Formaldehyde Resins. LXXVII. The Synthesis of Some Anthracene Derivatives as a Wavelength Shifter of a Plastic Scintillator*

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A liquid or plastic scintillator generally contains two kinds of organic compounds. One is called the primary solute, and the other, the secondary solute. They disperse themselves in the solute or the plastic to set one of their fluorescent wavelengths by the most sensitive wavelength of a photoelectron amplifier. As the primary solute, terphenyl, tetraphenylbutadiene or quaterphenyl are widely used, while for the second solute, many kinds of aromatic compound are used. POPOP (*p*-di-(5-phenyl-2-oxazol)benzene)[1] is said to be the best second solute.

Recently, one of the present authors synthesized 9, 10-bis(2, 4-dimethylbenzyl)anthracene (I)[2], which was proved to behave excellently as a second solute[3].

The present paper concerns the syntheses of three compounds similar to I and a study of their ultraviolet and fluorescent spectra. The first compound synthesized was 9, 10-di-*m*-xylylanthracene (II), in which the nucleus of benzene is attached directly to the nucleus of anthracene. The two other compounds are derivatives of I with methyl groups in different positions, 9, 10-bis(4-methylbenzyl)anthracene (III) and 9, 10-bis(2, 3, 5, 6-tetramethylbenzyl)anthracene (IV).

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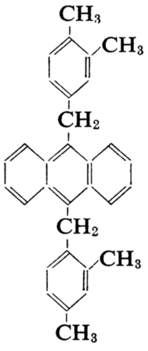
[*] LXXVI: M. Imoto and A. Ninagawa, in preparation.

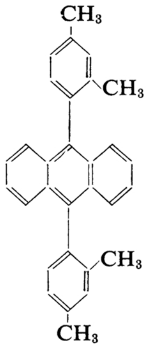
[1] W. C. Kaski and C. O. Jomas, *J. Chem. Phys.*, **79**, 1286 (1951).

[2] M. Imoto, K. Ko and F. Sakurai, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **65**, 622 (1962).

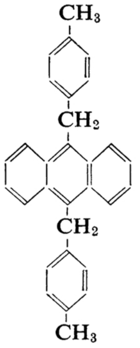
[3] K. Osio, private communication.



(I)



(II)



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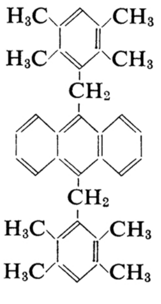

(IV)

These compounds have been little described in literature but have been proved by Osio et al.[3)] to be more usable as second solutes than POPOP.

Experimental

9, 10-Bis(2′, 4′-dimethylphenyl)anthracene(II).— 4-Iodo-*m*-xylene was obtained by the method described in the literature[4)]; b. p., 105°C/12 mmHg; yield, 44%. A mixture of anthraquinone (27 g.) and 200 ml. of tetrahydrofuran was gradually added to a Grignard solution prepared from the mixture of 102 g. of 4-iodo-*m*-xylene, 9.7 g. of magnesium, 200 ml. of tetrahydrofuran and a trace of iodine. After the mixture had been heated under reflux for 4 hr., a saturated solution of ammonium chloride was added to decompose the excess reagent. The solid product, 9,10-dihydroxy-9,10-(2′,4′-dimethylphenyl)anthracene, was twice extracted with ethyl acetate. The extract was then concentrated to give crystals. After recrystallization from a mixture of benzene and ethanol (1 : 1 in vol.), white needle crystals melting at 277∼288°C were obtained in a 76% yield.

Found: C, 85.22; H, 6.74. Calcd. for $C_{30}H_{28}O_2$: C, 85.72; H, 6.67%. IR: ν-OH 3620 cm^{-1} in Nujol mull.

9,10-Dihydroxy-9,10-(2′,4′-dimethylphenyl)anthracene was heated under reflux with 1 g. of zinc dust in 30 ml. of acetic acid for 1 hr. The mixture was then concentrated and cooled, and the crystals separated were extracted with toluene. Recrystallization was performed from a mixture of ethanol and benzene (2 : 1 in vol.). 9,10-Bis(2′,4′-dimethylphenyl)anthracene was obtained as pale yellow crystals melting at 289∼291°C. In the infrared spectrum, ν-OH was not observed in Nujol mull.

Found: C, 93.01; H, 6.89. Calcd. for $C_{30}H_{26}$: C, 93.21; H, 6.79%. UV absorptions: λ_{max}(mμ): 260, 356, 376, 397 in dioxane, as shown in Fig. 1.

9, 10 - Bis(4 - methylbenzyl)anthracene (III). — Twenty eight grams of *p*-xylylene chloride was added to 400 ml. of carbon disulfide already containing 17 g. of anthracene and 5 g. of zinc dust. The mixture was heated under reflux for 30 hr. while being stirred and then cooled. The precipitate was collected and recrystallized from benzene. Colorless crystals melting at 288∼289°C were obtained in a 22% yield.

Found: C, 93.02; H, 6.98. Calcd. for $C_{30}H_{26}$: C, 93.26; H, 6.74%. λ_{max} (mμ): 260, 357, 378, 400 in dioxane.

9, 10-Bis(2, 3, 5, 6-tetramethylbenzyl)anthracene (IV). — By a method similar to that which gave 9,10-bis(4-methylbenzyl)anthracene, the reaction of 16.9 g. of anthracene with 36.5 g. of tetramethylbenzyl chloride was carried out in 350 ml. of carbon disulfide under refluxing for 30 hr. Colorless powder with a m. p. of 369∼370°C was obtained from benzene in a 18% yield.

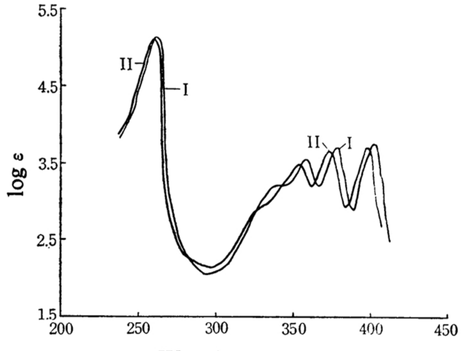

Fig. 1. UV absorption spectra of I and II in dioxane (concn. 2×10^{-4} mol./l.).

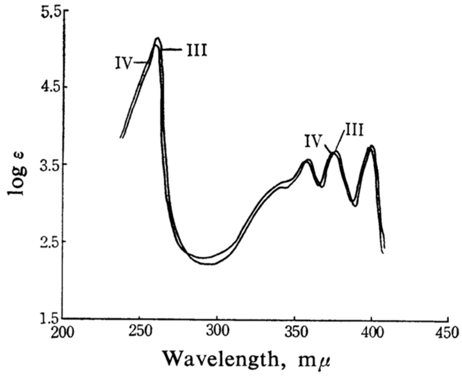

Fig. 2. UV absorption spectra of III and IV in dioxane (concn. 2×10^{-4} mol./l.).

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4) R. L. Datta and N. R. Chatterjee, *J. Am. Chem. Soc.*, **39**, 438 (1917).

Found: C, 91.96; H, 7.94. Calcd. for $C_{30}H_{38}$: C, 91.92; H, 8.08%. λ_{max} (mμ): 260, 356, 376, 397 in dioxane.

Discussion

Ultraviolet Absorption Spectra. — The ultraviolet absorption spectra of compounds I, II, III and IV are shown in Figs. 1 and 2. The O–O bands of the absorption spectra are tabulated in Table I. The O–O bands may be compared with the B-bands of the phenyl type and with benzyl-type derivatives of anthracene.

TABLE I. THE WAVELENGTHS OF THE O–O BANDS OF ULTRAVIOLET ABSORPTION SPECTRA

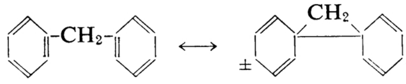
Compound	O–O, mμ	Log ε	Solvent
I	403	3.75	Dioxane
II	397	3.73	Dioxane
III	400	3.74	Dioxane
IV	397	3.73	Dioxane
Anthracene(5)	380	3.90	Ethanol

Comparing the absorption wavelengths of compound II with those of compounds I and III, it is clear that the CH_2 group between the anthracene and benzene rings shifts the absorption band toward longer wavelengths. In order to explain the fact that the extent of conjugation is greater when the CH_2-group was present between the nuclei, two interpretations may be possible. One of them is the concept of hyperconjugation by the CH_2-group; the other is the direct conjugation of the rings of anthracene and benzene.

From the identical values of the λ_{max} in compounds II and IV, it can not be possible that the hyperconjugation effect of the CH_2-group plays an important role.

Actually, when the model of 9, 10-bis(2′, 4′-dimethylphenyl)anthracene (II) was constructed by use of Stuart model, it was observed that the benzene and anthracene rings twist by an angle of about 60° to each other; it was therefore considered that the direct conjugation of the two rings may be very small. However, in the case of 9, 10-bis(2′, 4′-dimethylbenzyl)anthracene (I), the rings of anthracene and benzene are situated opposite one another at an angle of about 110°. Accordingly, the molecular orbitals of the anthracene ring and the benzene rings may directly interact; thus, the absorption bands may shift to longer wavelengths.

In 1950, Bartlett(6) considered a direct conjugation in the mode of the following formula:



Also, McClure and Coffman(7) and Stewart(8) observed the same phenomenon in polyphenylalkanes and agreed with the idea of direct conjugation.

As for the identical absorption maxima of compounds II and IV, it may be considarable that the 2′, 6′-dimethyl groups of the durene nucleus prevent the conjugation.

Fluorescence Spectra.—The fluorescence spectra measured are shown in Figs. 3 and 4. The O–O and O–1 bands are tablated in Table II, along with the differences in the wavelengths between the O–O bands of the fluorescence spectra and the O–O bands of the ultraviolet absorption spectra.

The fluorescence O–O bands shifted toward wavelengths longer by 5∼7 mμ than those of the ultraviolet absorption spectra. This may be ascribed to the fact that the conjugation between the anthracene and two benzene rings

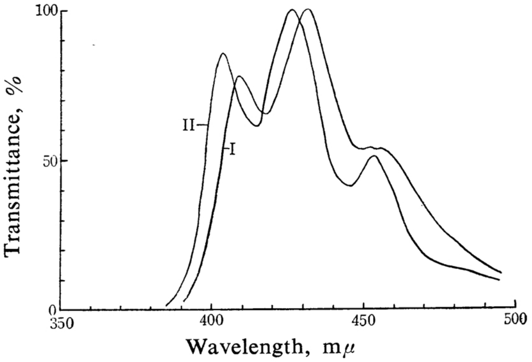


Fig. 3. Fluorescence spectra I and II in dioxane (concn. 2×10^{-4} mol./l.).

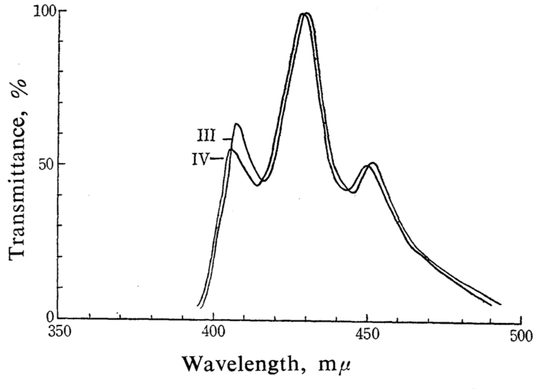


Fig. 4. Fluorescence spectra III and IV in dioxane (concn. 2×10^{-4} mol./l.).

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5) E. Clar, *Ber.*, **69**, 607 (1936).

6) P. D. Bartlett and E. S. Lewis., *J. Am. Chem. Soc.*, **72**, 1005 (1950).

7) D. S. McClure and R. Coffman, *Can. J. Chem.*, **36**, 48 (1958).

8) F. H. C. Stewart, *J. Org. Chem.*, **27**, 3374 (1962).

TABLE II. THE WAVELENGTHS OF THE O–O AND O–1 BANDS OF THE FLUORESCENCE SPECTRA

Compound	O–O mμ	O–1 mμ	Differences in O–O bands between fluores. and UV absorption, mμ
I	408	432	5
II	403	427	6
III	407	430	7
IV	404	428	7

occur more easily in the excited state than in the ground state, because the molecule is somewhat less strained in the excited state.

Since the best sensitivity of the photoelectron amplifier exists at the wavelength of about 450 mμ, it is desirable to have the fluorescence also in this region. While the strongest band of the POPOP is 417 mμ, those of compounds II and III are 429 and 430 mμ respectively. The compounds described in the present paper are, therefore, considered to be better second solutes of the plastic scintillator than POPOP[2].

Summary

Three anthracene derivatives, 9, 10-di-*m*-xylyl-anthracene (II), 9, 10-bis(4-methylbenzyl)-anthracene (III), and 9, 10-bis(2, 3. 5, 6-tetramethylbenzyl)anthracene (IV), have been synthesized and their ultraviolet and fluorescence spectra measured. The shift of the spectrum to the longer wavelength by the presence of methylene groups between anthracene and benzene rings may be explained in terms of direct conjugation between three rings.

According to the spectra, these compounds are believed to be better second solutes of the plastic scintillator.

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