Organic Liquid Scintillators. VI. Substituted Distyrylbenzenes: Scintillation Properties and Spectra of Absorption and Fluorescence

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Citation: The Journal of Chemical Physics **40**, 2839 (1964); doi: 10.1063/1.1724914 View online: http://dx.doi.org/10.1063/1.1724914 View Table of Contents: http://aip.scitation.org/toc/jcp/40/10 Published by the American Institute of Physics



given by sums of terms like (A16) and (A17) with p=0, q=kll'.

Most of the determinants and cofactors which appear are zero. They can be treated efficiently when it is noted that

$$(\Delta^{0,kll'})_{t,u} = (\lambda)_{t,u} (\mathbf{d}^{0,kll'})_{t,u}, \qquad (A21)$$

where λ is the overlap matrix for the orbitals φ_k and is independent of k, l, and l' while $\sigma^{0,kll'}$ is the overlap matrix for the spin functions and has only 0 and 1 as possible elements.

The nonzero coefficients in the components of interest are given in Tables V and VI. It should be noted that the expansion coefficients $\gamma_{s,0}^{\kappa}(t \mid v)$ and $\gamma^{\sigma}_{s,0}(tu \mid vw)$ are not the same as the matrix elements $\langle \varphi_t | \gamma^{\kappa}_{s,0} | \varphi_v \rangle$ and $\langle \varphi_t \varphi_u | \gamma^{\sigma}_{s,0} | \varphi_v \varphi_w \rangle$ because of the nonorthogonality of the basis. The normalization integral is given in (23).

In the tables, i and j have the significance mentioned previously and $\bar{\imath}=i+\mu$. The further convention i'>iis assumed. The summations for (A19) are to be taken over all the indices which appear with the ranges $1 \le i < i' \le \nu$, $1 \le j \le 2m$. The second-order components involve, in addition to A_k and $A_k(i)$,

$$A_{k}(i, i') = \sum_{i \neq i, i'}^{\binom{r-2}{k}} \prod_{i \neq i, i'}^{k} \{d_{i}^{2}\}$$
(A22)

defined on the set of $\nu - 2$ is excluding i and i'. Equations (A13) give the expansion coefficients for the projected state density matrix and these are readily converted to the matrix elements given in Table IV.

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 40, NUMBER 10

15 MAY 1964

Organic Liquid Scintillators. VI. Substituted Distyrylbenzenes: Scintillation Properties and Spectra of Absorption and Fluorescence

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The preparation, spectra of absorption and fluorescence, and the scintillation properties of 28 derivatives of trans, trans-p-distyrylbenzene are described.

Most of the soluble derivatives are efficient primary scintillators in alkylbenzene solutions and are highly efficient secondary scintillators in alkylbenzene solution of p-terphenyl. Solutions with efficiencies exceeding those of the best-reported liquid scintillation systems are described.

INTRODUCTION

DECENT computations by the LCAO–MO method **K** and observations on the structure of *trans*, *trans-p*distyrylbenzene indicated that the compound should be a fairly efficient liquid scintillation solute.¹

Distyrylbenzene was first prepared in 1917 by Kaufmann.² The compound is only slightly soluble in the solvents which are used in liquid scintillation counting (i.e., benzene, toluene, xylene, dioxane). In a study of fluorescent compounds, Pichat, Pesteil, and Clément suggested in 1954 the use of distyrylbenzene as a scintillation solute in plastic scintillators,^{3,4} but the compound did not attain practical importance because of its low solubility.

Several syntheses and derivatives of distyrylbenzene have been reported. Campbell and McDonald⁵ synthesized by the Wittig reaction of p-xylene-bis-triphenylphosphonium chloride and the corresponding aldehydes the 3,3'-diamino; 3,3'-dinitro; 4,4'-dimethyl; 4,4'dimethoxy; 4,4'-diamino; 4,4'-dinitro; 4,4'-diacetylamino; 4,4'-dichloro and 4,4'-dicarbomethoxy derivatives (Fig. 1).

Drefahl and Plötner⁶ prepared the 4-monomethyl and 4,4'-dimethyl derivatives via the Grignard reaction of the corresponding 4-stilbenaldehydes and benzylmagnesium chlorides. Schmitt and collaborators7.8 reacted two molecules of phenylacetylchloride under Friedel-Crafts conditions and obtained, on the addition of toluene or anisole to the reaction mixture diketones, which, on successive reduction and dehydration by

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⁷ J. Schmitt, P. Conroy, J. Boitard, and M. Suquet, Bull. Soc.

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aluminum isopropoxide, yielded 4-methyl and 4methoxydistyrylbenzene correspondingly. Ruggli and Wolff⁹ condensed 4-cvano-2-nitrotoluene and 2,4dinitrotoluene with terephthalaldehyde, to obtain the 4,4'-dicyano-2,2'-dinitro and the 2,2',4,4'-tetranitro derivatives. Other compounds carrying substituents in the α and β positions have been reported. In the above reactions, the yields are generally better than those obtained by the reaction of benzylmagnesium chloride with terephthalaldehyde and the dehydration of the resulting diol.

The theory which led to the re-examination of the scintillation properties of the distyrylbenzenes indicated that the 4-monomethyl, 4,4'-dimethyl, 4-methoxy, 4,4'-dimethoxy, and 4,4'-dichloro derivatives migh the efficient liquid scintillators, but examination of their solubilities showed that the compounds are unsuitable for most practical purposes because of their limited solubility. The other compounds which have been mentioned are not expected to be good scintillation solutes either because of the change in the π -electron system or because of the quenching properties of the substituents. Thus, it seemed desirable to prepare soluble derivatives with the desired electronic properties and structure.

METHOD OF PREPARATION

The method of Campbell and McDonald⁵ was used to prepare most of the distyrylbenzenes. This method was preferred to the other ones because of the commercial availability of the starting materials and because of the simplicity of the procedure, which consists of mixing an alcoholic solution of p-xylenebis-(triphenylphosphonium chloride) (obtained by refluxing triphenylphosphine and p-xylenedichloride in dimethylformamide¹⁰) with an aldehyde, followed by the addition of a solution of lithium ethoxide in alcohol. Under these conditions, a mixture of the three geometrical isomers separates within a few minutes. The desired trans, trans-isomer is obtained readily by refluxing the mixture of the isomers in an inert hydrocarbon (aliphatic or aromatic) with a trace of iodine.

An effort was made to improve the yields obtained by the Grignard reaction between substituted benzylmagnesium chlorides and terephthalaldehyde. Although various solvents (diethyl ether, tetrahydrofuran, dipropylether, benzene), and various organometallic compounds (magnesium, lithium, and cadmium derivatives) were tried, the temperatures of the reaction being varied within a wide range, the yields, after the dehydration of the diols (by refluxing these with iodine in xylene),¹¹ remained below 20%. Unexpectedly, small amounts of substituted benzaldehydes were obtained from the reaction mixtures.

Schmitt's method^{7,8} of reacting phenylacetylchloride with itself and later with an aromatic hydrocarbon or ether has been found to yield mixtures of ketones which were not easily separable. The yields of the desired diketones were severely decreased in the purification processes.

Condensations of *p*-phenylenediacetic acid with aromatic aldehydes under the conditions of either the Perkin reaction or those of the Dobbner-Miller reaction yielded the expected dicarboxylic acids in yields between 20%-35%, but the over-all yields were decreased in the decarboxylation by copper chromite in quinoline and in the isomerization by iodine.^{12,13}

SPECTRA OF ABSORPTION AND FLUORESCENCE

The maxima of the spectra of absorption and fluorescence of the distyrylbenzenes are summarized in Table I. Most of the spectra of the various compounds are similar in shape. The spectra of absorption consist of two strong bands at 350-370 m μ (ϵ =4.5-7.7×10⁴) and at 240-255 mµ (ϵ =1.2-1.5×10⁴ mµ). Substitution at the 2, 2', 6, and 6' positions, which interferes with the planarity of the compounds, tends to decrease the absorbance at the longer wavelengths. Introduction of alkyl, alkoxy, or chlorine groups in the 4 and 4' positions produces the expected bathochromic shifts in the spectra, while substitution in Positions 3 and 3' (or 5 and 5') does not influence strongly the wavelengths of absorption, as might be expected from elementary perturbation theory.^{14,15} Substitution by a methoxy group in the sterically interfering positions 2 or 2' (or 6 and 6') produces a shift to the longer wavelength, although substitution in the same positions by the more bulky methyl or chlorine groups decreases the planarity sufficiently to cause a hypsochromic shift in the spectra of absorption. When the molecules are substituted by methoxy groups, both at the 2 and 2' and at the 3 and 3' positions, the groups at Position 2 cannot assume their position of minimum interference by being pointed away from the centers of the molecules, and a hypsochromic shift, relative to the 2,2'-disubstituted compound, is observed. No similar shift is observed in the 2,2',4,4'-tetramethoxy derivative in which the spectrum is shifted strongly to longer wavelengths.

An extension of the aromatic system on the α carbon atoms shifts the spectra to the longer wavelengths. Although naphthyl groups attached in Position 1 are expected to produce a stronger shift than those attached in Position 2,15 the effects are inverted because



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		Spectr of absor in diox	rum ption cane	Spec of fluor in di	Separation of nearest maxima of absorption and fluores- cence in wavenumbers	
Compound	Formula	$\lambda_{max}(m\mu)$	e•10-4	Relative $\lambda_{max}(m\mu)$ intensity		
Distyrylbenzene	CH=CH CH=CH	232.5 245.5 251 357	2.71 1.98 1.69 5.70	394 414 (435)	0.92 1.00 (0.68)	2.63×10 ³
2,2'-Dimethyldistyrylben- zene	CH=CH CH=CH CH=CH CH3	244 (280) 350	1.50 2.20 5.20	395 420 (440)	0.99 1.00 (0.70)	3.25×10 ⁸
3,3'-Dimethyldistyrylben- zene	CH=CH CH3 CH=CH	242 (250) (280) 357	1.41 1.35 1.25 6.75	394 414 (435)	0.93 1.00 (0.71)	2.63×10³
4,4'-Dimethyldistyrylben- zene	CH ₃ CH=CHCHCHCH3CH ₃ CH=CH	359	5.80	397 414 (440)	0.91 1.00 (0.63)	2.67×10 ³
2, 2', 5, 5'-Tetramethyl- distyrylbenzene	CH ₃ CH ₃ CH=CH CH ₃ CH=CH CH ₃ CH=CH	246 358	2.30 5.30	405 427 (456)	0.96 1.00 (0.71)	3.24×10 ³
3,3',4,4'-Tetramethyl- distyrylbenzene	CH ₃ CH=CH CH=CH CH ₃ CH ₃	236 246 252 363	2.25 1.86 1.66 5.70	401 431 (445)	0.92 1.00 (0.66)	2.61×10 ^s
4,4'-Di-isopropyldistyryl- benzene	CH ₃ CH ₂ CH=CH CH ₃ CH=CH CH ₃ CH=CH CH ₃ CH=CH	247 362	2.10 7.35	400 420 (445)	0.91 1.00 (0.70)	2.62×10 ^s

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	TABLE I (Continued)					······
		Spect of absor in dio	rum ption xane	Spectrum of fluorescence in dioxane		Separation of nearest maxima of absorption
Compound	Formula	$\lambda_{\max}(m\mu)$	e•10-4	$\lambda_{max}(m\mu)$	Relative intensity	cence in wavenumbers
4,4'-Diphenyldistyrylben- zene	CH=CH CH=CH	360 376	• • • • #	419 444 (470)	1.00 0.95 0.42	2.73×10
1,4-bis-(1-Naphthyl- vinyl)benzene	CH=CH CH=CH	245 371	4.50 5.75	430° 449° (476)°	0.97 1.00 (0.64)	3.70×10³
1,4-bis-(2-Naphthyl- vinyl)benzene	CH=CHCHCHCH	242 373	7.00 ^b 4.00 ^b	414 435 (455)	0.95 1.00 (0.68)	2.66×10 ⁸
1,4-bis-(9-Anthrylvinyl)- benzene	CH=CH CH=CH	259 404	• • • 8 • • • 8	470°	•••	3.5×10³
2,2'-Dimethoxydistyryl- benzene	OCH3 CH=CH CH=CH CH4O	246 366	2.30 5.75	410 430 (462)	0.93 1.00 (0.66)	2.93×10 ⁸
4,4'-Dimethoxydistyryl- benzene	CH30 CH=CH CH=CH OCH3	358	7.30	405 428 (453)	0.96 1.00 (0.57)	3.24×10 ³
2,2',3,3'-Tetramethoxy- distyrylbenzene	CH ₃ O OCH ₃ CH ₃ O OCH ₃ CH=CH CH=CH	255 360	1.80 5.90	400 430 (441)	0.93 1.00 (0.69)	2.78×10 ³

					Spectrum of fluorescence in dioxane		
Compound	Formula	$\lambda_{\max}(m\mu)$	e•10 ⁻⁴	$\lambda_{max}(m\mu)$	Relative intensity	ence in wavenumbers	
3,3',4,4'-Tetramethoxy- distyrylbenzene	CH ₃ O CH ₃ O CH=CH CH=CH CH=CH OCH ₃	246 374	2.40 5.30	417 436 (460)	0.96 1.00 (0.62)	2.80×10 ³	
2,2',4,4'-Tetramethoxy- distyrylbenzene	CH ₃ O CH=CH CH=CH OCH ₃ OCH ₃	242 375	5.00 5.60	416 435 (458)	0.93 1.00 (0.54)	2.63×10 ³	
1,4-bis-(3,4-Methylene- dioxystyryl)benzene	CH ₂ —0 CH ₂ =CH CH=CH O CH ₂ CH ₂	246 373	1.90 7.10	414 434 (456)	0.90 1.00 (0.66)	2.66×10³	
4,4'-Diethoxy-3,3'-Di- methoxydistyrylbenzene	CH ₃ O C ₂ H ₆ O CH=CH CH=CH OCC ₂ H ₆	244 375	3.00 6.50	413 436 (457)	0.97 1.00 (0.60)	2.46×10 ³	
3,3',4,4',5,5'-Hexa- methoxydistyrylbenzene	CH ₃ O CH ₃ O CH ₃ O CH=CH CH=CH OCH ₃ OCH ₃	255 280 369	1.45 1.50 4.70	(420) 434 (458)	0.91 1.00 (0.74)	3.30×10³	
2,2'-Dichlorodistyryl- benzene	CH=CH CI	244 (280) 353	1.70 1.65 5.50	395 420 (440)	0.96 1.00 (0.65)	3.01×10 ³	
3,3'-Dichlorodistyrylben- zene	CI CH=CH CH=CH CI	242 356	3.60 5.60	394 411 (445)	0.89 1.00 (0.65)	2.71×10³	

TABLE I (Continued)

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	TABLE I (Continued)					
		Spectr of absor in diox	Spec of fluor in di	Separation of nearest maxima of absorption		
Compound	Formula	$\lambda_{\max}(m\mu)$	e•10 ⁴	$\lambda_{\max}(m\mu)$	Relative intensity	cence in wavenumbers
4,4'-Dichlorodistyrylben- zene	CI CH-CH CH-CH	243 361	2.10 7.70	398 419 (440)	0.96 1.00 (0.68)	2.58×10 ³
2, 2', 4, 4'-Tetrachloro- distyrylbenzene		245 280 358	1.40 1.40 4.60	406 428 (445)	0.93 1.00 (0.50)	3.30×10³
2, 2', 6, 6'-Tetrachloro- distyrylbenzene	CI CI CI CI	242 330	1.43 4.00	404° 421°	1.00 0.99	5.55×10³
3,3',4,4'-Tetrachloro- distyrylbenzene	CI CI CH=CH CH=CH CI CI	242 278 362	4.10 1.70 7.35	400 420 (440)	0.85 1.00 (0.58)	2.62×10³
1,4-bis-(2-Vinylpyridyl)- benzene	CH=CH-CH=CH-	244 356	1.20 6.35	395 413 (430)	0.88 1.00 (0.59)	2.76×10 ³
1,4-bis-(3-Vinylpyridyl)- benzene	N — СН=СН - СН=СН - К	243 353	0.91 2.26	390 408 (430)	0.93 1.00 (0.73)	2.69×10 ³
1,4-bis-(2-Vinylthienyl)- benzene		253 347	4.50 5.20	• • • 6		
4,4'-Dimethylamino- distyrylbenzene	CH ₃ CH ₃ CH ₃ CH=CH CH=CH CH=CH CH ₃	255 261 398	14.7 12.0 5.2	458 463	1.00 1.00	3.30×10 ³

^a The absorbance could not be determined because of the low solubility of the compound. ^b The values are only approximate because of the low solubility of the compound. ^c Very weakly fluorescent.

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Compound	Approxima solubilities 30°C (g/lite	at at er)	Solvent	Concen- tration (g/liter)	Relative pulse height (anthracene crystal= 100)	Solvent	Concen- tration (g/liter)	Relative pulse height (anthracene crystal = 100)
2,2'-dimethyldistyryl- benzene	Toluene Xylene Dioxane	4 ⁴ 3 ⁵	Toluene Toluene Toluene Toluene	2.0 2.6 3.2 4.0	56 56 56 53	Dioxane+10% naphthalene	5	46
2, 2', 5, 5'-tetramethyl- distyrylbenzene	Xylene 3	3.5	Xylene Xylene Xylene	2.2 2.5 2.8	59 61 58			
4,4'-di-isopropyldistyryl- benzene	Toluene Xylene Dioxane	2.5 2.5 1	Toluene Xylene	2.2 2.2	68 66			
2, 2'-dimethoxydistyryl- benzene	Xylene Toluene Dioxane	2 3 3	Toluene Toluene	2 3	57 66	Dioxane+10% naphthalene	3	51
2, 2', 3, 3'-tetramethoxy- distyrylbenzene	Xylene 2 Dioxane 10	20	Xylene Dioxane Dioxane Dioxane Dioxane Dioxane	2 2 4 6 8 10	62 10 16 18 20 20	Dioxane+10% naphthalene Dioxane+ 3%H ₂ O Dioxane+ 6% Dioxane+ 9% Dioxane+12%	2 4 10 10 10 10 10	44 43 46 42 38 31 25
3,3',4,4',5,5'-hexamethoxy-	Toluene Xylene	1.5 1	Toluene	1.5	57	Dioxane+15% Dioxane+10%	10 3	17 34
2, 2'-dichlorodistyryl- benzene	Toluene Xylene Dioxane	3 2 3	Toluene	3	57	Dioxane+10% naphthalene	3	34
3,3'-dichlorodistyryl- benzene	Toluene Xylene Dioxane	4 3 3	Toluene	4	61	Dioxane+10% naphthalene	1 2	42 42
2, 2', 4, 4'-tetrachlorodis- tyrylbenzene	Xylene Dioxane	0.5 3				Dioxane+10% naphthalene	3	44
3,3',4,4'-tetrachlorodis- tyrylbenzene	Toluene Xylene Dioxane	2 1.5 3	Toluene	2	60	Dioxane+10% naphthalene	3	44

TABLE II. Scintillation efficiencies of solutions of soluble substituted 1,4-trans,trans-distyrylbenzenes.

of the increased steric hindrance in the one-substituted compounds.

Introduction of nitrogen or sulfur atoms in the terminal rings shifts the spectra of absorption to shorter wavelengths.

Substituents in positions 3,3',4, and 4' influence the spectra of fluorescence to a similar extent to their influence on the spectra of absorption, with the exceptions of 4,4'-dimethoxy and 3,3',4,4',5,5'-hexamethoxydistyrylbenzene in which the shifts in the spectra of fluorescence are larger than in the spectra of absorption. In these molecules, the separation between the nearest maxima of absorption and fluorescence increases.

Since it might be assumed that the molecules in their excited states (from which they can reach geometrically different configurations) will be somewhat closer to linear than in the ground (*trans*, *trans*) state, and since the fluorescence photons are emitted by the sterically rearranged molecules (the molecules rearrange in a few vibrations, or 10⁻¹³ sec, while the lifetime of the excited states is about 10^{-9} sec), the difference in the spectra of absorption and fluorescence can be attributed to the difference in the structures of the molecules in the ground and in the excited states.^{1,16} In sterically hindered molecules, the hindrance will be decreased when the molecules assume a more linear structure. Thus, an increased shift in the spectra of fluorescence of the sterically hindered molecules might be expected, producing an increase in the separation of the nearest maxima of absorption and fluorescence. Such an effect has, indeed, been observed: while the separation in the unhindered compounds in which the terminal phenyl groups are free to rotate, is about 2.6×10^3 cm⁻¹ (7.3 kcal/mole) the separation increases in the most strongly hindered compound, 2,2',6,6'-tetrachlorodistyrylbenzene to 5.5×10^3 cm⁻¹ (15.4 kcal/mole). Substitu-¹⁶ A. Heller, J. Chem. Phys. 35, 1980 (1961).

Compound	Approxin solubilities (g/lite	nate at 30°C er)	Solvent	Concentrztion (g/liter)	Relative pulse height (anthracene crystal=100)
POPOP	Xylene Toluene	0.8 0.9	Xylene Toluene	$0.100 \\ 0.100$	76.5 76.5
Distyrylbenzene	Xylene Dioxane	0.15 0.2	Xylene Toluene	0.050 0.100	77 78
2,2'-dimethyldistyrylbenzene	Toluene Xylene Dioxane	4 3 5	Toluene	0.050 0.100 0.150 0.200 0.250	76 75 72 77 74
3,3'-dimethyldistyrylbenzene	Xylene Dioxane	1.5 1.5	Toluene	0.050 0.100 0.150 0.200	77 70 67 71
4,4'-dimethyldistyrylbenzene	Xylene	0.5	Toluene	0.150 0.200	78 78
2,2',5,5'-tetramethyldistyrylbenzene	Xylene	3.5	Xylene	0.100 0.150 0.180 0.200 0.250	69 74 79 77 73
4,4'-di-isopropyldistyrylbenzene	Xylene Dioxane	2.5 1.0	Xylene	0.200	81
			Toluene Toluene Toluene	0.050 0.100 0.150	75 73 73
2,2'-dimethoxydistyrylbenzene	Xylene Dioxane	2 3	Xylene	$\begin{array}{c} 0.025\\ 0.050\\ 0.075\\ 0.100\\ 0.125\\ 0.150\\ 0.175\\ 0.185\\ 0.200\\ 0.225\\ 0.250\\ \end{array}$	74 78 78 77 77 76 75 79 78 75
2,2',3,3'-tetramethoxydistyrylbenzene	Xylene Dioxane	2 10	Xylene	$\begin{array}{c} 0.50 \\ 0.75 \\ 0.100 \\ 0.150 \\ 0.200 \\ 0.250 \\ 0.300 \end{array}$	77 73 76 78 77 75 69
3,3',4,4',5,5'-hexamethoxydistyrlybenzene	Xylene Dioxane Toluene	1 4 1.5	Toluene	$\begin{array}{c} 0.050 \\ 0.025 \\ 0.100 \\ 0.150 \\ 0.200 \\ 0.250 \end{array}$	74 65 71 70 72 73
2,2'-dichlorodistyrylbenzene	Toluene Xylene Dioxane	3 2 3	Toluene	0.100 0.150 0.200	60 65 55
3,3'-dichlorodistyrylbenzene	Toluene Xylene Dioxane	4 3 3	Toluene	0.100 0.150 0.200	74 72 72
4,4'-dichlorodistyrylbenzene	Xylene Dioxane	<0.1 <0.1	Toluene	0.04	75

TABLE III. Scintillation efficiencies of 4 g/liter solutions of p-terphenyl in toluene and xylene containing substituted 1,4-trans,trans-distyrylbenzenes and related compounds.

Compound	Approxim solubilities a (g/liter	ate it 30°C :)	Solvent	Concentration (g/liter)	Relative pulse height (anthracene crystal=100)
2,2',4,4'-tetrachlorodistyrylbenzene	Xylene Dioxane	0.5 3	Toluene	0.100 0.150 0.200	61 65 65
3,3',4,4'-tetrachlorodistyrylbenzene	Toluene Xylene Dioxane	$ \begin{array}{c} 2 \\ 1.5 \\ 3 \end{array} $	Toluene	$\begin{array}{c} 0.100 \\ 0.150 \\ 0.200 \\ 0.250 \end{array}$	73 76 79 73
2, 2', 6, 6'-tetrachlorodistyrylbenzene	Xylene Dioxane	2 2	Toluene	0.100	0
1,4-bis-(2-vinylpyridyl)benzene	Xylene Dioxane	0.5 1.5	Toluene	0.100 0.150 0.200	40 39 36
1,4-bis-(3-vinylpyridyl)benzene	Xylene Dioxane	2 1	Toluene	0.100 0.150 0.200	65 65 65

TABLE III (Continued)

tion by two methyl groups in Positions 2 and 2' increases the separation to 3.25×10^3 cm⁻¹ (9.1 kcal/mole) and that by two chlorine atoms in the same positions to 3.1×10^3 cm⁻¹ (8.7 kcal/mole). Sterically interfering condensed aromatic rings, like those of the 1-naphthyl or of the 9-anthryl derivatives increase the separation from 2.66×10^3 cm⁻¹ (7.5 kcal/mole) for the 2-naphthyl derivatives (or from 2.63×10^3 cm⁻¹, 7.4 kcal/mole, of distyrylbenzene itself) to 3.7×10^3 cm⁻¹ (10.4 kcal/mole) in the 1-naphthyl derivative or 3.5×10^3 cm⁻¹ (9.8 kcal/mole) in the 9-anthryl derivative.

The 2-methoxy-substituted distyrylbenzenes present an interestingly different case; here, the molecules are not strongly hindered and the oxygen atoms are bonded to the hydrogen atoms on the near β -carbon atoms (Fig. 2). Due to the hydrogen bond, there are no repulsive forces of steric hindrance in these molecules, wherefore, they do not tend to assume more linear structures in the excited states and no increase in the separation of the nearest maxima of absorption and fluorescence is produced.

Severe deformation of the planar structure of the molecules decreases the efficiency of fluorescence. 1,4-bis-(1-naphthylvinyl)benzene, 1,4-bis-(9-anthrylvinyl)benzene and 2,2',6,6'-tetrachlorodistyrylbenzene have only a hardly observable fluorescence. Introduction of sulfur atoms in the aromatic rings, as in the case of 1,4-bis-(2-thienyl)benzene, makes the compound nonfluorescent.

RADIATIVE LIFETIMES

The radiative lifetimes of 4,4'-di-isopropyldistyrylbenzene and of 2,2',3,3'-tetramethoxydistyrylbenzene

FIG. 2. Hydrogen bonding in 2-methoxy-substituted distyrylbenzenes.



in toluene were measured by R. M. Walsh at the Department of Chemistry, University of California, Berkeley. A technique developed by Berg¹⁷ was used.

Assuming a single exponential decay law the lifetime of the first compound is $(1.7\pm0.2)\times10^{-9}$ sec and that of the second $(1.4\pm0.1)\times10^{-9}$ sec. These lifetimes are short as compared to those of the known scintillators.

SCINTILLATION PROPERTIES

The scintillation properties of organic liquid scintillators are governed by (a) the efficiency of the transfer of energy from the solvent used to the solutes; (b) by their quantum efficiency of fluorescence; (c) by the probability of reabsorption of the photons emitted, or the separation of the spectra of absorption and fluorescence, and (d) by the solubility of the compounds.

Prior computations indicated a fairly good quantum efficiency of fluorescence and energy transfer from alkylbenzenes to distyrylbenzenes.¹ Computations by the same method did not predict similar transfer properties and high quantum efficiencies of fluorescence for distyrylbenzene derivatives in which the benzene rings contain heteroatoms. The calculations predicted little influence for a heteroatom in the meta positions of the benzene rings, though an important influence was predicted for a heteroatom in the ortho positions. Such effects have, indeed, been found in the present study. Thiophene rings decreased the scintillation and the fluorescence efficiencies to nil. Nitrogen atoms in Posi-

FIG. 3. Conformation of 2-chloro or methyl-substituted distyrylbenzenes.



¹⁷ Robert Berg, "The Measurement of Radiative Lifetimes," Ph.D. thesis, University of California, Berkeley, March 1962.

Compound	mp (°C)	Appearance and solvents for recrystallization	yield (%)	Empirical formula	Analysis: calculated	Analysis: found
2,2'-Dimethyldistyrylbenzene	178	lemon yellow plates with blue- green fluorescence from methylcyclohexane	16	$C_{24}H_{22}$	С, 92.85; Н, 7.15	С, 93.03; Н, 7.08
3,3'-Dimethyldistyrylbenzene	191	lemon yellow plates with blue- green fluorescence from toluene	24	$C_{24}H_{22}$	С, 92.85; Н, 7.15	С, 92.83; Н, 6.95
4,4'-Dimethyldistyrylbenzene	202	yellow–green crystals from phenylcyclohexane	32	$C_{24}H_{22}$	C, 92.85; H, 7.15	С, 92.69; Н, 7.38
2, 2', 5, 5'-Tetramethyldistyryl- benzene	181	yellow needles from xylene	31	$C_{26}H_{26}$	С, 92.30; Н, 7.70	С, 92.10; Н, 7.78
3,3',4,4'-Tetramethyldistyryl- benzene	239-40	yellow plates with green fluores- cence from benzene or toluene	25	$C_{26}H_{26}$	С, 92.30; Н, 7.70	С, 92.24; Н, 7.79
4,4'-Di-isopropyldistyrylbenzene	238	yellow leaflets with green fluores- cence from xylene	40	$C_{28}H_{30}$	С, 91.80; Н, 8.20	С, 91.82; Н, 8.28
4,4'-Diphenyldistyrylbenzene	>320	light yellow crystals with green fluorescence from tetralin	40	$C_{34}H_{26}$	С, 93.97; Н, 6.03	С, 93.97; Н, 6.30
1,4-bis-(1-naphthylvinyl)benzene	210-2	deep yellow crystals from xylene	30	$C_{30}H_{22}$	С, 94.20; Н, 5.80	С, 94.38; Н, 5.80
1,4-bis-(2-naphthylvinyl)benzene	>230	yellow plates with green fluo- rescence from o-dichloro- benzene	71	$C_{80}H_{22}$	С, 94.20; Н, 5.80	С, 94.33; Н, 6.17
1,4-bis-(9-anthrylvinyl) benzene	> 300	deep yellow crystals from phenylcyclohexane	83	$C_{38}H_{26}$	С, 94.57; Н, 5.43	С, 94.27; Н, 5.50
2,2'-Dimethoxydistyrylbenzene	207	green-yellow needles with green fluorescence from trichloro- ethylene or dioxane	40	$C_{24}H_{22}O_2$	С, 84.19; Н, 6.48	С, 84.53; Н, 6.41
2, 2', 3, 3'-Tetramethoxydistyryl- benzene	175	colorless crystals with violet fluorescence from dioxane or xylene	21	$C_{26}H_{26}O_4$	С, 77.59; Н, 6.51	С, 77.40; Н, 6.58
2,2',4,4'-Tetramethoxydistyryl- benzene	184–6	lemon-yellow plates from xylene or dioxane	47	$C_{26}H_{26}O_4$	С, 77.59; Н, 6.51	С, 77.30; Н, 6.75
3,3',4,4'-Tetramethoxydistyryl- benzene	272	deep yellow plates with green fluorescence from toluene or dioxane	33	$C_{26}H_{26}O_4$	С, 77.59; Н, 6.51	С, 77.67; Н, 6.33
1,4-bis-(3,4-methylenedioxy- styryl)benzene	264	yellow crystals from chloroben- zene or dioxane	70	$C_{24}H_{18}O_4$	С, 77.82; Н, 4.90	С, 77.82; Н, 5.20
4,4'-Diethoxy-3,3'-dimethoxydis- tyrylbenzene	270	yellow plates from cyclohexa- none	70	$C_{28}H_{30}O_4$	С, 78.12; Н, 7.02	С, 78.02; Н, 7.02
3,3',4,4',5,5'-Hexamethoxydis- tyrylbenzene	202	yellow crystals with green fluo- rescence from 2-butanone or toluene	14	C ₂₈ H ₈₀ O ₆	С, 72.71; Н, 6.53	С, 72.86; Н, 6.57

Compound	mp (°C)	Appearance and solvents for recrystallization	Over-all yield (%)	Empirical formula	Analysis: calculated	Analysis: found
2,2'-Dichlorodistyrylbenzene	175	deep yellow needles with green fluorescence from carbon tetrachloride	28	$\mathrm{C}_{28}\mathrm{H}_{16}\mathrm{Cl}_2$	C, 75.23; H, 4.58; Cl, 20.19	C, 75.52; H, 4.71; Cl, 20.68
3,3'-Dichlorodistyrylbenzene	186	lemon green plates from dioxane or toluene	1	$\mathrm{C}_{22}\mathrm{H}_{16}\mathrm{Cl}_2$	C, 75.23; H, 4.58; Cl, 20.19	C, 75.18; H, 4.49; Cl, 20.64
4,4'-Dichlorodistyrylbenzene	301	green yellow plates with green fluorescence from o-dichloro- benzene	61	$\mathrm{C}_{22}\mathrm{H}_{16}\mathrm{Cl}_2$	C, 75.23; H, 4.58; Cl, 20.19	С, 75.26; Н, 4.65; Сl, 20.59
2,2',4,4'-Tetrachlorodistyryl- benzene	234	lemon yellow needles with green fluorescence from toluene or dioxane	58	$\mathrm{C}_{22}\mathrm{H}_{14}\mathrm{Cl}_{4}$	С, 62.89; Н, 3.36; Сl, 33.75	С, 62.71; Н, 3.27; Сl, 33.46
2,2',6,6'-Tetrachlorodistyrylbenzene	200	light yellow needles with green fluorescence from carbon tetrachloride	44	$C_{22}H_{14}Cl_4$	C, 62.89; H, 3.36; Cl, 33.75	C, 62.88; H, 3.26; Cl, 33.70
3,3',4,4'-Tetrachlorodistyrylbenzene	214	green yellow needles with green fluorescence from dioxane or toluene	12	$\mathrm{C}_{22}\mathrm{H}_{14}\mathrm{Cl}_{4}$	C, 62.89; H, 3.36; Cl, 33.75	С, 63.35; Н, 3.37; Сl, 33.93
1,4-bis-(2-vinylpyridyl)benzene	230	light green-yellow plates with bluish-green fluorescence from xylene or toluene	1	$C_{20}H_{16}N_2$	C, 84.49; H, 5.66; N, 9.85	C, 84.59; H. 5.44; N, 10.37
1,4-bis-(3-vinylpyridyl)benzene	195	light yellow plates with bluish- green fluorescence from toluene or xylene	1	$C_{20}H_{16}N_2$	C, 84.49; H, 5.66; N, 9.85	C, 84.64; H, 6.03; N, 10.36
1,4-bis-(2-thienyl)benzene	275	yellow needles from trichloro- ethylene or toluene	61	$C_{18}H_{14}S_2$	С, 73.44; Н, 4.79	С, 73.46; Н, 4.93
4,4'-Dimethylaminodistyrylbenzene	>320	yellow crystals from dimethyl- formamide	quantitative	C ₂₆ H ₂₈ N ₂	C, 84.75; H, 7.65; N, 7.60	C, 85.06; H, 7.92; N, 7.59

TABLE IV (Continued)

tion 2 decreased the scintillation efficiency strongly, while only a slight decrease was found in the compound with nitrogen atoms in Position 3.

Substitution by alkyl or alkoxy groups or by chlorine did not influence significantly the energy transfer of the compounds or their quantum efficiency of fluorescence as long as the molecules remained planar. Introduction of four bulky substituents in Positions 2,2',6, and 6' decreased the fluorescence and the scintillation efficiencies in 2, 2', 6, 6'-tetrachlorodistyrylbenzene and in 1,4-bis-(9-anthrylvinyl)-benzene, which were expected to be good receptors of energy and compounds with high quantum yields of fluorescence, if their structures were planar. If only two substituents are introduced in either Positions 2,2' or 6,6', the molecules are not necessarily hindered sterically in the ground state, since the substituents can be pointed away from the double bonds (Fig. 3). In this case, the terminal phenyl rings are not free to rotate along their bond with the α carbon atoms and exert, in certain vibrations, a pressure on the hydrogens on the β -carbon atoms. This pressure increases the linearity of the molecule in the excited state and produces a better separation between the spectra of absorption and fluorescence. (This is not the case with the 2-methoxy-substituted compounds, which assume in their ground states the conformation indicated in Fig. 2.)

The separation of the maxima of the spectra of absorption and fluorescence in the distyrylbenzenes is of the order of 7.5 kcal/mole, at room temperature.

Since the spectral curves of both absorption and fluorescence decrease sharply on approaching each other, the spectra do not overlap significantly and the solutions may be considered practically transparent to their own fluorescent radiation. This feature makes the distyrylbenzenes superior to the known "wavelength shifters" (or secondary scintillation solutes) like POPOP, and makes them extremely useful in largevolume liquid scintillators where the photons emitted have to traverse a thick layer of solution before reaching the phototube. The perfect matching of the spectra of fluorescence with the maximum sensitivity region of the S-11 and S-13 type photosurfaces, which are used in most of the commercial photomultipliers manufactured for use in liquid scintillation counters, increases the measured scintillation efficiencies of the solutions still further. Some of the solutions obtained have an efficiency higher than that of any liquid scintillation system known to the author.

The primary scintillation efficiencies of the distyrylbenzenes in alkylbenzenes range from 62% to 68% on the anthracene scale (Table II). The efficiencies are only weakly concentration dependent, because of the separation of the spectra of absorption and fluorescence which diminishes the reabsorption of photons even in fairly concentrated solutions. The scintillation efficiencies seem to level off or decrease slightly at a concentration of 2.5 g/liter in most of the toluene or xylene solutions. 4,4'-Di-isopropyldistyrylbenzene is the most efficient primary liquid scintillation solute in toluene, with a yield of 68% on the anthracene scale.

Addition of naphthalene to the dioxane solutions which are used in the counting of aqueous samples of radio-isotopes, increases the scintillation efficiencies of the solutions.^{18,19} Efficiencies in the dioxane-10%-naphthalene system range between 42%-51% on the anthracene scale for the various compounds, the best being 2,2'-dimethoxydistyrylbenzene, at a concentration of 3 g/liter. As might be expected, introduction of water into the solution decreases the efficiencies, though reasonably good efficiencies are still obtained for water concentrations as high as 15%.

It has already been mentioned that the present group of compounds yields solutions of the highest scintillation efficiencies observed. The best of these is a xylene or pseudocumene solution containing 200 mg/liter 4,4'-di-isopropyldistyrylbenzene and 4 g/liter p-terphenyl; this solution has an efficiency of 81% on the anthracene scale, as compared with 76.5% of a xylene solution containing 0.1 g/liter POPOP and 4 g/liter p-terphenyl. As seen in Table III, most of the distyrylbenzenes are highly efficient secondary liquid scintillation solutes, the efficiencies ranging between 74%-81% on the anthracene scale.

In some of the compounds presented in Table III, the efficiency of the solutions increases very sharply on the addition of small amounts of the secondary solute, decreases when more of the compound is added, increases with a further addition of the solute and decreases again at high concentrations. No explanation has been found for the existence of the two maxima.

Compounds which do not dissolve to an extent of 1 g/liter in the solvents used have not been included in Table II. Table III contains data on compounds which have solubilities of 0.04 g/liter or better.

EXPERIMENTAL

Preparation

The method of Campbell and McDonald⁵ has been used for the preparation of the various compounds. *p*-Xylene-bis-(triphenylphosphonium chloride) was obtained by refluxing *p*-xylylenedichloride (obtained from Diamond Alkali Company, Cleveland, Ohio) with triphenylphosphine (Metal and Thermit Company, Rahway, New Jersey) in dimethylformamide.¹⁰ 0.025 mole (17.4 g) of the phosphonium salt and 0.06 moles of an aldehyde ("Purum" from Fluka, Buchs, Switzerland) were dissolved in 50 ml of absolute alcohol by heating and stirring. To the solution obtained, 250 ml of a 0.2*M* solution of lithium ethoxide in absolute

¹⁸ M. Furst, H. Kallman, and F. H. Brown, Nucleonics 13 (4), 58 (1955).

¹⁰ H. Werbin, I. L. Chaikoff, and M. R. Imada, Proc. Soc. Exptl. Biol. N. Y. **102**, 8 (1959).

ethanol was added. Although the reaction was completed in a few hours, the solutions were left to stand overnight at room temperature, whereafter 150 ml of water was added to complete the precipitation. The precipitates were filtered and dried in vacuo at room temperature. The mixtures were isomerized by refluxing for 3 h in a xylene or methylcyclohexane solution containing a trace of iodine. On cooling, crystals of the compounds separated.

Table IV summarizes the melting points, the appearance, the solvents used for the recrystallization, the yields, and the analyses of the compounds. The yields are those of the scintillation pure crystals, obtained by recrystallizing the compounds at least three times (once with active charcoal). When possible, the solvent of recrystallization was varied during the purification. Little attention was paid to the yields, and those indicated in the table should be regarded only as minimum values. The melting points are all corrected.

Spectra of Absorption and Fluorescence

All the spectra were measured with a Cary 14 automatic recording spectrophotometer at 24°C. The fluorescence attachment supplied with the instrument was used to measure the spectra of fluorescence.

Scintillation Efficiencies

Scintillation efficiencies were determined as described previously.²⁰ Optical contact between the photomultiplier and the flask containing the solution was formed directly by an analytical-grade paraffin oil. Magnesium oxide powder enclosed in a double layer of glass was used as reflector in all the experiments.

20 A. Heller and D. Katz, J. Chem. Phys. 35, 1987 (1961).

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 40, NUMBER 10

15 MAY 1964

Gaseous Ion Recombination Rates. II

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An analysis of the mechanics of three-body ion recombination is given. The relative efficiencies of various gases in promoting ion recombination are calculated and found to be in satisfactory agreement with experiment. The calculations lead to qualitative conclusions about how mass, relative velocity, and the nature of the deactivation criterion affect the magnitude of the recombination rate.

N an earlier publication¹ we presented experimental L evidence that suggested that three-body recombination of gaseous ions proceeds by the following mechanism:

$$A^{+}+B^{-} \rightarrow (A^{+}B^{-})^{*},$$

$$(A^{+}B^{-})^{*} \rightarrow A^{+}+B^{-},$$

$$(A^{+}B^{-})^{*}+M \rightarrow (A^{+}B^{-})+M \rightarrow neutrals.$$

The species $(A+B^{-})^*$ is a pair of ions in an unbound orbit about each other, but in a condition such that if one of them collides with a neutral molecule M, a bound ion pair in an elliptical orbit will be formed. The most probable fate of this bound ion pair is charge transfer followed by dissociation to neutral fragments. If neither member of the unbound pair (A+B-)* undergoes a collision, the two ions separate via their hyperbolic

orbit. A steady state treatment of the mechanism gives

$$-\frac{d[n]}{dt} = \frac{k_1 k_3 [A^+] [B^-] [M]}{k_2 + k_3 [M]} \equiv \alpha_t [A^+] [B^-],$$

where α_t is the ion recombination coefficient that refers to this three-body process only.

The above mechanism is essentially a restatement of the process proposed by Thomson² for three-body ion recombination. Thomson developed an expression for α_i using a simplified description of the mechanics of the three-body collision. He first assumed that although two ions in proximity would have abnormally large kinetic energies due to the action of the Coulomb force, a collision of one of these ions with a neutral molecule would restore the ion kinetic energy to the average value characteristic of thermal equilibrium, $\frac{3}{2}kT$. This suggested that if either of two ions undergoes a collision while the two ions are closer than a distance d defined by $e^2/d = \frac{3}{2}kT$, a bound ion pair and, eventually, neutral fragments will result. Thomson calculated this collisional deactivation rate under the assumption that the ions travel past each other on straight lines and at con-

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[‡] Inorganic Materials Research Division. ⁴ B. H. Mahan and J. C. Person, J. Chem. Phys. (to be published).

² J. J. Thomson, Phil. Mag. 47, 337 (1924).