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CATION RADICALS OF DIBENZO-p-DIOXIN AND RELATED COMPOUNDS

Masao Tomita and Shin-ichi Ueda

Faculty of Pharmacy, Kyoto University, Kyoto, Japan

and

Yasuto Nakai, Yasuo Deguchi and Hideo Takaki

Faculty of Science, Kyoto University, Kyoto, Japan

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COMPOUNDS having a skeleton of dibenzo-p-dioxin (Ia) show the characteristic colour (mostly blue or greenish blue and sometimes violet) in sulphuric acid (98%) with an oxidizing agent. A series of systematic work[1-7] has established the generality of these phenomena, dibenzo-p-dioxin reaction, except for a few species[3] which happened to be insoluble in the solvent. An ESR study has seemed to reveal that the colouring was due to formation of the cation radicals such as (Ib).

In the dibenzo-p-dioxin reaction, the quinoid formation was not expected since the octamethyl derivative (VI)[7] being unable to take any quinoid forms did also give the characteristic colour as other derivatives.

The colouring reaction was instantaneous and could be reversed by addition of water. For example, 1,6-dibromodibenzo-p-dioxin[3] was coloured in sulphuric-nitric acid, then recovered quantitatively on pouring into water[6]. The colouring also took place generally in oxidizing, strong

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[1] M. Tomita, J. Pharm. Soc. Japan **52**, 889 (1932): Ibid. **54**, 891 (1934).

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[5] M. Tomita and S. Ueda, J. Pharm. Soc. Japan **81**, 724 (1961).

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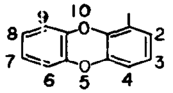
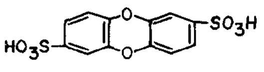


Ia



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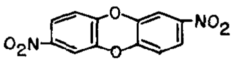

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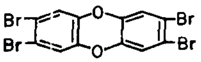

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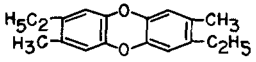

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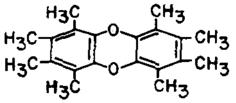

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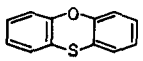
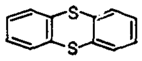
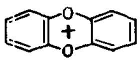


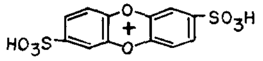
VIIa



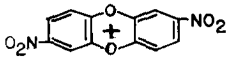
VIIIa



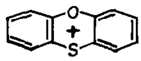
Ib



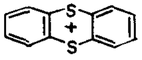
IIb



IIIb



VIIb



VIIIb

acidic media such as antimony pentachloride, fuming nitric acid, or trichloroacetic acid together with a usual oxidizing agent, whereas dibenzo-p-dioxin (Ia) and its octamethyl derivative (VI)[7] gave blue colour and ESR signals in concentrated sulphuric acid solution without addition of any oxidizing materials. The g-values were about 2.0036. The spectrum of (Ib) consisted of five distinct lines with intensity ratios of 1:4:6:4:1 (with an anisotropic effect[8] of the viscous solvent), like thianthrene (VIIIa)[9], indicating a coupling of an unpaired electron spin with a set of four equivalent hydrogen nuclei in either 1,4,6,9- or 2,3,7,8- positions respectively. Phenoxathiin (VIIa) with less molecular symmetry, however, showed hyperfine structure contributed by probably all protons in the molecule. An additional information was obtained from the result of the following derivative.

Dibenzo-*p*-dioxin-2,7-disulphonic acid (IIa)[4] in concentrated sulphuric acid with potassium nitrate gave only three line spectrum in exactly 1:2:1 intensity ratios. Therefore, there must be a strong contribution from 3,8- protons to give the major pattern of the spectrum of (IIb). Hence it was inferred that the contribution of 2,3,7,8- protons predominated over that of 1,4,6,9- protons in the case of (Ib), whereas the spectra of the 2,7-dinitro derivative (IIIa)[2] or octamethyl derivative (VI), however, did not allow a straightforward interpretation. 2,7-Dimethyl-3,8-diethyl (V)[10], 2,3,7,8-tetrabromo (IV)[3], and octamethyl derivative (VI) in sulphuric acid (98%) with potassium nitrate all gave the ESR spectra.

Further studies on 2-methyl[11], 2,7-dimethyl[12] and 1,2,3,6,7,8-hexamethoxy-4,9-diethyldibenzo-*p*-dioxin[5] (having no hydrogen atom on the dibenzo-*p*-dioxin ring) are under way and results will be published in due course.

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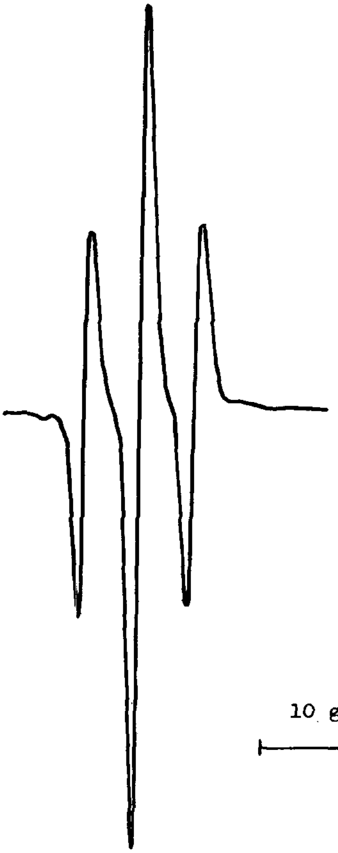
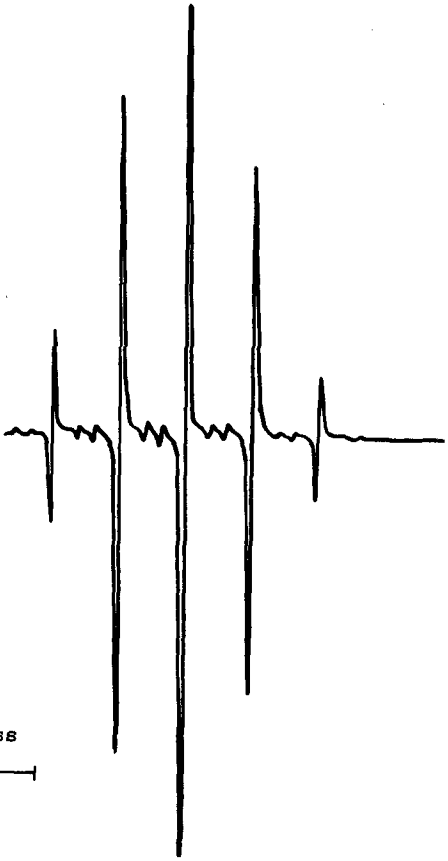
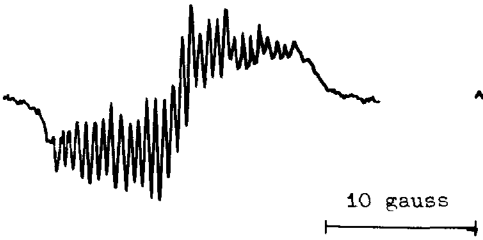


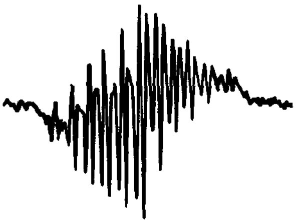
ESR spectrum of dibenzo-p-dioxin-2,7-disulphonic acid (IIa) in sulphuric acid with potassium nitrate



ESR spectrum of dibenzo-p-dioxin (Ia) in sulphuric acid

ESR spectrum of octamethyldibenzo-p-dioxin (VI) in sulphuric acid





ESR spectrum of phenoxathiin (VIIa) in sulphuric acid

ESR spectrum of 2,7-dinitrodibenzo-p-dioxin (IIIa) in sulphuric acid with potassium nitrate

ESR Spectra.--JES-3B spectrometer (Japan Electron Optics Laboratory Co., Ltd.) was used with 100 Kc. field modulation. In all spectra, the field sweep increased in the same rate from left to right on the figures and a modulation amplitude of 0.1 gauss. The spectra were calibrated with aqueous solution of potassium peroxylamine disulphonate.[13]

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