

Thus the charge densities determined from proton shifts show a remarkable good correspondence with the HMO charge distributions to indicate that the HMO is valid in predicting the reactivities of the ring protons.

The authors express their gratitude to Dr. K. Takeda, Director of this laboratory, for his encouragement.

Summary

Proton magnetic resonance spectra of the *s*-triazolo[1,5-*a*]pyrimidine derivatives are recorded to give the positional order of $H_6 > H_2 > H_5 > H_7$ for the ring proton chemical shifts in τ -value. The methyl substituent effect on the proton chemical shifts and the correlation between the proton chemical shift and the local π -electron density on the carbon atom to which the proton is bonded, are discussed. Thus the charge densities determined from proton chemical shifts show a remarkably good correspondence with the charge distributions calculated by the simple Hückel MO method.

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29. Shin-ichi Ueda : Studies on the Dibenzo-*p*-dioxin (Diphenylene Dioxide) Derivatives. XL.*¹ Electron Spin Resonance Spectra of Dibenzo-*p*-dioxin-2,7-dicarboxylic Acid and 2,7-Disulfonic Acid.

(Faculty of Pharmaceutical Sciences, Kyoto University*²)

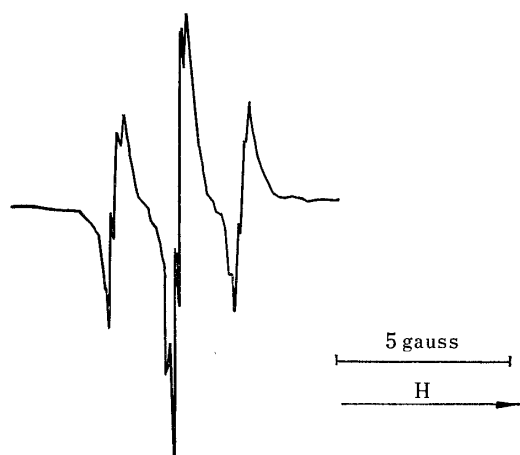


Fig. 1. Electron Spin Resonance Spectrum of Dibenzo-*p*-dioxin-2,7-disulfonic Acid (II) in conc. Sulfuric Acid with Potassium Nitrate

The author previously reported that dibenzo-*p*-dioxin (I) derivatives in concentrated sulfuric acid with an oxidizing agent such as potassium nitrate gave electron spin resonance (ESR) absorption spectra.*^{1,1)} Dibenzo-*p*-dioxin-2,7-disulfonic acid (II)²⁾ in concentrated sulfuric acid gave no color and no ESR absorption, while after the addition of potassium nitrate into the sulfuric acid solution, it colored blue and the ESR spectrum gave a triplet with the intensity ratios of 1:2:1, indicating a coupling of an unpaired electron spin with a set of two equivalent hydrogen nuclei. The *g*-value was 2.0038 (Fig. 1).

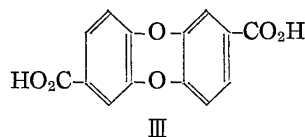
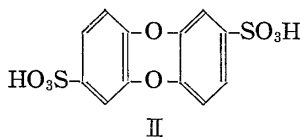
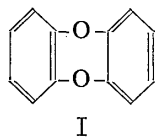
*¹ This paper constitutes Part XL of the series entitled "M. Tomita : Studies on the Dibenzo-*p*-dioxin Derivatives." Part XXXIX. M. Tomita, S. Ueda : This Bulletin, 12, 40 (1964).

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1) M. Tomita, S. Ueda, Y. Nakai, Y. Deguchi, H. Takaki : Tetrahedron Letters, No. 18, 1189 (1963); M. Tomita, S. Ueda : This Bulletin, 12, 33 (1964).

2) M. Tomita, S. Ueda : Yakugaku Zasshi, 80, 796 (1960).

From the studies on the spectra of many dibenzo-*p*-dioxin derivatives, the author assumed that there must be a strong contribution from 3,8-protons to give the major pattern of the spectrum of II.^{*1,1)}



This time, the author measured the ESR spectrum of dibenzo-*p*-dioxin-2,7-dicarboxylic acid (III)³⁾ which also has two electron attractive groups at 2,7-positions. The spectrum of III gave a triplet whose intensity ratios were 1:2:1 and the *g*-value was just the same as that of II. (The *g*-value was 2.0038) (Fig. 2). The coupling constant of the spectrum of III was about the same as that of II. Therefore, there must be a strong contribution from 3,8-protons to give the major pattern of the spectrum of III, and it was inferred that the distribution of the spin-density of the odd electron was quite similar to that of II.

The author²⁾ already reported that when dibenzo-*p*-dioxin (I) was treated with concentrated sulfuric acid, it gave dibenzo-*p*-dioxin-2,7-disulfonic acid (II) with some amount of the recovery of I.

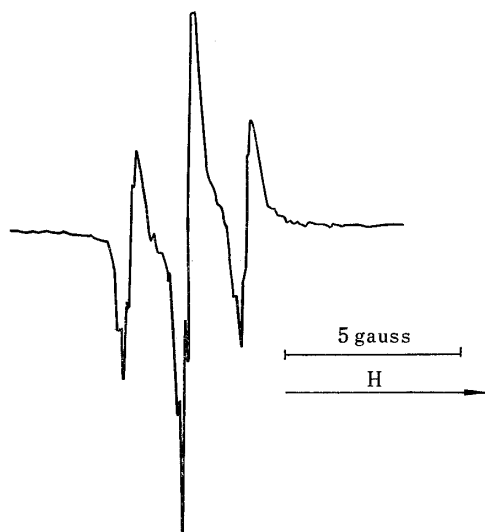


Fig. 2. Electron Spin Resonance Spectrum of Dibenzo-*p*-dioxin-2,7-dicarboxylic Acid (III) in conc. Sulfuric Acid with Potassium Nitrate

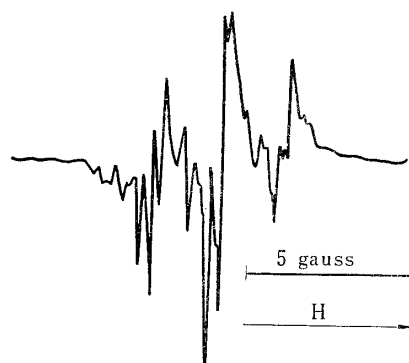


Fig. 3. Electron Spin Resonance Spectrum of Dibenzo-*p*-dioxin (I) treated with conc. Sulfuric Acid and after 1 Hour Potassium Nitrate was added

By the way, unless potassium nitrate was added, the concentrated sulfuric acid solution of II gave no ESR absorption, while the concentrated sulfuric acid solution of I gave ESR absorption of quintet with intensity ratios of 1:4:6:4:1.^{*1,1)}

Soon after the addition of concentrated sulfuric acid into I, potassium nitrate was added to the solution and immediately the ESR spectrum was measured. The ESR spectrum of the solution gave the quintet which was just the same as that of I in concentrated sulfuric acid.

On the other hand, dibenzo-*p*-dioxin (I) was dissolved in concentrated sulfuric acid and the solution was kept standing for an hour at room temperature (25°). Then potassium nitrate was added to the solution. It colored deep blue and the ESR spectrum of

3) M. Tomita : Yakugaku Zasshi, **52**, 889 (1932); S. Ueda : *Ibid.*, **82**, 714 (1962).

4) G.E. Pake, J. Townsend, S.I. Weissman : Phys. Rev., **85**, 682 (1952).

the solution gave a similar absorption as that of II in concentrated sulfuric acid with potassium nitrate (Fig. 3). Therefore, in this case, the ESR spectrum of the solution indicated the formation of dibenzo-*p*-dioxin-2,7-disulfonic acid (II) by standing dibenzo-*p*-dioxin (I) in concentrated sulfuric acid at room temperature.

Experimental

Electron Spin Resonance Spectra—A 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. An aqueous solution of potassium peroxyamine disulfonate⁴⁾ was used as a standard of the magnetic field and the *g*-value.

The author express his gratitude to Prof. M. Tomita, Faculty of Pharmaceutical Sciences, Kyoto University, for his kind encouragement and advices. He is also appreciative of the encouragement of Prof. H. Takaki, Dr. Y. Deguchi, and Mr. Y. Nakai, Faculty of Science, Kyoto University.

Summary

Dibenzo-*p*-dioxin-2,7-dicarboxylic acid (III) in concentrated sulfuric acid with potassium nitrate gave an electron spin resonance spectrum which was considerably similar to that of dibenzo-*p*-dioxin-2,7-disulfonic acid (II).

Therefore, the spectra indicated that the distributions of the spin densities of the odd electron were quite similar in both cases.

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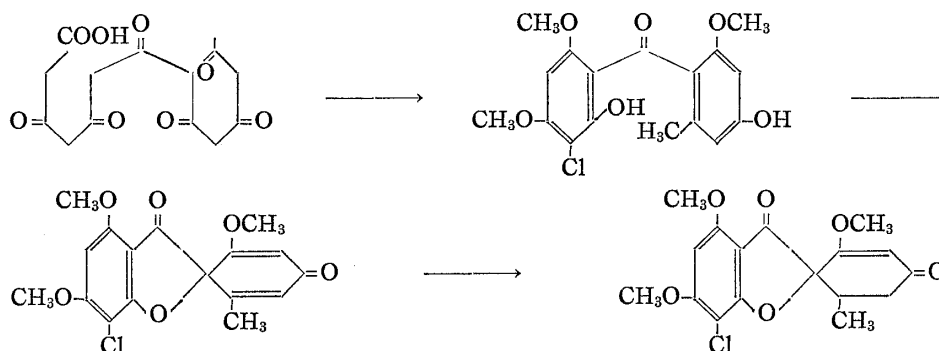
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30. Tadasu Tanaka : Synthesis of the Compounds Containing Grisan Ring.*¹

(Osaka Research Laboratory, Tanabe Seiyaku Co., Ltd.*²)

In 1958, Birch and his co-workers¹⁾ demonstrated that the mould metabolite griseofulvin was derived from β -poly carbonyl system through "head to tail" condensation of seven units of acetic acid.



*¹ The paper reported at the 82nd annual meeting of the Pharmaceutical Society of Japan, Nov. 3rd. 1962.

*² 960, Kashimacho, Higashiyodogawa-ku, Osaka (田中 雅).

1) A. J. Birch, R. A. Massy Westropp, R. W. Richards, H. Smith: J. Chem. Soc., 1958, 360.