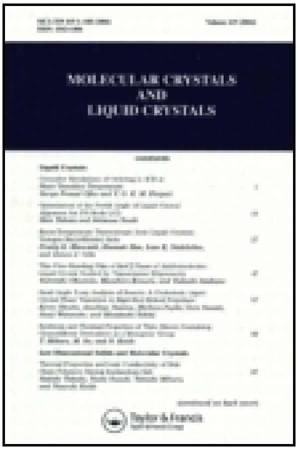

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On the Correlations Between Constitution and Scintillation Properties in the p-Oligophenylene Series

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Abstract—The paper deals with the problem: What properties are requested from an organic scintillator solute and what structural principles are given to realize, or at least to influence them especially by looking at the p-oligophenylene series? According to their importance and also in respect to more or less special purposes one can distinguish the following sequence:

1) An organic scintillator solute must have a sufficient solubility in all types of solvents used for this counting method. As a result of extensive systematic studies substitution of larger alkyl groups has been recognized as a very effective principle of solubilization. By use of branched, particularly long-chain branched groups, even extremely insoluble substances can be solubilized to any extent in homopolar solvents. While substitution of alkyl groups is only effective for nonpolar solvents, the use of oxa-alkyl groups (derived from ethylene oxide) affords solubility also in polar solvents. It seems that with these two types of substituents almost all solubility problems in low molecular organic chemistry can be solved.

2) In any case a high light output is of greatest importance. In the *p*-coligophenylene series the scintillation efficiency increases with the degree of condensation (number of rings). Thus, with the higher homologs light yields could be obtained which were unknown up until now. Substituents disturbing the coplanarity cause a decrease in light output.

3) The fluorescence wavelengths should be in a favorable range in order to match the response of the commonly used phototubes. In the *p*-oligophenylene series with increasing degree of condensations the absorption and therefore also the fluorescence bands are shifted into longer wavelengths. Because of the convergency phenomena in connection with the lower accessibility of the higher homologs it is difficult to reach the range of 400 mμ. By introducing other chromophoric systems, such as pyrene or fluoranthene, very long fluorescence wavelengths can be established.

4) For many measurements, especially in high energy physics, a short decay time is of greatest interest. For the *p*-oligophenylene series the decay time decreases as the degree of condensation increases. This can be easily understood, according to Förster, since in the same direction the molar extinction coefficient increases.

5) A large mean free path between absorption and fluorescence band (Stokes shift) guarantees a high optical transparency. In the *p*-oligophenylene series there

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is almost no overlap in these two bands. Substitution of alkyl groups seems to be a generalizable provision to further enhance the Stokes shift.

6) Organic scintillator solutes should have a low sensitivity to all types of quenching processes. So far, it is only known how to eliminate the self quenching. The solubilization groups, namely, affording on the one hand the necessary solubility seduce, or even completely exclude, the self quenching on the other hand.

1. Introduction

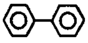
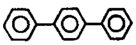
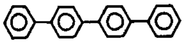
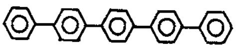
The progress in the field of organic scintillators both in scientific and in practical directions depends on extensive cooperation between physicists, nuclear chemists and organic chemists. This paper is a contribution to this field from the organic chemistry. Its subject is the correlation between chemical constitution and physical properties, especially in respect to scintillator solutes. In Table 1 these properties are listed using a sequence which may correspond to their importance. It will be shown that almost all of these properties can be correlated with fundamental structural concepts by using the *p*-oligophenylenes as model substances. Table 2 gives information on the chemical constitution and also on some of the most important physical properties of this homologous series.

TABLE 1 Properties requested from an organic scintillator solute

Desirable properties of an organic scintillator solute
1. Sufficient solubility
2. High light output
3. Favorable fluorescence wavelength
4. Short decay time
5. Big STOKES Shift
6. Low quenching sensitivity

Because of the rapid decline in solubility with increasing degree of condensation (number of rings) this class of substances could not be investigated more extensively for a long time. It was found some years ago that their solubility can be greatly enhanced by substituting methyl- or methoxyl groups. We have already reported on this subject in many publications.[1]

TABLE 2 Melting points, solubilities (toluene, 20°C), wavelengths of the UV-absorption bands (conjugation bands) and corresponding molar extinction coefficients (chloroform) of the unsubstituted *p*-oligophenylene series

Structural formula	Melting point [°C]	Solubility [g/l]	UV-absorption λ max [Å]	ε max 10^{-3}
	71	414	2510	17.2
	214	7.4	2800	31.1
	320	0.12	2980	46.1
	395	<0.003	3100	>60

These methyl- or methoxyl-substituted *p*-oligophenylenes proved finally to have favorable scintillation properties. Results on these have also been published.[2] On the basis of these results a more systematic research in the scintillator field could be started. Something about this has been published, too.[3,4] This paper is a review of the present state of these investigations using the sequence of topics given in Table 1.

2. Scintillation Properties and Their Correlation to the Chemical Constitution

Solubility

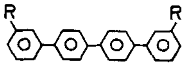
An organic scintillator solute must have a sufficient solubility in all types of solvents used for this counting method. An insoluble compound has no interest for this application in spite of the fact that its scintillation properties may be extremely favorable.

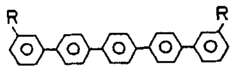
As a result of extensive systematic investigations on the correlations between constitution and solubilities of organic compounds, an effective and widely generalizable solubilization principle has been developed. This subject was discussed quite extensively last year.[4] Because of its immense importance even for the whole organic luminescence field, it may be helpful to outline once more the fundamental facts in a brief manner. In the meantime also some new approaches have been included.

Alkyl Groups and Their Solubilizing Effect

Substitution of larger alkyl groups has been recognized as a very effective provision of solubilization for all nonpolar solvents. This may be demonstrated by the following examples.

TABLE 3 Solubilities (toluene, 20°C) and melting points of $1^2,4^3$-dialkyl-*p*-quaterphenyls and of $1^2,5^3$-dialkyl-*p*-quinquiphenyls with groups of the n-alkyl series





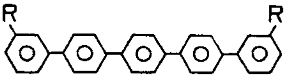
R	Solubility		Melting point	Solubility		Melting point
	[g/l]	[mMol/l]	[°C]	[g/l]	[mMol/l]	[°C]
H	0.12	0.39	320	<0.005	<0.013	395
Methyl	3.7	11.1	213	0.1	0.24	313
Ethyl	7.5	20.7	194	0.18	0.41	291
n-Butyl	43	103	165	0.48	0.97	268
n-Hexyl	46	97	157	0.52	0.94	259
n-Octyl	48	90	150	0.55	0.91	253

The *p*-quaterphenyl is an interesting scintillator solute (Table 3). Unfortunately, its solubility is very poor. (In this connection it should be said that for scintillation purposes a solubility of about 30 mMol/l is desirable. This corresponds, on the average—depending, of course, on the molecular weight—to about 10 g/l.) By substitution of alkyl groups of increasing size in the positions of *p*-quaterphenyl designated by *R* one attains easily the desired solubility range. Since these groups have to be seen as ballast on the molecule, the molar solubility—expressed in mMol/l—is the more exact measure. It seems that the peak in the molar solubility of the *p*-quaterphenyls is reached with the butyl derivative. We have to point out that in these positions alkyl groups have almost no influence on the optical properties of the basic molecules.

With increasing solubility a concomitant decrease in melting point can be observed. This is to be expected since both these properties are correlative to each other (see page 327).

With *p*-quinquiphenyl (Table 3) the substitution of linear alkyl groups also causes a considerable increase in solubility. However, the desired value of about 30 mMol/l thus cannot be realized. This example shows that the solubilization effect of linear alkyl groups is limited. By going to longer alkyl groups no further increase in solubility is to be expected also in this case.

TABLE 4 Solubilities (toluene, 20°C) and melting points of $1^2, 5^3$-dialkyl-*p*-quinquiphenyls with long-chained branched alkyl groups

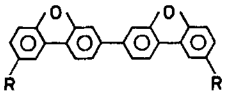
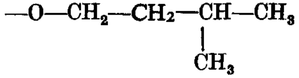
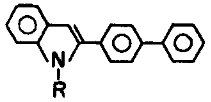
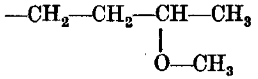
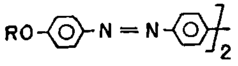
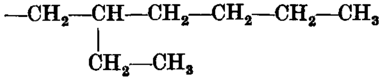


R	Solubility		Melting Point
	[g/l]	[mMol/l]	[°C]
H	<0.005	<0.013	395
t-Butyl	0.57	1.15	283
3-Amyl	8.6	16.4	236
5-Nonyl	34	53.5	177
7-Tridecyl	227	304	127
9-Heptadecyl	>500	>600	80

By using long-chain branched alkyl groups we finally succeeded also in getting highly soluble *p*-quinquiphenyl derivatives (Table 4). One even comes quickly into a range where it is impossible to measure exact values. The molar solubility of the 7-tridecyl derivative (no. 5) is already more than 23,000 times that of the basic substance. In addition it is of interest to point out at the enormous difference between the melting point of the heptadecyl derivative and the basic compound which is more than 300°C.

Table 5, finally, shows that this solubilization principle is not limited to the oligophenylenes. Also, with other substances, one reaches an increase in solubility of several orders of magnitude depending, of course, on the number, the position, the size, and the structure of these groups. We have already enough experience to know what group is needed to

Table 5 Comparison of solubilities (toluene, 20°C) and melting points of alkyl derivatives of different types of organic compounds with those of their basic molecules

Structural formula	R	Solubility [g/l]	Solubility [mMol/l]	Melting point [°C]
	H	0.8	2.4	252
	 $-O-CH_2-CH_2-CH(CH_3)-CH_3$	19.7	38.9	156
	H	<0.1	<0.3	300
	 $-CH_2-CH_2-CH(O-CH_3)-CH_3$	>300	>850	85
	$-CH_3$	0.035	0.083	258
	 $-CH_2-CH(CH_2-CH_3)-CH_2-CH_2-CH_2-CH_3$	35	56.5	163

give a favorable but not excessive solubility; one also overshoot over the goal (see page 324).

Oxa-alkyl Groups and Their Solubilizing Effect

Pure alkyl groups are only effective for nonpolar solvents. The use of oxa-alkyl groups—derived from ethylene oxide—however, affords solubility also in polar solvents. This can be demonstrated with a further example.

Table 6 allows a comparison of the solubility properties of the n-alkyl ethers with the chain-analogous oxa-alkyl ethers of 4,4'-dihydroxybiphenyl in solvents of different polarity. There is a great decline in the solubility of the pure alkyl derivatives by going from toluene to methanol. The oxa-alkyl derivatives, however, show an increasing solubility in the polar solvents with growing size of these groups. The value of the 3,6,9-trioxa-undecyl derivative (Table 6) in nitromethane is extremely high.

From experience in the chemistry of polyethylene oxide[5] one can gather that the solubility of any organic compound in a polar solvent—water included—is only a question of the length of a substituted oxa-alkyl group.

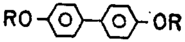
It is to be expected that scintillator solutes substituted with oxa-alkyl groups will be very favorable in the counting technique of water-containing samples. We have found that such groups cause a high water compatibility with the corresponding liquid scintillator mixtures used for this purpose.

Melting Point and Crystallizability

In general, the groups which increase the solubility cause at the same time a decline in melting point. The extent of this decline depends mainly on the structure of these groups. It is no problem, therefore, to obtain compounds with melting points below room temperature.

Frequently the decline in melting point is accompanied by a reduced tendency to crystallize to the extent that compounds can be obtained without any crystallizability. We have several of these, but they are very difficult to handle. Since the crystallization is still the most important and most effective purification method for compounds of a higher molecular weight, one, of course, will try to avoid such situations. We

TABLE 6 Solubilities (20°C) of oxa-alkyl ethers and of the chain-analogous n-alkyl ethers of 4,4 -dihydroxybiphenyl in different solvents

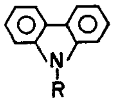
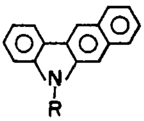
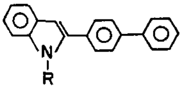
	Solubilities [mMol/]				
R	Toluene	Dioxane	Nitro-methane	Methanol	Melting point [°C]
$CH_3—CH_2—CH_2—CH_2—CH_2—$	113	46.3	1.2	0.84	134
$CH_3—CH_2—O—CH_2—CH_2—$	138	204	60.4	8.77	120
$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—$	43.4	7.3	0.84	<0.1	117.5
$CH_3—CH_2—O—CH_2—CH_2—O—CH_2—CH_2—$	56.1	111	69.9	4.8	100
$CH_3—CH_2—CH_2—CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—$	4.45	0.46	0.28	<0.1	114
$CH_3—CH_2—O—CH_2—CH_2—O—CH_2—CH_2—O—CH_2—CH_2—$	243	497	802	21.2	68

have now enough experience to know how this can be done. However, there is not enough space to discuss this.

On the other hand such oily, highly viscous or even glassy aromatic compounds are quite interesting to study, e.g. electronic interaction processes between molecules at very short distances but, which is very important, outside of a lattice. We recently found another way to get substances of this type without missing the crystallizability.

By mixing different but crystallizable alkyl derivatives of one and the same basic molecule and melting them together, one can obtain an eutecticum-like system which no longer crystallizes. Since the size or structure of the alkyl groups has no influence on the electronic properties of the basic molecule, it doesn't make any difference whether there is a mixture or not. In Table 7 only three examples are shown, but this principle seems to have a general applicability. The consistency of such mixtures depends

TABLE 7 Alkyl derivatives of organic fluors forming a noncrystallizable (amorphous) mixture

General structural formula	Derivatives		Consistency of the noncrystallizable mixture of the alkyl derivatives at 20°C
	R	Melting points [°C]	
	n-Octyl	22	Rather fluid liquid
	n-Decyl	12	
	i-Butyl	50	
	H	247	
	n-Hexyl	39	High viscous oil
	n-Tetradecyl	49	
	i-Propyl	110	
	H	335	
	n-Butyl	110	Tar-like mass
	3-Methoxy-n-butyl	85	
	H	300	

on the size, or better, rigidity of the basic molecules. Thus, one can get either a rather fluid liquid or even a sticky glass-like mass.

In summarizing one can emphasize once more that the solubility problem in organic luminescence field is solved now in a comprehensive manner. Even extremely insoluble compounds can be solubilized to any degree in all common solvents. In addition, also the melting and crystallizing behavior of organic fluors can be changed rather arbitrarily. Simple and widely generalizable procedures for substituting the mentioned groups have been developed. This means that the solubility and melting point problems are not only solved theoretically but experimentally as well.

Finally, we have to say that these solubilization and "liquification" principles, respectively, can be related to familiar structural concepts such as molecular asymmetry (static entropy effect), internal molecular mobility (dynamic entropy effect) and molecule bulkiness (enthalpy effect). From these also the universal applicability can be deduced. All in all, the results make possible a much better understanding of the correlation between constitution, solubility and melting point of organic compounds in general.

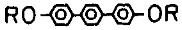
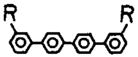
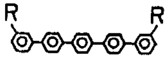
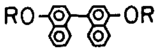
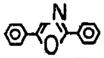
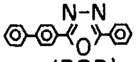
Light output

In any case a high light output is of greatest importance. For a long time the RPH value of PBD (2-phenyl-5-biphenylyl-oxadiazole) could not be surpassed (Table 8, no. 7). In this connection it is worth mentioning that this compound has been developed in the Los Alamos Group of Hayes.[6] With our methyl- and methoxyl-substituted *p*-oligophenylenes we found efficiencies very close to that of PBD but none of these proved to be better.[2]

By application of the above discussed solubilization principle (see page 324), we were able to make soluble the higher *p*-oligophenylenes but without disturbing the conjugation system; with these compounds we succeeded finally in getting RPH values higher than 1.28. The *p*-quinquiphenyl derivative (no. 4) has a light output which is even more than 40% higher than that of PPO (no. 6). All our relative pulse heights were measured and compared to a standard solution of PPO, 3 g/l in toluene, equal to according to the method of Hayes *et al.*[6]

It is interesting that auxochromes like alkyloxy groups substituted in the *p*-positions of the terminal rings have a very favorable effect on the relative pulse heights (nos. 1 and 2). This can be seen as a confir-

TABLE 8 Relative pulse heights (toluene), corresponding optimal solute concentrations, mean fluorescence wavelengths (toluene, at 5 g/l), wavelengths of the absorption maxima (chloroform), solubilities and melting points of p-oligophenylenes and related compounds

Structural Formula	Relative Pulse Height	Optimal Concentration		λ (Fluoresc.)	λ_{max} (Absorpt.)	Solubility		Melting Point
		[g/l]	[mMol/l]	[Å]	[Å]	[g/l]	[mMol/l]	[°C]
 R : 2-Ethylhexyl	1.32	13	27	3650	2950	295	607	95
 R : 2-Butyloctyl	1.41	16	24	3855	3090	63	93	163
 R: n-Octyl	1.37	15	28	3735	2980	48	90	150
 R: 7-Tridecyl	1.45	28	37	3880	3110	227	304	127
 R: n-Octyl	1.06	14	27	3910	3080	174	341	146
 (PPO)	1.03 (1.00)	6 (3)	27 (14)	3760	3060	~250	~1130	72
 (PBD)	1.28	10	33.5	3730	2990	11.1	37	169

mation that there is a close correlation between the length of the chromophor and the light output. Auxochromes in these positions greatly increase the strength of the chromophor of the basic molecule.

The binaphthyl derivative in Table 8 (no. 5) has an RPH value only slightly higher than that of PPO. However, this compound has some other advantages. Its fluorescence band is already in a range where it matches very well the recently developed phototubes. That means it can be used without a secondary solute. In addition, it has an unusually large mean free path between the fluorescence and absorption band, which is very important when used as sole solute, and last but not least, it is easily accessible; it is even commercially available. The same is true—which may be worth mentioning in this connection—for the dialkyloxy-*p*-quaterphenyl (no. 2).

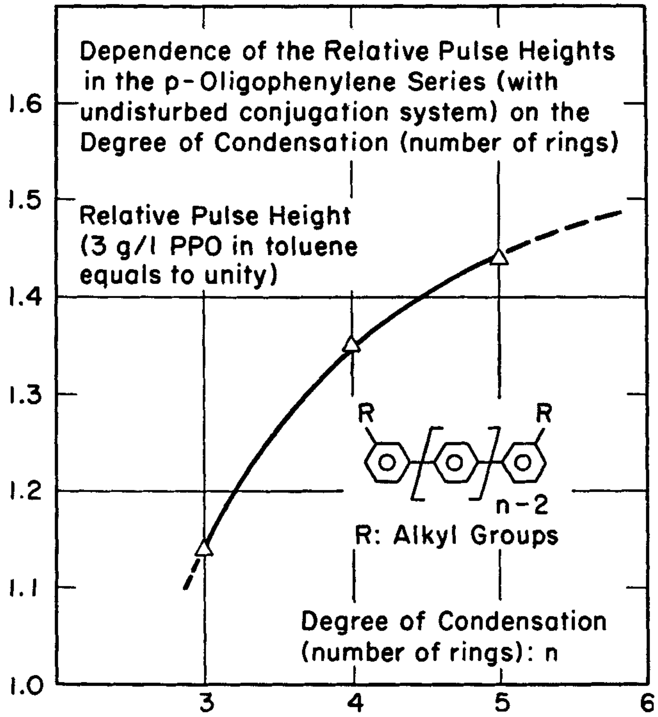
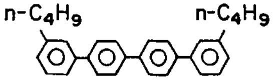
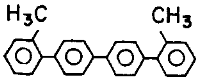
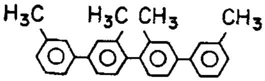
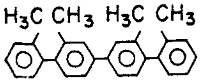


Figure 1. Dependence of the Relative Pulse Heights in the *p*-Oligophenylene Series (with undisturbed conjugation system) on the Degree of Condensation (number of rings).

Is it still possible to get a further increase in the relative pulse height? This question may be answered by Fig. 1, in which are plotted the RPH values of the p-oligophenylene series with undisturbed conjugation system against the number of rings. According to this curve, one can guess that by going to the higher homologs there will be a further increase.

TABLE 9 Relative pulse heights (toluene, 3 g/l PPO equals unity), corresponding optimal solute concentrations, mean fluorescence wavelengths (toluene, 5 g/l) and wavelengths of the absorption maxima (chloroform) of *p*-quaterphenyl derivatives possessing different coplanarity

Structural Formula	Relative Pulse Height	Optim. Conc. [g/l]	λ mean (Fluoresc.) [Å]	λ max. (Absorpt.) [Å]
	1.35	11	3740	3000
	1.25	35	3625	2810
	1.17	25	3585	2690
	0.89	15	3445	2670

Substituents disturbing the coplanarity of the oligophenylene molecules cause a decrease in light output. This can be seen in Table 9. The more the coplanarity is disturbed the lower the RPH values become. From this comparison we could easily deduce that the p-oligophenylenes with undisturbed conjugation systems must have the highest scintillation efficiencies. With methyl substitution only, however, we did not reach the necessary solubility. Thus, the idea was born to develop the solubilization principle discussed above. With that we came finally to the highly soluble dibutyl-*p*-quaterphenyl (no. 1) with the RPH value of 1.35. This whole story has already been reported extensively.[4]

Fluorescence Properties

Organic scintillator solutes must have a favorable fluorescence wavelength. It depends, of course, on their application e.g. as primary or secondary solutes or, in general, on the response of the phototubes.

A brief discussion of the UV absorption behavior of the *p*-oligophenylenes at first makes possible a much better understanding of their fluorescence properties.

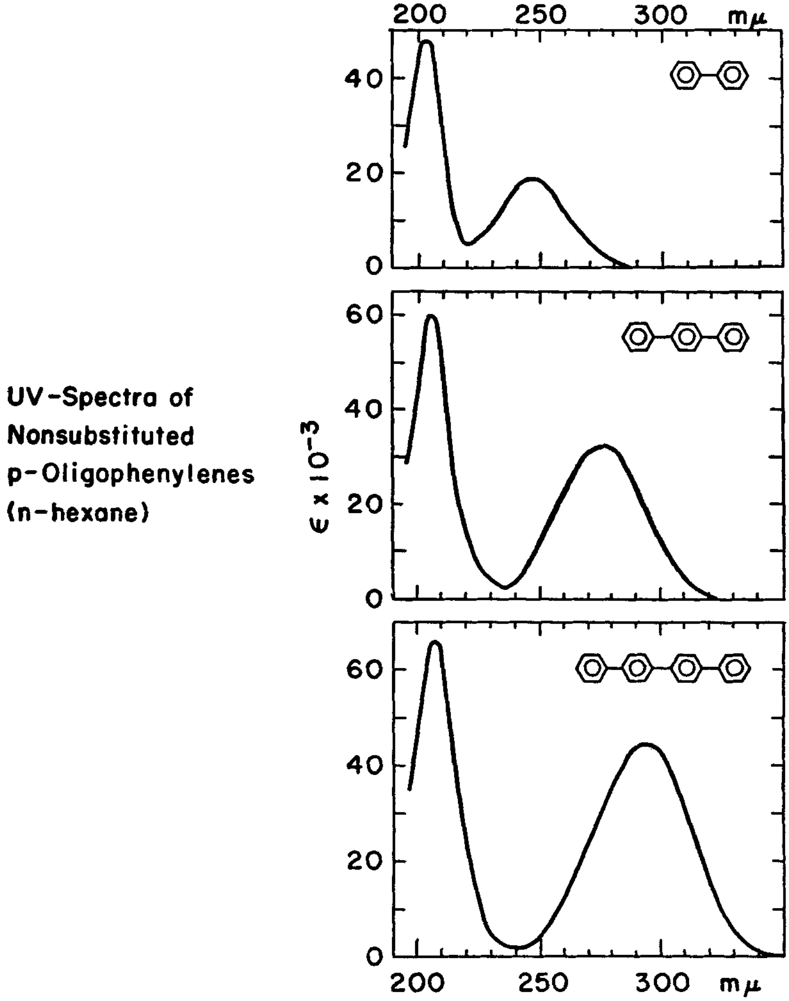


Figure 2. UV-Spectra of Nonsubstituted *p*-Oligophenylenes (*n*-hexane)

The *p*-oligophenylenes have—as already shown by different authors[7]—two distinct absorption bands; both are structureless (Fig. 2). The position of the short wavelength band is almost independent of the length of the molecules. One, therefore, has to assume that it is caused by a transition process located in the single benzene rings.

With the long wavelength band, however, a red-shift occurs as the degree of condensation increases. One can see this shift in Fig. 2. This is evidence enough that these bands must be caused by a chromophor which is identical with the whole molecule. The red-shift of these bands takes place, though, in the sense of a converging series and this can be seen more obviously in Fig. 3.

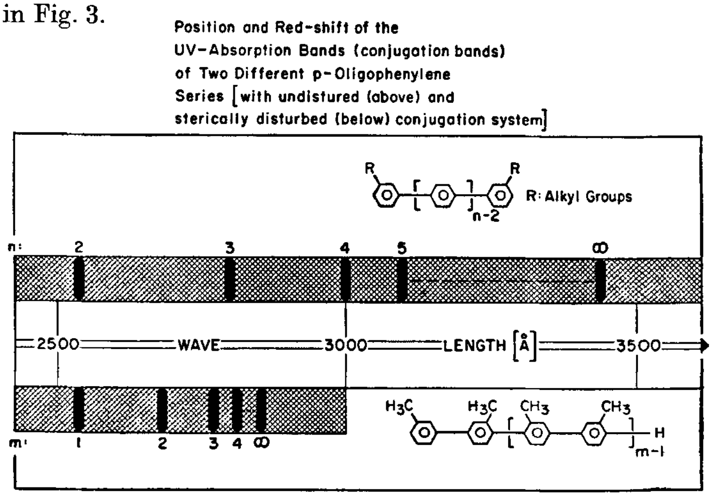


Figure 3. Position and Red-shift of the UV-Absorption Bands (conjugation bands) of two Different *p*-Oligophenylene Series [with undisturbed (above) and sterically disturbed (below) conjugation system].

With a formula developed by Kuhn[8] one can calculate a threshold value of 3450 Å. That means a polyphenylene with a condensation degree of infinity still absorbs in ultraviolet and therefore must be colorless.

The absorption behavior of the methyl substituted *p*-oligophenylene series can also be described as a converging series. The range of absorption is much narrower, however, and the threshold value of the corresponding polyphenylene is already 2870 Å. This is easily understandable since the methyl groups sterically disturb the coplanar adjustment of the rings and therefore interfere with the cooperation of these single chromophores.

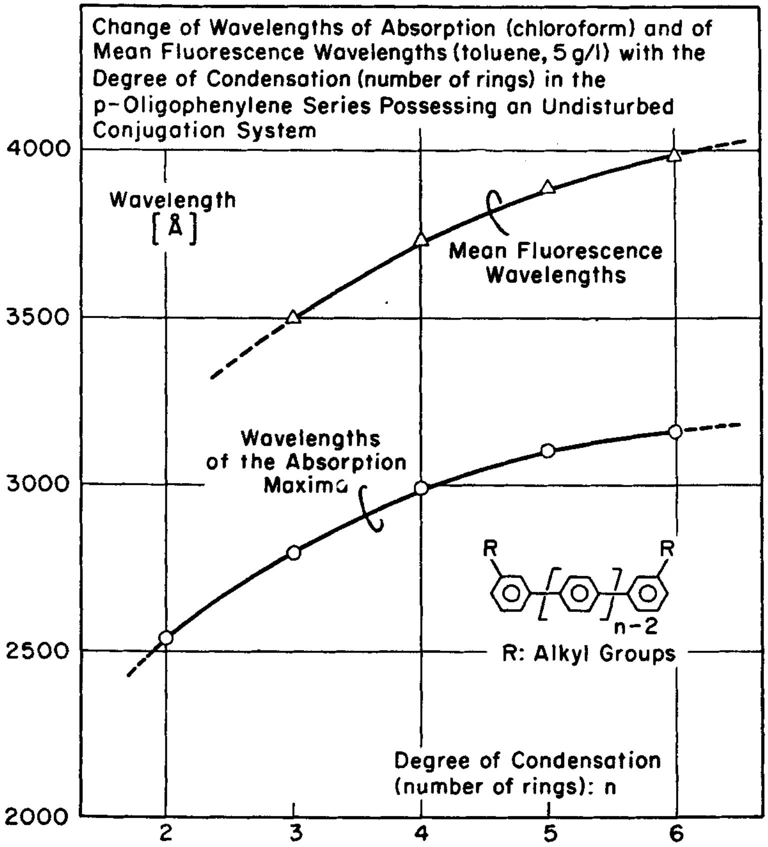


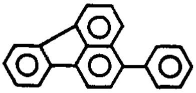
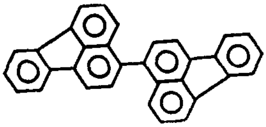
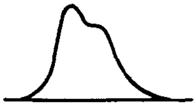
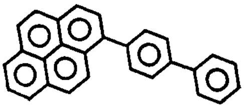
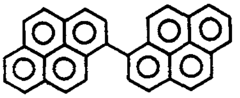
Figure 4. Change of Wavelengths of UV Absorption Maxima (chloroform) and of Mean Fluorescence Wavelengths (toluene, 5 g/l, with the Degree of Condensation (number of rings) in the *p*-Oligophenylene Series Possessing an Undisturbed Conjugation System.

The fluorescence bands of the *p*-oligophenylenes are correlated to the long wavelength absorption bands, also called conjugation bands. On the graph in Fig. 4, there are now plotted the maxima of absorption wavelengths and the mean fluorescence wavelengths of the series with undisturbed conjugation system against the number of rings. The similarity of these two curves is evident. With increasing degree of condensation one can also observe a red-shift of the fluorescence bands and, according to the expectations, this red-shift is subject to the convergency phenomena, too. Using the formula of Kuhn one can calculate a threshold value of about 4300 Å. That means, finally, in this series one never can get a fluorescence band longer than 4300 Å.

We have already made attempts to shift the fluorescence bands into longer wavelengths by bridging the oligophenylenes, e.g. with oxygen.[1] Even this proved to be effective. But unfortunately, other properties such as the light output were influenced thereby very unfavorably.

Recently we found the solution of this problem. By combining chromophoric systems like pyrene or fluoranthene with the oligophenylene structure one can very easily produce fluorescence radiation in a long wavelength range (Table 10). Thus, the mean fluorescence band of the 4-phenylfluoranthene (no. 1) is at 4630 Å. An appropriate combination makes it possible to establish any desired fluorescence range at least up to about 5000 Å. According to our preliminary results these compounds have quite favorable scintillation properties.

TABLE 10 Fluorescence Properties of Aromatic Compounds (related to oligophenylenes) which Emit at Longer Wavelengths

Structural Formula	λ max. [Å]	λ mean [Å]	Shape of the Spectrum $\rightarrow \lambda$
	4525	4630	
	4390 4555	4585	
	4250	3450	
	4245	4360	

Decay Time†

For many measurements such as particle discrimination, β-ray spectrometry, etc., a short decay time is of greatest interest. According to investigations of Berlman[9] with decreasing decay time the oxygen quenching is also reduced. The limit at which the oxygen quenching can be neglected is about 1 nsec. It would be very interesting to study whether sample quenching can thus be excluded as well.

Kallmann and his coworkers[10] measured time constants of some methyl substituted *p*-oligophenylenes 5 years ago. Greenberg[11] reported more detailed results last year. Recently Schmillen‡ renewed this study with a series of about 40 compounds, mainly oligophenylenes. He has, however, published nothing yet. Thus detailed time constants cannot be presented. However, it is possible to correlate the constitution of the oligophenylene series with the decay time in a more qualitative or, better, indirect manner using UV absorption data.

According to an equation developed by Förster[12] and simplified and proved by Berlman,[13] the natural decay time of a molecule is inversely proportional to the corresponding molar extinction coefficient.

In the *p*-oligophenylene series there is a linear relationship between the molar extinction coefficients and the degree of condensation (number of rings), as shown by Fig. 5. In a series with sterically disturbed conjugation this increase is considerably smaller. One can easily understand this fact.

In the Fig. 6 there are now plotted the reciprocal molar extinction coefficients for the series with undisturbed conjugation system against the number of rings, and this curve represents the real change of the natural decay time with the degree of condensation. That means, by going to the higher homologs the decrease in the natural decay time becomes smaller and smaller. However, there are still hopeful expectations, or, expressed in other words, unused possibilities. Just to give an idea, Berlman[14] found for the nonsubstituted *p*-quaterphenyl a decay time of about 0.8 nsec. That means with the sexiphenyl we should come in the range of perhaps 0.6 nsec.

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† Very stimulating discussions on this subject with Dr. Berlman, Argonne National Laboratory, are gratefully acknowledged.

‡ Prof. Dr. A. Schmillen, I. Physikalisches Institut der Universität Giessen, Germany.

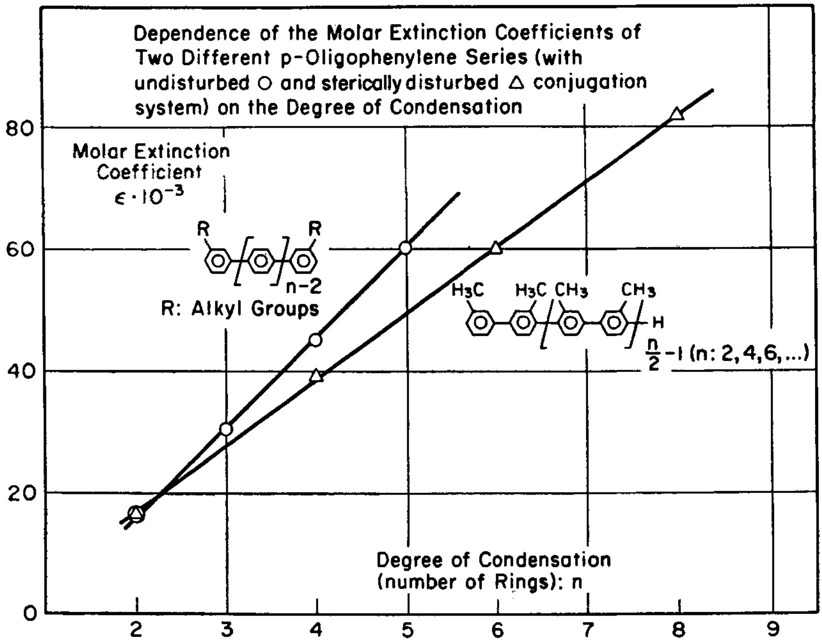


Figure 5. Dependence of the Molar Extinction Coefficients of Two Different *p*-Oligophenylene Series (with undisturbed ○ and sterically disturbed △ conjugation systems) on the Degree of Condensation.

The most important conclusion one can make then is: Decay times of organic scintillator solutes can be influenced in a controlled manner by the constitution. That means, finally, there is also a certain arbitrariness in the choice of a time constant.

Mean free path between the Absorption and Fluorescence Bands

A large mean free path between the absorption and fluorescence bands of organic scintillator solutes is very favorable. If there is no overlap in the two bands, a high optical transparency results. This is very important, but especially so for large volume scintillators. In spite of this fact, no systematic work has been done in this direction up to this date.

The binaphthyl derivative of Table 8 (no. 5) has already been mentioned as having an unusually long free path between absorption and fluores-

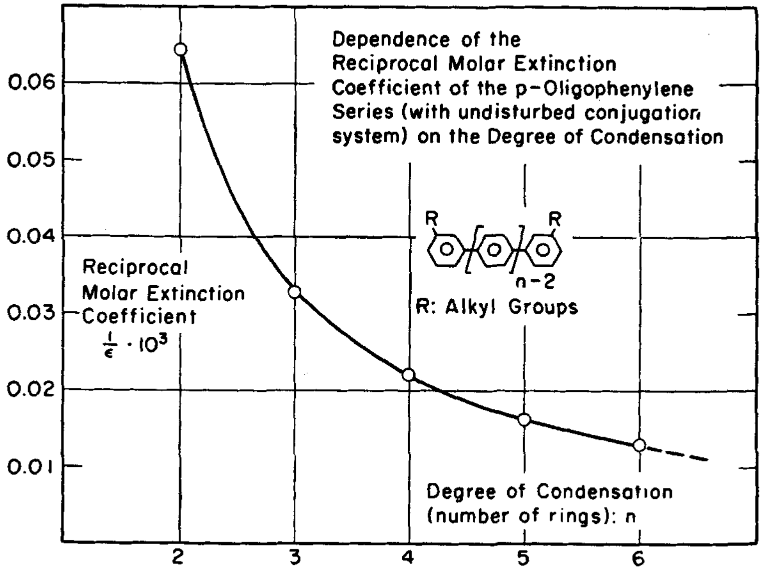
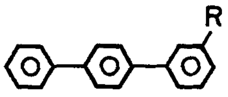
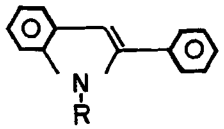


Figure 6. Dependence of the Reciprocal Molar Extinction Coefficient of the p-Oligophenylene Series (with undisturbed conjugation system) on the Degree of Condensation.

Table 11 Comparison of the Optical Data of p-Terphenyl and 2-Phenylindole with Both of Their Methyl Derivatives

Structural Formula	R	Wavelengths [Å]			$\Delta\Delta$
		λ_{max} (Absorpt.)	λ_{mean} (Fluoresc.)	Δ $\lambda_{fl}-\lambda_{abs}$	
	H	2790	3485	695	
	CH_3	2800	3530	730	35
	H	3005	3715	710	90
	CH_3	3010	3810	800	

cence bands; but this compound was found occasionally. We know also that there is a big shift of the fluorescence bands away from the absorption bands in the *p*-oligophenylene series; much larger even than in the oxazole and oxadiazole series. However, we have only very little knowledge as yet by what structural principles this shift can be further increased. We just know that the substitution of alkyl groups has a certain effect. This may be explained now with two examples (Table 11).

In these two compounds the substitution of a methyl group has almost no influence on the absorption bands but the fluorescence bands of the methyl derivatives appear at longer wavelengths. With the 2-phenylindole (below) this shift is even 90 Å which is quite considerable.

In summarizing one can only say there is still a lot to do in order to make real progress in this direction.

Quenching Sensitivity

Organic scintillator solutes should have a low sensitivity to all types of quenching processes, the sample's quenching included. So far we know only how to eliminate the self quenching. It has been found, namely, that alkyl groups affording on the one hand a high solubility reduce or even exclude completely the self quenching on the other hand. These results can only be explained in connection with a shielding effect caused by these groups. In the next paper[15] more information about this shielding effect will be given. It seems to be very interesting to learn whether such groups are also active against foreign quenchers. We are intending to study this in the near future.

3. Conclusions

The preceding explanations may have shown that it is possible to correlate so far almost all properties requested from an organic scintillator solute with controllable structural concepts in the oligophenylene series. This class of substances—which seems worth mentioning in this connection—is especially suited for systematic research. By variation of the type of condensation, the degree of condensation, the number of substituents, the position of substituents, and finally also the type of substituents, one obtains always broad spectra of compounds falling in a homologous relation to each other. This, finally, is an essential supposition for systematic investigations on a phenomenological base.

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