo-*p*-dioxin derivatives in antimony pentachloride were measured.

Dibenzo-*p*-dioxin (I) in sulfuric acid gave five-line spectrum, whereas in antimony pentachloride it gave only one band spectrum with the g-value of 2.0054.

Dibenzo-*p*-dioxin-2,7-disulfonic acid (II),[1] 1,6-dibromodibenzo-*p*-dioxin (III)[2] and 2,3,7,8-tetrabromodibenzo-*p*-dioxin (V)[2] also gave one band spectra and their g-values were about the same as those in sulfuric acid with potassium nitrate.

2,7-Dimethyldibenzo-*p*-dioxin (VI),[3] soon after the addition of antimony pentachloride, gave an asymmetric spectrum. It evidently seemed to be the spectrum of the mixture but it gradually changed and after two and a half hours at room temperature it gave a symmetric spectrum. The shape of this spectrum was a little different from that of 2,7-dimethyl-3,8-dichlorodibenzo-*p*-dioxin (VII).[4]

2,7-Dibromodibenzo-*p*-dioxin (IV)[2] in antimony pentachloride gave an asymmetric spectrum which seemed to be the spectrum of the mixture. In this case chlorination of 2,7-dibromodibenzo-*p*-dioxin (IV) must have taken place, whereas the less reactive 1,6-dibromodibenzo-*p*-dioxin (III) gave a symmetric spectrum.

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*1 Part XXXVIII. M. Tomita, S. Ueda : This Bulletin, **12**, 33 (1964).

*2 Yoshida-konoe-cho, Sakyo-ku, Kyoto (富田真雄, 上田伸一).

1) M. Tomita, S. Ueda : Yakugaku Zasshi, **80**, 796 (1960).
2) M. Tomita, S. Ueda, M. Narisada : *Ibid.*, **79**, 186 (1959).
3) M. Tomita : *Ibid.*, **52**, 900 (1932).
4) M. Tomita, S. Ueda : *Ibid.*, **80**, 353 (1960).

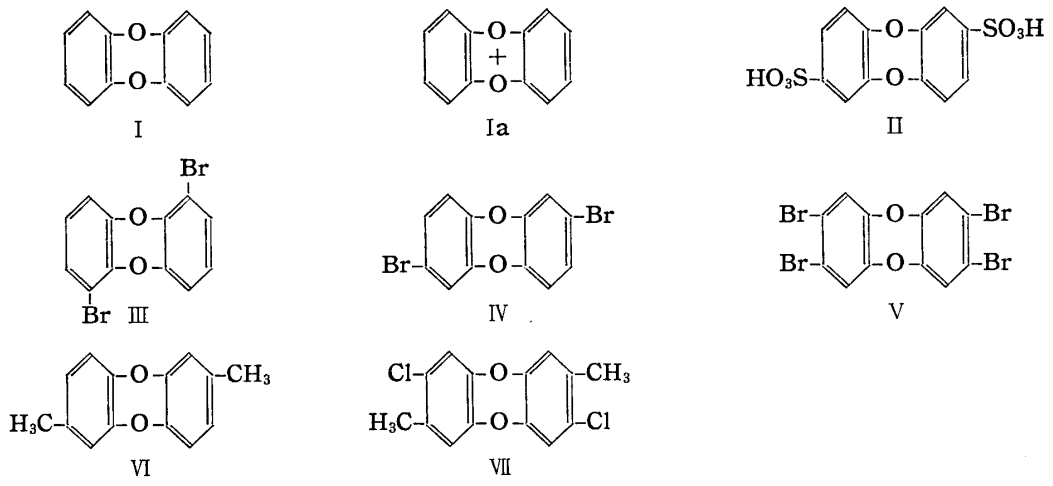

Chart 1.

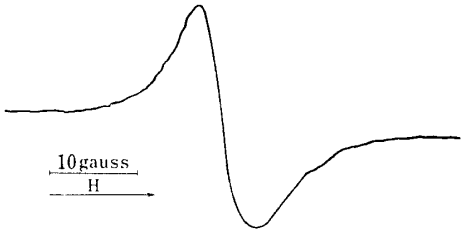

Fig. 1. Electron Spin Resonance Spectrum of Dibenzo-*p*-dioxin (I) in Antimony Pentachloride

Fig. 2. Electron Spin Resonance Spectrum of Dibenzo-*p*-dioxin-2,7-disulfonic Acid (II) in Antimony Pentachloride

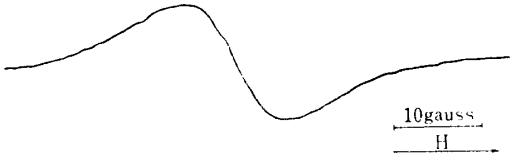

Fig. 3. Electron Spin Resonance Spectrum of 2,3,7,8-Tetrabromodibenzo-*p*-dioxin (V) in Antimony Pentachloride

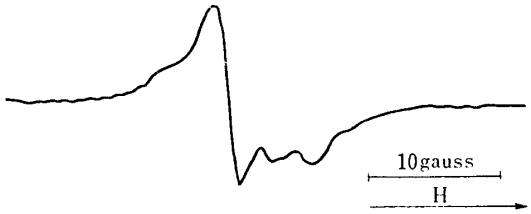

Fig. 4. Electron Spin Resonance Spectrum of 2,7-Dimethyldibenzo-*p*-dioxin (VI) (soon after the addition of $SbCl_5$)

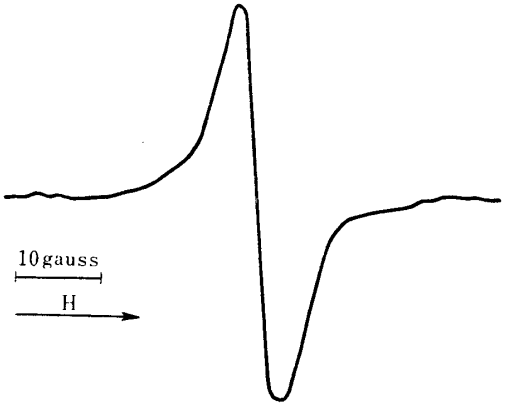

Fig. 5. Electron Spin Resonance Spectrum of VI (2.5 hr. after the addition of $SbCl_5$)

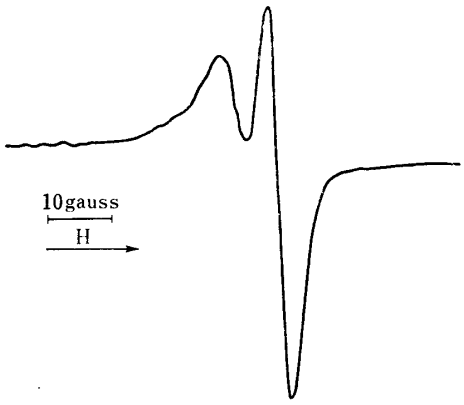

Fig. 6. Electron Spin Resonance Spectrum of 2,7-Dibromodibenzo-*p*-dioxin (IV) in Antimony Pentachloride

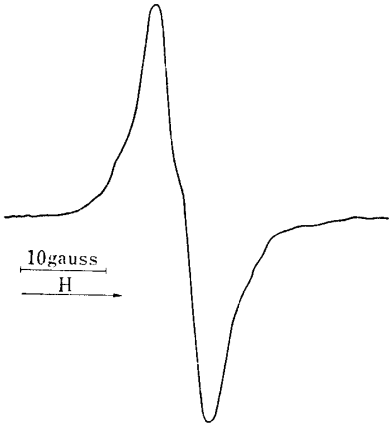

Fig. 7. Electron Spin Resonance Spectrum of 1,6-Dibromodibenzo-*p*-dioxin (III) in Antimony Pentachloride

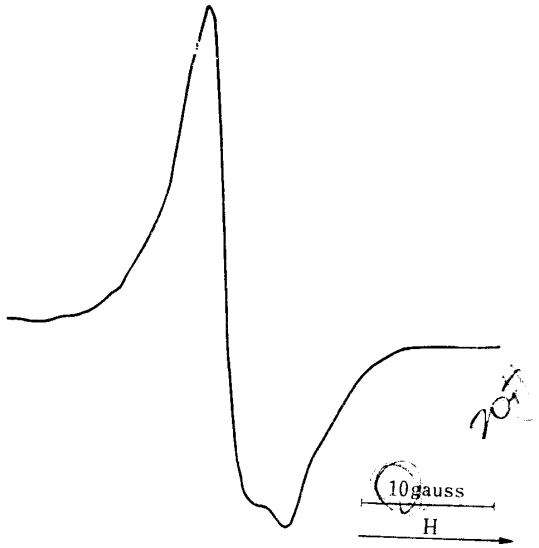

Fig. 8. Electron Spin Resonance Spectrum of 2,7-Dimethyl-3,8-dichlorodibenzo-*p*-dioxin (VII) in Antimony Pentachloride

From these results in antimony pentachloride solution, the formation of the cation radicals such as Ia was confirmed. But in these cases the spectra were not so clear as those of concentrated sulfuric acid solution with the addition of potassium nitrate.

Experimental

Electron Spin Resonance Spectra——A JES-3B-spectrometer (Japan Electron Optics Co., Ltd.) was used with 100 Kc. field modulation and a modulation amplitude of 0.1 gauss. In all spectra, the field sweep increased in the same rate from left to right on the figures. An aqueous solution of potassium peroxylamine disulfonate was used as a standard of the magnetic field and the g-value. All the sample tubes were sealed at both ends.

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Summary

Dibenzo-*p*-dioxin (I) derivatives showed blue color in antimony pentachloride. These colored solutions gave electron spin resonance absorption spectra and the formation of the cation radicals such as Ia was confirmed.

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