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Plastic Scintillators. III. The Synthesis of Some Anthracene Derivatives as Wavelength Shifters in Plastic Scintillators

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Fifteen anthracene derivatives have been synthesized, and their absorption and fluorescence spectra have been measured. The spectra will be discussed in this paper. According to the spectra, some of anthracene derivatives synthesized here are better wavelength shifters than the compounds previously described in the literature.

In the first paper of this series,[1] we described the synthesis of some anthracene derivatives and their absorption and fluorescence spectra.

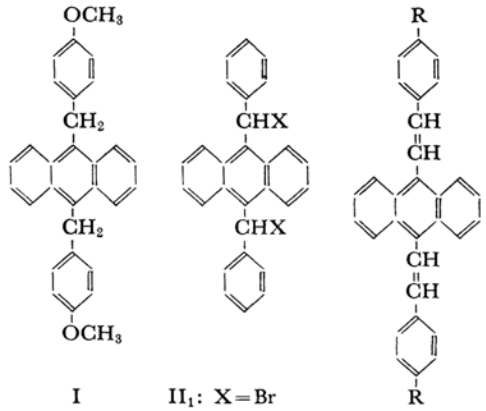
We have now synthesized fifteen more derivatives of anthracene; they are listed below.

9, 10-Bis(4-methoxybenzyl)anthracene (I) was obtained by the reaction of anthracene with 4-methoxybenzylalcohol. 9, 10-Bis(α-bromobenzyl)-anthracene (II_1), 9, 10-bis(α-*o*-toluidinobenzyl)-anthracene (II_2) and 9, 10-bis(α-acetoxybenzyl)-anthracene (II_3) were, respectively, obtained with the successive bromination, amination and acetoxylation of 9, 10-dibenzylanthracene. The derivatives of 9, 10-*trans*, *trans*-distyrylanthracene (III_1—III_2) were synthesized by the Wittig reaction of 9, 10-anthracenedimethyl-bis(triphenylphosphonium chloride) with the corresponding aldehydes. 9, 10-Anthracene-dimethanol diacetate (IV_1) and 9, 10-anthracene-dimethanol (IV_2) were prepared by the procedure described by Miller and his co-workers.[2]

9-Anthraldehyde tosylhydrazone (V) was synthesized by the reaction of 9-anthraldehyde with tosylhydrazine. The derivatives of 9, 10-dihydro-9, 10-*cis*-di(phenylcarbamoyl)anthracene (VI_1—VI_7) were obtained by the treatment of

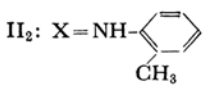
1) M. Imoto and T. Nakaya, This Bulletin, **36**, 785 (1963).

2) M. W. Miller, R. W. Amison and P. O. Tawney, *J. Am. Chem. Soc.*, **77**, 2845 (1955).



I

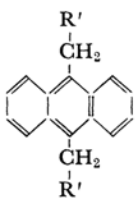
II_1: X=Br



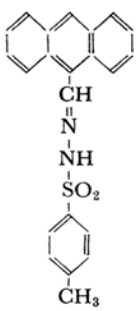
II_2: X=NH-

II_3: X=OCOCH$_3$

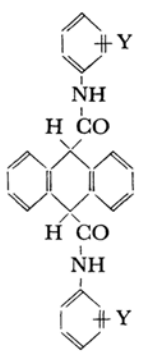
III_1: R=H
III_2: R=NO$_2$



IV_1: R′=OCOCH$_3$
IV_2: R′=OH



V



VI_1: Y=H
VI_2: Y=*p*-Cl
VI_3: Y=*m*-OCH$_3$
VI_4: Y=*o*-OCH$_3$
VI_5: Y=*o*-CH$_3$
VI_6: Y=*p*-NO$_2$
VI_7: Y=*m*-NO$_2$

9, 10-dihydro-9, 10-*cis*-dicaroxylic chloride with substituted anilines.

This paper is concerned also with the absorption and fluorescence spectra of the compounds synthesized here. Some of them have been proved by Osio and his co-workers[3] to be superior to the wavelength shifters described in the literature.[4-6]

Experimental

9, 10-Bis(4-methoxybenzyl)anthracene (I).—1.7 g. of anthracene and 2.5 g. of 4-methoxybenzylalcohol were added to 50 ml. of acetic acid, and then the mixture was heated under reflux with a current of nitrogen gas for 4.5 hr. After the reaction mixture had been concentrated to removed the excess acetic acid, pale yellow crystals began to separate from the solution. The crystals were recrystallized several times from benzene to give I, with a m. p. of 223—224.5°C, in a 65% yield.

Found: C, 86.28; H, 6.33. Calcd. for $C_{30}H_{26}O_2$: C, 86.12; H, 6.22%.

9, 10-Bis(α-bromobenzyl)anthracene (II_1).—9, 10-Dibenzylanthracene was obtained by a method similar to that described in the previous paper.[1] A mixture of 9, 10-dibenzylanthracene (3.8 g.) and *N*-bromosuccinimide (4.0 g.) was heated in 250 ml. of oxygen-free carbon tetrachloride. To take off the *N*-bromosuccinimide, the mixture was filtered. The mixture was then concentrated by distillation under reduced pressure to give yellow crystals. The separated crystals were washed twice with diethylether, dried in vacuo, and crystallized from carbon tetrachloride to give II_1, melting at 193—195°C, in a 60% yield.

Found: Br, 30.8. Calcd. for $C_{28}H_{20}Br_2$: Br, 31.0%.

9, 10-Bis(α-*o*-toluidinobenzyl)anthracene (II_2).—Three grams of 9, 10-bis(bromobenzyl)anthracene and 3 g. of *o*-toluidine were added to 80 ml. of benzene, and then the mixture was heated for 9 hr. at the boiling point of the solvent. The reaction mixture was then chilled. The crystals which separated were collected and washed with cold benzene. The pale yellow crystalline solid was recrystallized from benzene to give II_2, with a m. p. of 261—262°C, in a 39% yield.

Found: C, 89.08; H, 6.01; N, 4.91. Calcd. for $C_{42}H_{36}N_2$: C, 88.93; H, 6.34; N, 4.93%.

9, 10-Bis(α-acetoxybenzyl)anthracene (II_3).—Two grams of 9, 10-bis(bromobenzyl)anthracene and 1.5 g. of silver acetate were added to 30 ml. of benzene, and then the mixture was heated under reflux for 1.5 hr. The reaction mixture was filtered at about 50°C. The mother liquor was concentrated to separate white crystals. The separated crystals were recrystallized several times from benzene to give II_3, with a m. p. of 227—229°C, a 52% yield. This compound showed the infrared absorption of the carbonyl group at 1735 cm^{-1}.

Found: C, 80.74; H, 5.94. Calcd. for $C_{32}H_{26}O_4$: C, 81.01; H, 5.48%.

9, 10-Anthracenedimethyl-bis(triphenylphosphonium chloride).—A solution of 2.7 g. of 9, 10-dichloromethylanthracene and 7.0 g. of triphenylphosphine in 350 ml. of dry xylene was heated at the boiling point of the solvent with stirring for 9 hr. The yellow crystals began to separate after 15 min. The mixture was then cooled to room temperature. The crystals were filtered, washed several times with excess dry xylene, and then dried in a vacuum desiccator at 10 mmHg and 60°C. The solid product, melting at 298—300°C, was obtained in a yield of 85%.

Found: Cl, 9.1. Calcd. for $C_{52}H_{42}Cl_2P_2$: Cl, 8.9%.

9, 10-*trans*, *trans*-Distyrylanthracene (III_1).—To a solution of 2.0 g. of 9, 10-anthracenedimethyl-bis(triphenylphosphonium chloride) and 0.8 g. of benzaldehyde in 30 ml. of absolute ethanol, 70 ml. of a 0.2 M lithium ethoxide solution was added. A yellow crystalline solid began to separate from the solution after 7 hr. After the solution had stood for 15 hr., the solid was collected on a filter glass and dried in vacuo. The

3) T. Osio, private communication.
4) R. C. Sangster and J. W. Irvine, *J. Chem. Phys.*, **24**, 670 (1956).
5) V. N. Kerr, F. N. Hayes, D. G. Ott and E. Hansbury, *J. Org. Chem.*, **24**, 1861 (1959); **24**, 1864 (1959).
6) A. Heller and D. Katz, *J. Chem. Phys.*, **35**, 1987 (1961).

solid product was crystallized from benzene. The solid, which was a mixture of cis and trans isomers, was recrystallized several times from boiling benzene containing a trace of iodine to give III_1 as yellow crystals, m. p.>310°C in a 24% yield.

Found: C, 93.19; H, 6.81. Calcd. for $C_{30}H_{22}$: C, 92.79; H, 7.21%.

9, 10-*trans*, *trans* - Bis(*p*-nitrostyryl)anthracene (III_2).—To a solution of 4.4 g. of 9, 10-anthracenedimethyl-bis(triphenylphosphonium chloride) and 2.0 g. of 4-nitrobenzaldehyde in 80 ml. of absolute ethanol, 110 ml. of a 0.2 M lithium ethoxide solution was added. A yellow red crystalline solid began to separate from the solution after a while. After the solution had stood for 10 hr, the solid was collected on a filter glass and dried in vacuo. The solid was then treated as above. The solid product was recrystallized several times from benzene in the presence of a trace of iodine to give III_2 as yellow red crystals, with a m. p. of >320°C, in a 28% yield.

Found: N, 5.90. Calcd. for $C_{30}H_{20}N_2O_4$: N, 5.93%.

9, 10-Anthracene-dimethanol Diacetate (IV_1).—This compound was prepared by the procedure reported by Miller and his co-workers.[2] A solution of 20 g. of 9, 10-dichloromethylanthracene and 25 g. of anhydrous sodium acetate in 400 ml. of glacial acetic acid was heated at reflux for 5 hr. The mixture was then allowed to cool to room temperature; yellow crystals were filtered out and dried in vacuo. The solid product was recrystallized from benzene to give IV_1 as yellow needles, melting at 220—222°C, in a 70% yield.

Found: C, 74.75; H, 6.07. Calcd. for $C_{20}H_{18}O_4$: C, 74.31; H, 5.66%.

9, 10-Anthracene-dimethanol (IV_2).—This compound was also prepared by the procedure reported by Miller and his co-workers.[2] To 4.9 g. of IV_1 in 400 ml. of methanol, 15 g. of 85% potassium hydroxide was added. After the mixture had been stirred under reflux for 2 hr., it was poured into 500 ml. of cold water. The solid products were collected, dried in vacuo, and recrystallized from benzene to give IV_2 as yellow prisms, melting at 280—282°C, in a 75% yield.

Found: C, 80.23; H, 6.10. Calcd. for $C_{16}H_{14}O_2$: C, 80.07; H, 5.88%.

9-Anthraldehyde Tosylhydrazone (V).—Anthraldehyde (2 g.) was added to a solution of 2g. of *p*-toluenesulfonylhydrazine in ethanol by an adaptation of the method described by Depuy and Froemsdolf.[7] The reaction mixture was kept at 70—80°C for 3 hr. and then chilled to room temperature. The solid product was collected and crystallized from ethanol. Recrystallization from ethanol gave V as yellowish prisms, melting at 183—184°C, in a 75% yield.

Found: C, 70.59; H, 5.13; N, 7.55. Calcd. for $C_{22}H_{18}N_2O_2S$: C, 70.67; H, 4.81; N, 7.49%.

9, 10-Dihydroanthracene-9, 10-*cis*-dicarboxylic Chloride.[8]—Two grams of 9, 10-dihydroanthracene-9, 10-*cis*-dicarboxylic acid[9] in thionyl chloride was heated under a nitrogen atmosphere for 2 hr. The reaction mixture was concentrated to remove the thionyl chloride. The yellow crystals, with a melting point of 169—170°C, were obtained in a 80% yield.

Found: Cl, 23.2. Calcd. for $C_{16}H_{10}O_2Cl_2$: Cl, 22.9%.

Derivatives of 9, 10-Dihydro-9, 10-*cis*-di(phenylcarbamoyl)anthracene (VI_1—VI_7).—To a solution of 0.01 mol. (3.1 g.) of the dicarboxylic chloride in benzene was 0.05 mol. of the corresponding substituted aniline at room temperature. An immediate precipitate formed. The mixture was then stirred at room temperature. The crystalline solid was collected, washed with benzene and water, and dried in vacuo. The solid was recrystallized from ethanol. The melting points and analysis of the compounds VI_1—VI_7 are tabulated in Table I. The yields of the compounds were quantitative.

Spectra and Discussion

Absorption Spectra.—The absorption spectrum of compound I closely resembles that of 9, 10-dibenzylanthracene, as is shown in Fig. 1. The shapes of the absorption spectra of II_1, II_2 and II_3, in which the hydrogen atoms of the methylene

Table I. Derivatives of 9, 10-dihydro-9, 10-*cis*-di(phenylcarbamoyl)anthracene (VI_1—VI_7)

Sample No.	Substitute Y	M.p. °C	Molecular formula		Analysis, % C	H	N	Cl
VI_1	H	297—298	$C_{28}H_{22}N_2O_2$	Calcd.	80.36	5.30	6.98	
				Found	80.02	5.36	6.93	
VI_2	*p*-Cl	>360 (decomp.)	$C_{28}H_{20}Cl_2N_2O_2$	Calcd.	68.99	4.11	5.75	14.8
				Found	68.62	4.50	5.83	14.1
VI_3	*m*-OCH_3	283—284	$C_{30}H_{26}N_2O_4$	Calcd.	75.31	5.44	5.85	
				Found	74.98	5.91	5.99	
VI_4	*o*-OCH_3	303—304	$C_{30}H_{26}N_2O_4$	Calcd.	75.31	5.44	5.85	
				Found	75.74	5.52	6.23	
VI_5	*o*-CH_3	336—337	$C_{30}H_{26}N_2O_2$	Calcd.	81.44	5.88	6.27	
				Found	80.89	6.06	6.27	
VI_6	*p*-NO_2	>360 (decomp.)	$C_{28}H_{20}N_4O_6$	Calcd.	66.14	3.94	11.02	
				Found	66.04	3.77	10.81	
VI_7	*m*-NO_2	280—282	$C_{28}H_{20}N_4O_6$	Calcd.	66.14	3.94	11.02	
				Found	65.82	4.28	10.91	

7) C. H. Depuy and D. H. Froemsdolf, *J. Am. Chem. Soc.*, **82**, 634 (1960).
8) P. J. Mathien, *Ann. Chim.*, **20**, 215 (1945).
9) A. H. Beckett, R. G. Ligard and B. A. Mulley, *J. Chem. Soc.*, **1953**, 3328.

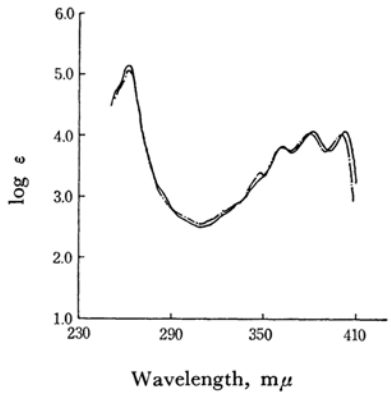


Fig. 1. Absorption spectra of 9, 10-bis(4-methoxybenzyl)anthracene (I): —— and 9, 10-dibenzylanthracene: —·— (in dioxane).

TABLE II. THE WAVELENGTHS AND MOLAR EXTINCTION COEFFICIENTS OF THE LONGEST-WAVELENGTH ABSORPTION MAXIMA OF COMPOUNDS I—IV_2 (IN DIOXANE)

Compound	Appearance	λ_{max} mμ	log ε
I	colorless	403	4.09
II_1	yellow	415	4.00
II_2	pale yellow	406	4.01
II_3	colorless	397	4.03
III_1	yellow	417	—a)
III_2	yellow red	428	—a)
IV_1	yellow	394	4.06
IV_2	yellow	393	3.98
9, 10-Dibenzylanthracene	colorless	400	4.03

a) The molar extinction coefficient could not be determined because of the low solubility.

groups of 9, 10-dibenzylanthracene are replaced by bromine, *o*-toluidino and acetoxy groups respectively, are also similar to that of 9, 10-dibenzylanthracene. The wavelengths and molar extinction coefficients of the longest-wavelength absorption maxima of II_1, II_2 and II_3 are shown in Table II. The spectra of III_1 and III_2 indicate some resemblance to that of the parent anthracene, except for the considerable red shift, although the molar extinction coefficients could not be determined because of the low solubilities in organic solvents. The spectra of IV_1 and IV_2 are very similar to that of 9, 10-dimethylanthracene.[10] The wavelengths and molar extinction coefficients of the longest-wavelength absorption maxima of IV_1 and IV_2 are shown in Table II. When the longest-wavelength absorption maximum of II_3 are compared with those of II_1, II_2 and 9, 10-dibenzylanthracene, it is obvious that the introduction of acetoxy groups shifts the absorption band toward a shorter wavelength. As the reason for this blue shift, two interpretations are possible. One is that the acetoxy groups withdraw the π electron in the anthracene ring, since we would expect that the introduction of an electron-attracting group such as an acetoxy group increases the energy difference between the highest occupied and lowest vacant orbitals of the molecule; the other is the deformation of conjugation by the steric hindrance between the acetoxy groups and the hydrogen atoms at the 1, 4, 5 and 8 positions of the anthracene nucleus. Probably, both the effects play important roles. The spectrum of V is given in Fig. 2. The spectra of VI_2 and VI_5 are shown in Fig. 3. The wavelengths and molar extinction coefficients of the longest-wavelength absorption maxima of compounds V—VI_7 are tabulated in Table III.

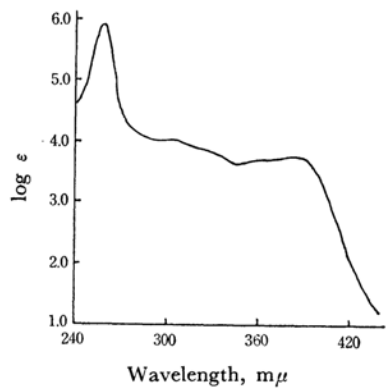


Fig. 2. Absorption spectrum of 9-anthraldehyde tosylhydrazone (V). (in dioxane)

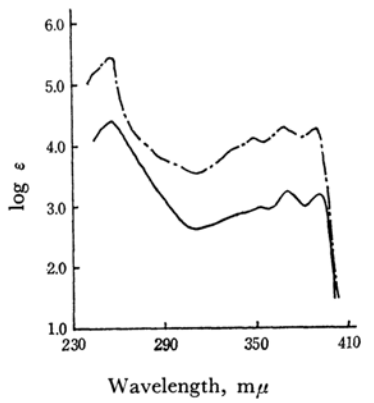


Fig. 3. Absorption spectra of 9, 10-dihydro-9, 10-*cis*-di(*p*-chlorophenylcarbamoyl)anthracene (VI_2): —— and 9, 10-dihydro-9, 10-*cis*-di(*o*-toylcarbamoyl)anthracene (VI_5): —·—. (in dioxane)

Within compounds VI_1—VI_7, the absorption intensities of VI_3, VI_4 and VI_5 are higher than those of the other compounds. It is apparent

10) H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley & Sons, New York (1962), p. 323.

Table III. The wavelengths and molar extinction coefficients of the longest-wavelength absorption maxima of compounds V—VI_7 (in dioxane)

Compound	Appearance	λ_{max} mμ	log ε
V	yellow	388	4.08
VI_1	colorless	392	—a)
VI_2	colorless	385	3.28
VI_3	colorless	393	4.22
VI_4	colorless	393	4.32
VI_5	colorless	390	4.08
VI_6	yellow	392	3.80
VI_7	yellow	390	3.81

a) The molar extinction coefficient could not be determined because of the low solubility.

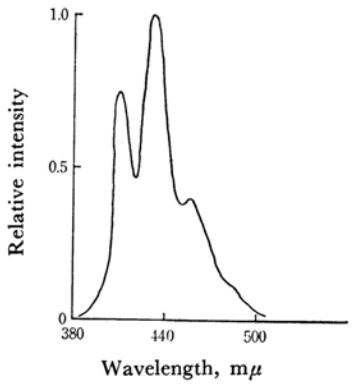


Fig. 4. Fluorescence spectrum of 9,10-bis(4-methoxybenzyl)anthracene (I). (2.5×10^{-5} mol./l. in dioxane)

Table IV. Fluorescence spectra (in dioxane)

Compound	Maxima of fluorescence spectra mμ	Relative intensity	Separation of nearest maxima of absorption and fluorescence mμ
I	411	0.75	8
	431	1.00	
	456	0.46	
II_3	405	0.77	8
	424	1.00	
	445	0.55	
IV_1	404	0.75	10
	424	1.00	
	448	0.53	
IV_2	405	0.63	12
	424	1.00	
	448	0.49	
V	(460)	(1.00)	—

that the methoxy or methyl groups increase the intensities of those compounds, because the methoxy or methyl groups exert electron-donating and conjugative effects on the anthracene nucleus.

Fluorescence Spectra. — The fluorescence spectrum of I are shown in Fig. 4. The shortest-wavelength fluorescence maxima and the difference in wavelength between the nearest maxima of the absorption and the fluorescence are given in Table IV.

The differences are 8—12 mμ, as is shown in Table IV. This may be ascribed to the fact that the conjugation of the molecules occurs more easily in the excited state than in the ground state, because the molecules are somewhat less strained in the excited state.

The fluorescence intensity of II_1 was very weak. This may be due to the effect of the heavy atoms of bromine in the molecule.[11] The fluorescence intensity of II_2 was also weak, as the substituents of the bulky *o*-toluidino groups prevent the conjugation between anthracene and benzene rings. The intensity of the fluorescence spectrum of II_3 was strong, because the acetoxy groups in the molecule should increase the intensity of the fluorescence in spite of the introduction of the bulky acetoxy groups.

The fluorescence intensities of III_1, III_2 and VI_1—VI_7 were also too weak to be observed.

The fluorescence spectrum of IV_2 is given in Fig. 5. The fluorescence spectrum of IV_1 closely resembles that of IV_2. The strongest fluorescence maximum of I is near the maximum sensitivity region of the widely-used photoelectron amplifier. In addition, the separation of the nearest maxima of the spectra of absorption and of fluorescence is sufficient. Therefore, there is a small probability of the reabsorption of photons, and a good scintillation property is predicted for it. This compound attains practical importance because of its high solubility in an alkylbenzene solution.

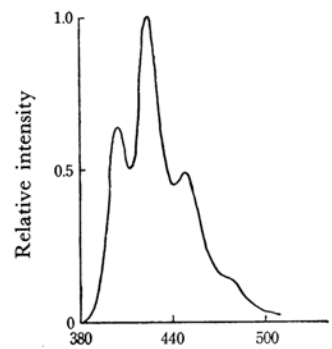


Fig. 5. Fluorescence spectrum of 9,10-anthracenedimethanol (IV_2). (2.3×10^{-5} mol./l. in dioxane)

The scintillation properties of II_3, IV_1 and IV_2 are also good in undergoing conformational changes in the excited states and in high solubilities in an alkylbenzene solution. In the case of V, the broad peak of fluorescence covers the maximum

11) J. Ferguson, *J. Mol. Spectroscopy*, **3**, 177 (1959).

sensitivity region of the phototube. The compound shows a greenish fluorescence in the crystals. Furthermore, it has a very good solubility in an alkylbenzene solution.

The authors are indebted to Professor Takahumi Osio and his coworkers for measuring the absorption and fluorescence spectra and the helpful discussion.