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Plastic Scintillators. II. The Synthesis of Some Distyrylbenzene Derivatives as Wavelength Shifters in Plastic Scintillators

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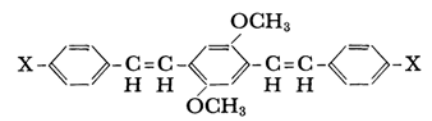
The synthesis and the absorption and fluorescence spectra of 2, 5-dimethoxy-1, 4-distyrylbenzene derivatives and the related compounds are reported on. Their absorption and their fluorescence spectra, are then discussed. According to the spectra, some of the compounds synthesized here are better wavelength shifters in plastic scintillators that the compounds described in the literature.

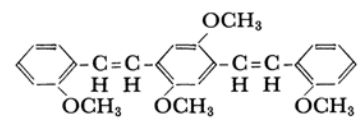
The use of some anthracene derivatives as efficient wavelength shifters in plastic scintillators were described in our previous paper.[1] In 1954, Pichat and Pesteil[2] showed that distyrylbenzene acts as a scintillation solute in plastic scintillators. Recently, Heller[3] suggested that substituted distyrylbenzenes would be highly efficient wavelength shifters in organic liquid scintillators. In the present paper, in order to increase the fluorescent intensity, the solubility in alkylbenzene solution, and the separation of the nearest maxima of the absorption and fluorescence spectra, two methoxy groups were introduced into the central benzene nucleus of the substituted distrylbenzenes. Ten derivatives of 2, 5-dimethoxy-1, 4-distyrylbenzene were synthesized by Wittig reaction.[4]

In order to ascertain the effect of substituents in the *meta* position on the absorption and fluorescence spectra, we also prepared some derivatives of *meta*-distyrylbenzene. The compounds synthesized here may be summarized as follows:



(I)

X=H(1), CH_3(2), OCH_3(3), NO_2(4), $N(CH_3)_2$(5), Cl(6), $CH(CH_3)_2$(7)



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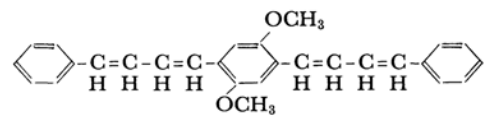

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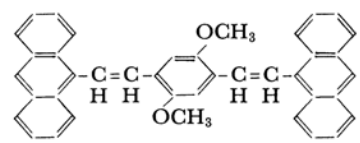

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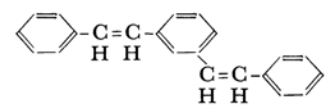

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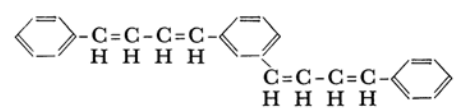
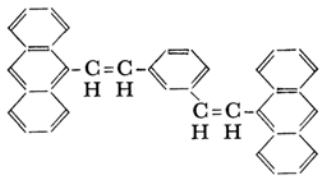


(VI)

1) Part I of this series: M. Imoto and T. Nakaya, This Bulletin, **36**, 785 (1963).
2) L. Pichat and P. Pesteil, French Pat. 1071794 (1954); *Chem. Abstr.*, **53**, 3904 (1959).
3) A. Heller, *J. Chem. Phys.*, **36**, 2858 (1962); **40**, 2839 (1964).
4) T. W. Campbell and R. W. McDonald, *J. Org. Chem.*, **24**, 1246 (1959).



(VII)

These compounds all have *trans*-forms with the exception of 1, 4-bis(*p*-dimethylaminostyryl)-2, 5-dimethoxybenzene; they have been little described in the literature, as far as we have been able to determine. Some of the compounds synthesized here have been proved by Osio and his co-workers[5] to be equal to the wavelength shifters reported in the literature.[6-7]

Experimental

1, 4-Dichloromethyl - 2, 5 - dimethoxybenzene. — Thirty-five grams of *p*-dimethoxybenzene was added at 0°C to a mixture of 230 ml. of a 37% formaldehyde solution and 600 ml. of concentrated hydrochloric acid. The temperature was kept below 35°C while the mixture was stirred for 4 hr. The solid was then collected, washed twice with water, and dried in vacuo. It was recrystallized from carbon tetrachloride to give 23 g. of 1, 4 - dichloromethyl - 2, 5 - dimethoxybenzene (43% yield), melting at 164—165°C.[8]

Found: C, 51.20; H, 5.36; Cl, 30.0. Calcd. for $C_8H_{10}Cl_2O_2$: C, 51.06; H, 5.11; Cl, 30.2%.

2, 5 - Dimethoxy - *p* - xylylene-bis(triphenylphosphonium chloride).—A solution of 2.3 g. of 1, 4-dichloromethyl-2, 5-dimethoxybenzene and 7.4 g. of triphenylphosphine in 350 ml. of dry xylene was refluxed at the boiling point of the solvent while being stirred for 11 hr. A crystalline solid began to separate after 10 min. The reaction products were collected, washed with dry xylene, and then dried in a vacuum desiccator at 10—20 mmHg and 60—70°C. Yield, 6.5 g. (85%); m. p. 271—275°C.

Found: Cl, 9.1. Calcd. for $C_{46}H_{42}O_2Cl_2P_2$: Cl, 9.4%.

The Derivatives of 2, 5-Dimethoxy-1, 4-distyrylbenzene (I_1—I_7).—To a solution of 0.01 mol. of the 2, 5 - dimethoxy - *p* - xylylene-bis(triphenylphosphonium chloride) and 0.028 mol. of the corresponding *p*-substituted benzaldehyde in 100 ml. of absolute ethanol, 150 ml. of a 0.3 M lithium ethoxide solution was added. After 10 hr., the excess ethanol was removed by distillation under reduced pressure. The crystalline solid which separated was collected and dried in vacuo. The solid was crystallized from cyclohexane. The *cis-trans*-mixture was changed to a *trans*-compound by refluxing it in cyclohexane which contained a trace of iodine. However, 1, 4-bis(*p*-dimethylaminostyryl)-2, 5-dimethoxybenzene (I_3) could not be isomerized, because of the formation of a complex between the compound and iodine in cyclohexane or benzene. The melting points, yields, and analysis of the compounds are shown in Table I.

1, 4 - Bis(*o* - methoxystyryl) - 2, 5 - dimethoxybenzene (II). — To a solution of 3.2 g. of 2, 5-dimethoxy-*p*-xylylene-bis(triphenylphosphonium chloride) and 2.0 g. of *o*-methoxybenzaldehyde in 100 ml. of absolute ethanol, 100 ml. of a 0.3 M lithium ethoxide solution was added. After a while, yellow crystals began to separate from the solution. After 15 hr., the yellow crystalline solid was collected and dried in vacuo. Recrystallization from cyclohexane containing a trace of iodine gave II with a m. p. of 178—179°C in a yield of 80%.

Found: C, 77.72; H, 6.82. Calcd. for $C_{26}H_{26}O_2$: C, 77.49; H, 6.44%.

1, 4 - Bis(4-phenylbutadienyl)-2, 5- dimethoxybenzene (III).—250 ml. of a 0.25 M lithium ethoxide solution was added to a solution of 5.5 g. of 2, 5-dimethoxy-*p*-xylylene-bis(triphenylphosphonium chloride) and 5 g. of cinnamaldehyde in 150 ml. of absolute ethanol. After a while, deep yellow crystals began to separate from the solution. The crystals were collected, washed with ethanol, and dried in vacuo. Recrystallization from benzene containing a trace of iodine gave III as a deep yellow powder with a m. p. of 229—231°C in a yield of 75%.

Found: C, 85.14; H, 6.68. Calcd. for $C_{28}H_{26}O_2$: C, 85.28; H, 6.60%.

1, 4-Bis (9-anthrylvinyl) - 2, 4 - dimethoxybenzene (IV).—To a solution of 6 g. of 2, 5-dimethoxy-*p*-xylylene-bis(triphenylphosphonium chloride) and 5.5 g. of 9-anthraldehyde in 380 ml. of absolute ethanol, 200 ml. of a 0.25 M lithium ethoxide solution was added. After a while, a deep yellow crystalline solid began to separate from the solution. After 10 hr., the mixture

TABLE I. DERIVATIVES OF 2, 5-DIMETHOXY-1, 4-DISTYRYLBENZENE

Compound	Substitute X	M.p. °C	Yield %	Molecular formula	Analysis, % Found	Calcd.
I_1	H	177—178	72	$C_{24}H_{22}O_2$	C: 84.11 H: 6.74	C: 84.21 H: 6.44
I_2	CH_3	176—178	70	$C_{26}H_{26}O_2$	C: 84.14 H: 7.40	C: 84.32 H: 7.03
I_3	OCH_3	209—210	73	$C_{26}H_{26}O_4$	C: 77.38 H: 6.82	C: 77.49 H: 6.47
I_4	NO_2	274—278	80	$C_{24}H_{20}N_2O_6$	C: 66.25 H: 4.98	C: 66.67 H: 4.63
					N: 6.51	N: 6.45
I_5	$N(CH_3)_2$	238—248	75	$C_{28}H_{32}N_2O_2$	C: 78.29 H: 7.55	C: 78.50 H: 7.45
					N: 6.49	N: 6.54
I_6	Cl	214—216	48	$C_{24}H_{20}Cl_2O_2$	C: 70.27 H: 5.35	C: 70.08 H: 4.87
I_7	$CH(CH_3)_2$	181—183	68	$C_{30}H_{34}O_2$	C: 84.14 H: 7.40	C: 84.32 H: 7.03

5) T. Osio, private communication.
6) R. C. Sangster and J. W. Irvine, *J. Chem. Phys.*, **24**, 670 (1956).
7) A. Heller and D. Katz, ibid., **35**, 1987 (1961).
8) S. E. Hunt and A. S. Lindseg, *J. Chem. Soc.*, **1962**, 4550.

was filtered, washed with ethanol, and dried in vacuo. The solid product was recrystallized several times from benzene in the presence of a trace of iodine to give IV as deep yellow prisms with a m. p. of 298—299°C in a yield of 78%.

Found: C, 88.11; H, 5.76. Calcd. for $C_{40}H_{30}O_2$: C, 88.56; H, 5.53%.

***m*-Xylylene-bis(triphenylphosphonium bromide).**—A solution of 25 g. of *m*-xylylene dibromide and 58 g. of triphenylphosphine in dry xylene was heated under reflux for 10 hr. After a while, white crystals began to separate from the solution. The solid product was collected, washed with dry xylene, and dried in a vacuum desiccator at 10 mmHg and 60°C for 15 hr. The white crystals, melting at 275—278°C were obtained The white crystals, melting at 275—278°C, were obtained in a yield of 83%.

Found: Br, 6.3. Calcd. for $C_{42}H_{34}Br_2P_2$: Br, 6.6%.

1, 3-Distyrylbenzene (V).—To a solution of 2.1 g. of *m*-xylylene-bis(triphenylphosphonium bromide) and 2.9 g. of benzaldehyde in 50 ml. of absolute ethanol, 50 ml. of a 0.2 M lithium ethoxide solution was added. After 15 hr., 110 ml. of water was added to the reaction mixture. The crystals then began to separate from the solution. The separated crystals were dried in vacuo and recrystallized from *n*-hexane in the presence of a trace of iodine to give V as white prisms, with a m. p. of 167—168°C and in a yield of 55%.

Found: C, 93.81; H, 6.18. Calcd. for $C_{22}H_{18}$: C, 93.62; H, 6.38%.

1, 3-Bis(4-phenylbutadienyl)benzene (VI).—To a solution of 2.0 g. of *m*-xylylene-bis(triphenylphosphonium bromide) and 2.9 g. of cinnamaldehyde in 50 ml. of absolute ethanol, 50 ml. of a 0.2 M lithium ethoxide solution was added. After 10 hr., a solid product was collected and recrystallized from benzene in the presence of a trace of iodine to give VI as white prisms, with a m. p. of 189—190°C and in a yield of 60%.

Found: C, 92.86; H, 6.73. Calcd. for $C_{26}H_{22}$: C, 93.41; H, 6.51%.

1, 3-Bis(9-anthrylvinyl)benzene (VII).—To a solution of 2.4 g. of *m*-xylylene-bis(triphenylphosphonium bromide) and 2.8 g. of anthraldehyde in 150 ml. of absolute ethanol, 100 ml. of a 0.2 M lithium ethoxide solution was added. After 8 hr., the yellow crystals were collected and recrystallized from benzene containing a trace of iodine to give VII, melting at 229—231°C, in a yield of 40%.

Found: C, 94.17; H, 5.59. Calcd. for $C_{38}H_{26}$: C, 94.60; H, 5.40%.

Spectra and Discussion

Absorption Spectra.—The absorption spectrum of 2, 5-dimethoxy-1, 4-distyrylbenzene (I_1) is given in Fig. 1. This compound exhibits, in the ultraviolet and visible region, three absorption maxima, at 233 mμ (ε=27900), 324 mμ (ε=33100) and 390 mμ (ε=48600).

The absorption spectra of the derivatives of 2, 5-dimethoxy-1, 4-distyrylbenzene (I_2—I_7), are similar in shape to that of I_1.

The wavelengths and molar extinction coefficients of the longest-wavelength absorption maxima of compounds I_1—IV and 1, 4-distyrylbenzene are summarized in Table II.

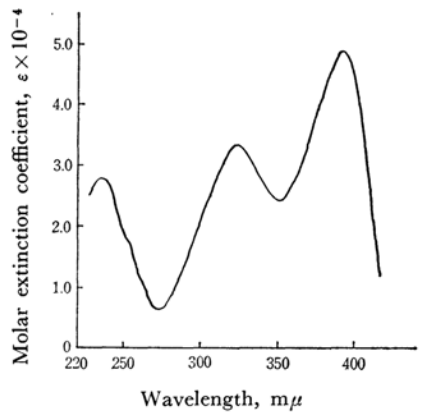
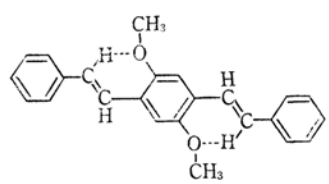


Fig. 1. The absorption spectrum of 2, 5-dimethoxy-1, 4-distyrylbenzene (I_1). (in dioxane)

Table II. The wavelengths and molar extinction coefficients of the longest-wavelength absorption maxima of 2, 5-dimethoxy-1, 4-distyrylbenzene and the related compounds (I_1—IV) (in dioxane)

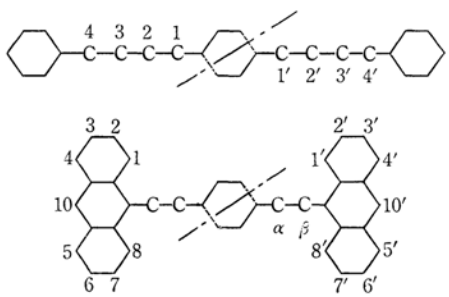
Compound	Color	λ_{max}, mμ	$\varepsilon\times10^{-4}$
I_1	yellow	390	4.86
I_2	yellow	392	3.70
I_3	yellow	396	3.60
I_4	pink yellow	431	3.51
I_5	pink yellow	420	4.20
I_6	deep yellow	395	4.62
I_7	yellow	390	6.45
II	yellow	396	4.49
III	deep yellow	419	3.21
IV	deep yellow	413	4.36
1, 4-Distyryl-benzene[3]	colorless	357	5.70

The absorption maximum of 2, 5-dimethoxy-1, 4-distyrylbenzene shifts toward a longer wavelength than that of 1, 4-distyrylbenzene, as is shown in Table II. As the cause of this red shift, the full participation of lone pair electrons on the oxygen atoms of the methoxy groups in the π electron system of the benzene rings may be considered. Furthermore, this red shift may be due to the effect of hydrogen bonds between the oxygen atoms of the methoxy groups and the hydrogen atoms on the near β-carbon atoms:



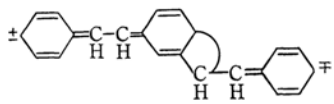
The maximum wavelength of compound III shifted to a wavelength longer than that of compound IV. The longest-wavelength bands of III and IV may be both associated with the *p*-band.

According to a method developed by Dewar,[9] if the methoxy groups are disregarded, the π electron systems of III and IV can be considered to be formed by joining up two odd-AH radicals as follows:



The magnitude of the splitting of the NBMO's of the two odd-AH radicals corresponds to the energy of the *p*-band. The splitting values for III and IV were 16/19 and 16/22, in units of β-(resonance integral), respectively. From the results of the calculation, the longest-wavelength band of III is expected to be at a shorter wavelength than that of IV.

However, the calculated values seem to be inconsistent with the experimental finding that the longest-wavelength band of III is observed in a longer-wavelength region than that of IV. Regarding the cause of this phenomenon, it may be considered that IV has a less planar structure than III, because of the repulsive forces of steric hindrance between the hydrogen atoms on the β-carbon atoms and the hydrogen atoms at the 1, 1′, 8 and 8′ positions of the terminal anthracene rings. The longest-wavelength absorption maxima and the molar extinction coefficients of compounds V—VII and *trans*- and *cis*-stilbene are shown in Table III. In the case of *meta*-substituted compounds, the conjugation between two terminal substituents is unimportant because it involves a structure with long, or ineffective, bonds, as in the following figure:



For example, 1, 3-distyrylbenzene and *trans*-stilbene absorbed at nearly the same wavelength, as is shown in Table III.

Fluorescence Spectra. — The fluorescence spectra of compounds I_1 and I_7 are shown in Figs. 2 and 3. The fluorescence spectra of the other compounds of the I series are similar in shape to those of I_1 and I_7. The shortest-wavelength fluorescence maxima and the difference in wavelength between the nearest maxima of fluorescence

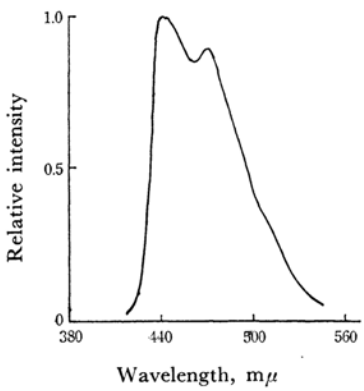


Fig. 2. Fluorescence spectrum of 2,5-dimethoxy-1,4-distyrylbenzene (I_1). (1.0×10^{-5} mol./l. in dioxane)

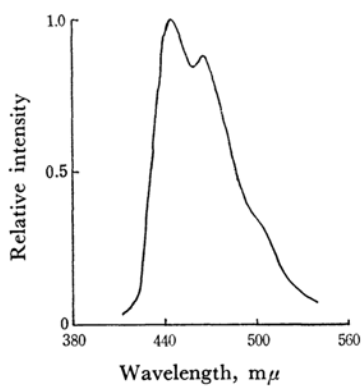


Fig. 3. Fluorescence spectrum of 1,4-bis(*p*-isopropylstyryl)-2,5-dimethoxybenzene (I_7). (1.1×10^{-5} mol./l. in dioxane)

TABLE III. THE WAVELENGTHS AND MOLAR EXTINCTION COEFFICIENT OF THE ABSORPTION MAXIMA OF THE COMPOUNDS (V—VII)

Compound	Color	λ_{max} mμ	$\varepsilon\times10^{-4}$	Solvent
V	colorless	325	2.33	dioxane
VI	colorless	356	4.53	dioxane
VII	yellow	390	2.46	dioxane
trans-Stilbene[α]	colorless	320.5	1.60	heptane
cis-Stilbene[β]	colorless	280	1.05	ethanol

α: H. Suzuki, This Bulletin, **33**, 381 (1960).
β: R. N. Beale and E. M. F. Roe, *J. Chem. Soc.*, **1953**, 2755.

9) M. J. S. Dewar, *J. Chem. Soc.*, **1950**, 329; **1952**, 3529.

Table IV. The shortest-wavelength fluorescence maxima and difference in nearest maxima of spectra between fluorescence and absorption (in dioxane)

Compound	Shortest-wavelength fluorescence maximum mμ	Difference in nearest maxima between fluorescence and absorption mμ
I_1	440	50
I_2	445	53
I_3	460	64
I_4	(525)	—
I_5	477	57
I_6	442	47
I_7	444	49
II	439	43
III	(444)	—
IV	466	53
V	370	45
VI	395	39
VII	478	88
Distyrylbenzene[3]	394	37

and the absorption of the compounds synthesized here are tabulated in Table IV.

The separation of the maxima of absorption and fluorescence spectra for I_1 is larger than that of 1, 4-distyrylbenzene. Since it is desirable that there be little probability of the reabsorption of the photons emitted, the separation of the maxima of absorption and fluorescence is required. This requirement is fully satisfied in I_1 and in the other compounds synthesized here, as is seen in Table IV. The compounds are of practical use because of their high solubilities. Furthermore, the derivatives of 2, 5-dimethoxy-*p*-distyrylbenzene are better wavelength shifters in plastic scintillators, because the strongest-fluorescence maxima of these compounds match the most sensitive region of a phototube. Except for VII, the difference in wavelength between the nearest maxima of fluorescence and the absorption of the derivatives of *meta*-distyrylbenzene is nearly equal to those in *para*-distyrylbenzene derivatives.[3]

The authors wish to express their hearty thanks to Professor Takahumi Osio and his co-workers for their helpful advice.