

>7.5. Equation 10 may now be reexpressed as

$$(b/a) = 6r(\text{IDA}) \quad \text{pH} > 7.5 \quad (11)$$

From Figure 2 we have $r(\text{IDA}) \approx 0.11$ at $\text{pH} > 7.5$ leading, therefore, to a value of ~ 0.66 for (b/a) . This value of 0.66 for (b/a) indicates that the deactivating efficiency of a bound NH oscillator is only about two-thirds that of a bound water OH oscillator.

Essential to our calculation of the $(b/a) = 0.66$ value (given above) are the assumptions of nine-coordination and tris-terdentate Tb^{3+} -IDA chelation at high pH (>7.5). These assumptions would appear to be amply justified by the independent results presented in this study and by the expected isostructural behavior of the $\text{Tb}(\text{MIDA})$ and $\text{Tb}(\text{IDA})$ complexes at high pH.

Conclusion

In this study we have used potentiometric titration data, absorption spectra, and luminescence decay measurements to examine the formation and structure of $\text{Tb}(\text{IDA})$ and $\text{Tb}(\text{MIDA})$ complexes in aqueous solution as a function of pH. Analysis of the various experimental data reveals that Tb^{3+} -IDA chelation occurs primarily over the pH region 4-7, with tris-terdentate $\text{Tb}(\text{IDA})_3^{3-}$ complexes being the dominant species at high pH (>8.0). It was found that Tb^{3+} -MIDA chelation occurs primarily over the pH region 3.5-9.0, with tris-terdentate $\text{Tb}(\text{MIDA})_3^{3-}$ complexes being the dominant species at $\text{pH} > 9.0$. In both the $\text{Tb}^{3+}/\text{IDA}$ and $\text{Tb}^{3+}/\text{MIDA}$ systems, the region of chelation corresponds closely to the pH region over which terbium-induced early deprotonation of ligand ammonium groups occurs. Finally, an analysis of the luminescence decay data on the $\text{Tb}^{3+}/\text{IDA}$ and $\text{Tb}^{3+}/\text{MIDA}$ systems obtained in the high pH region allowed calculation of the

relative radiationless deactivation efficiencies of NH oscillators vs. OH oscillators belonging to ligand donor groups or to bound water molecules. This latter determination will make possible the extension of the luminescence decay "water-counting" method for Tb^{3+} complexes in aqueous solution to ligand systems containing primary amine or secondary amine donor groups. An important class of such systems are protein molecules in which the lanthanide ion binding sites may present amine donor groups.

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Effect of Substituents on the Melting Points and Spectroscopic Characteristics of Some Popular Scintillators

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The melting points of several fluorescent chromophores, such as anthracene, several *p*-oligophenylenes, and BBD, have been dramatically reduced by the addition of alkyl or vinyl substituents. In the case of anthracene and *p*-terphenyl, the melting points of a number of derivatives are below room temperature. Some of the desirable characteristics that accompany these structural modifications are a dramatic increase in solubility in aromatic solvents and a greater immunity to self-quenching and quenching by high *Z* atoms. In all cases, the substituents have been so positioned that the favorable fluorescence characteristics of the parent chromophore have not been impaired.

Introduction

It has been demonstrated that the addition of methyl or ethyl substituents on the *p*-oligophenylenes will greatly increase their solubility in aromatic solvents.¹ This work has been extended to investigate the effect of substituents on the melting points. In particular, it was of interest to learn whether it was possible to decrease the melting point of a chromophore to a value below room temperature and

whether the chromophore would continue to maintain its favorable fluorescence characteristics. To date, there are no well-known liquid chromophores that have a short decay time and/or a high fluorescence quantum yield; e.g., the quantum yield of 1-methylnaphthalene is about 0.25 and that of 3,3'-dimethylbiphenyl is about 0.21.²

Our major effort has been directed toward investigating the *p*-oligophenylenes, compounds that have very desirable

TABLE I

| compound | $\lambda_{\text{max}}^{\text{fl}}$, nm | $\lambda_{\text{max}}^{\text{ab}}$, nm | L/L_0 | L_B/L_{B_r} | quantum yield, $\pm 10\%$ | decay time, ns | mp, °C |
|--------------------------|---|---|---------|---------------|---------------------------|-----------------|---------|
| <i>p</i> -terphenyl | 340 | 277 | 1.09 | 3.7 | 0.93 | 1.10 ± 0.05 | 212 |
| SG-15 | 351 | 287 | 1.08 | | 0.93 | 1.06 ± 0.05 | 30 |
| SG-52 | 375 | 298 | 1.06 | 1.3 | 0.99 | | oil |
| SG-53 | 351 | 287 | 1.06 | 2.2 | 0.93 | | oil |
| SG-56 | 375 | 293 | 1.07 | 1.3 | 0.99 | | oil |
| SG-57 | 367 | 295 | 1.05 | 1.6 | 0.99 | | oil |
| SG-58 | 351 | 287 | 1.06 | 2.1 | 0.93 | 1.07 ± 0.05 | oil |
| SG-59 | 354 | 290 | 1.04 | 1.7 | 0.93 | | oil |
| SG-63 | 348 | 283 | 1.10 | 1.9 | 0.93 | | 52 |
| SG-136 | 378 | 299 | 1.08 | 1.3 | 1.00 | 0.94 ± 0.05 | oil |
| <i>p</i> -quaterphenyl | 365 | 294 | 1.03 | 1.4 | 0.89 | 0.8^2 | 300 |
| SG-87 | 371 | 301 | 1.07 | 1.4 | 1.00 | 0.85 ± 0.05 | 48 |
| SG-80 | 401 | 316 | 1.10 | 1.4 | 1.00 | 0.75 ± 0.05 | 350 dec |
| BBD | 379 ^a | 318 ^a | | | 1.00 | 1.00 ± 0.05 | 229 |
| SG-122 | 397 | 325 | 1.04 | 1.5 | 1.00 | 0.97 ± 0.05 | 109 |
| anthracene | 400 | 357 | 1.25 | 14.5 | 0.36 ² | 5.0^2 | 216 |
| 9,10-diphenyl-anthracene | 429 | 373 | 1.38 | 1.2 | 1.00 | 7.58^{10} | 248 |
| SG-35 | 421 | 362 | 1.26 | 5.2 | 0.36 | | oil |
| SG-37 | 430 | 378 | 1.67 | 1.2 | 0.83 | | 105 |
| SG-38 | 421 | 362 | | | | | oil |
| SG-40 | 428 | 379 | 1.64 | 1.2 | 0.94 | | 88 |
| SG-41 | 430 | 378 | 1.60 | 1.2 | 0.94 | | oil |
| SG-44 | 428 | 379 | 1.55 | 1.2 | 0.90 | | oil |
| SG-45 | 430 | 378 | 1.44 | 1.2 | 0.89 | | oil |
| SG-46 | 410 | 368 | 1.30 | 1.8 | 0.42 | | 47 |

^a In benzene.

fluorescence characteristics such as high fluorescence quantum yields, fast decay times, and large Stokes shifts. Three chromophores of this set of compounds have been investigated—*p*-terphenyl, *p*-quaterphenyl, and *p*-sexi-phenyl.

Anthracene as a crystal has a much larger scintillation quantum yield than any other organic crystal, commercial scintillation cocktail, or plastic scintillator. In solution, however, its fluorescence quantum yield is not very impressive. At low solute concentrations, the quantum yield is about 0.36, and the decay time is about 5 ns.² At high concentrations, these parameters are even smaller because of strong self-quenching. When phenyl groups or alkyl chains are attached to the 9 and 10 positions, the fluorescence quantum yield is improved and the self-quenching is greatly reduced. It was of interest to learn whether there were any surprises when the melting point of an anthracene derivative was reduced to below room temperature.

Various oxazole and oxadiazole compounds have been extensively employed in scintillation detectors. One of these, BBD, has been investigated² but not used because of its low solubility. Since this compound has a shorter decay time than other similar chromophores and its fluorescence quantum yield is close to unity, it follows that if the solubility could be sufficiently increased, this compound would become a popular candidate as a component in scintillation cocktails and scintillation plastics.

Measurements

The new compounds that were synthesized and their spectroscopic characteristics are tabulated in Table I. The chemical nomenclature of each compound is listed in the Appendix.

The fluorescence and absorption measurements were made with a Beckman DK-2A spectrophotometer, and the measurements were made on dilute cyclohexane solutions.² In Table I, the values of the fluorescence maximum, $\lambda_{\text{max}}^{\text{fl}}$, and of the absorption maximum, $\lambda_{\text{max}}^{\text{ab}}$, are recorded.

The fluorescence quantum yields of the derivatives were determined by comparing them with the parent chromo-

phores. The techniques and corrections employed are similar to those reported in ref 2.

The fluorescence decay times were measured with a new and versatile apparatus that has just been completed.³ In brief, this apparatus consists of a high gain photomultiplier (56 UVP), a pulse sampling oscilloscope, a small on-line computer, and a data storage disk. Measurements can be made either with pulsed UV excitation or with ionizing particles. To analyze the data, programs are available for the deconvolution and the convolution of pulse contours. A very desirable feature of this equipment is that the data can be conveniently recorded, stored, and/or immediately evaluated on demand.

To determine the sensitivity of these compounds to quenching by oxygen, we first measured the fluorescence intensity from a dilute nitrogen-bubbled solution and then we measured the intensity from an aerated solution (L_0). The value of the ratio L/L_0 is an indication of the sensitivity of the compound to oxygen quenching. Generally, this ratio is linearly related to the lifetime of the excited state.⁴

A measure of the sensitivity of these new compounds to heavy atom quenching is given by the ratio L_B/L_{B_r} , where L_B is the fluorescence intensity from a dilute benzene solution and L_{B_r} is that from a bromobenzene solution of the same concentration. Both solutions were nitrogen bubbled to remove oxygen.

Results

Eight substituted anthracenes, ten substituted *p*-oligo-phenylenes, and one substituted BBD compound have been synthesized.⁵ In each case there is a dramatic reduction of the melting point. Of special interest were the four anthracene derivatives and six *p*-terphenyl derivatives whose melting points were below room temperature.

The melting point of anthracene has been reduced from about 216 °C to below room temperature for the compounds labeled SG-35, SG-38, SG-41, SG-44, and SG-45 (see Table I and Appendix). In other cases, the effect was less; e.g., the melting point of SG-37 is about 105 °C, that of SG-40 is about 88 °C, and that of SG-46 is about 47 °C.

As expected, two similar substituents have a larger effect on lowering the melting point than a single one (cf. SG-45 and SG-46), and two nonidentical substituents are more effective than two similar ones (cf. SG-38 and SG-45). Since substituents on the 9 and 10 positions of anthracene are effective in increasing the fluorescence yield as well as depressing the melting point, most of our effort was directed toward the investigation of these types of derivatives.

The melting point of *p*-terphenyl (about 212 °C) has been reduced to below room temperature for the compounds as listed in Table I: SG-52, SG-53, SG-56, SG-57, SG-58, and SG-59. Each of these *p*-terphenyl derivatives has a substituent on both para positions. When only one para position is occupied by an alkyl chain, as in SG-63, the melting point is about 52 °C.

The melting points of the larger chromophores of the *p*-oligophenylenes starting with *p*-quaterphenyl are much higher, and it becomes more difficult to depress the melting point to below room temperature. As an example, the melting point of *p*-quaterphenyl is >300 °C, and it has been reduced to about 48 °C by the addition of 5-eicosyl substituents on both para positions (e.g., SG-87). In the case of *p*-sexiphenyl, whose melting point is about 465 °C, the melting point has been reduced to about 350 °C by the substitution of 5-(2-methyldodecyl) on both para positions, as in SG-80. Work is still in progress to reduce even further the melting point of these larger chromophores.

The melting point of BBD is about 230 °C. In the case of the derivative of BBD, i.e., SG-122, the melting point is about 110 °C.

The spectroscopic data were without any surprises. Both the absorption and fluorescence spectra of the derivatives generally are slightly red-shifted relative to those of the parent chromophore, but the shapes and intensities of the band structures are similar. The spectra from derivatives with two substituents are more red-shifted than those from derivatives with only one substituent (cf. SG-59 and SG-63). When a substituent contains a vinyl group, not only does it produce a larger shift but it also produces a measurable increase in the value of the molar extinction coefficient, as would be expected from an increase in the size of the chromophores.

A characteristic of the *p*-oligophenylenes and BBD is that the absorption spectra are not structured, whereas the fluorescence spectra are slightly structured. This result is explained by the fact that the chromophore is more planar in the first excited singlet state than in the ground state. The large Stokes shift found in these spectra and the resultant large transparency of these compounds to their own radiation may also be explained by this difference in planarity between the two electronic states. Since the spectra of the derivatives and other characteristics are so similar to those of the parent chromophore, except for the small red shift, it is assumed that the substituents do not interfere with the planarity of the chromophore.

In the case of the anthracenes, the spectra of the substituted derivatives are also red-shifted with respect to the parent chromophore. Both spectra are highly structured and the Stokes shift is small, with the result that these compounds are subject to strong self-absorption. These results are consistent with the fact that these chromophores are planar in both the ground and the first excited singlet state.

The values of the quantum yield and the decay time are intimately related. In the case of alkyl substituents on the *p*-oligophenylenes and on BBD, there is no significant change in molar extinction coefficient or in the transition

moment, so that the values of the decay time and the quantum yield remain essentially those of the parent chromophore. When the substituent on *p*-terphenyl contains a vinyl group, there is an increase in the value of the transition moment so that there is a decrease in the natural fluorescence lifetime. There is a concurrent small increase in the quantum yield which cancels the change in the lifetime, so that the measured decay time is approximately that of the parent chromophore.

In the case of the anthracene derivatives, other factors, such as self-quenching and intersystem crossing, must be considered. The quantum yield and therefore the decay time are strongly dependent on the number, position, and type of substituent. When the substituent is on the 1 position as in SG-35, the quantum yield is similar to that of anthracene, i.e., about 0.36. However, if the substituent is on the 9-position, the quantum yield is slightly larger, i.e., about 0.49 for 9-phenylanthracene² and about 0.42 for 9-butylanthracene. When substituents are positioned on both 9 and 10 positions, the quantum yield approaches unity. If the quantum yield of 9,10-diphenylanthracene is taken as unity,^{2,6} then the quantum yields of SG-41, SG-44, and SG-45 are about 0.94, 0.90, and 0.89, respectively. Since the natural lifetimes are approximately unchanged, the measured decay times are correspondingly increased.

Whereas the fluorescence quantum yield of anthracene as a crystal is unity, the quantum yield in dilute solution is much smaller. This large difference in quantum yield is explained by Kellogg⁷ as being due to a shift in energy of the second triplet level, ³L_b, with respect to the lowest excited singlet level, ¹L_a, in the two cases. The triplet level is below the singlet level in solutions and is above the singlet level in the crystal. Likewise, the high quantum yield of 9,10-diphenylanthracene and the other 9- and 10-substituted derivatives is explained by Ting⁸ as being due to the same mechanism. The rate of intersystem crossing is a function of the position of this second triplet level.

The values of quantum yield and decay time as shown in Table I are for dilute cyclohexane solutions with excitation by UV radiation. Although the quantum yields of alkyl-substituted *p*-terphenyls in the neat condition are approximately those of the compounds, in dilute solutions, this is not the case for alkyl-substituted anthracenes. Surprisingly, the quantum yields of the latter compounds are less than a percent in the neat condition. A possible explanation for these low yields is that these compounds are photochemically unstable, as they readily turn yellow even when kept in the dark and under nitrogen conditions. Under irradiation and in the neat condition, the photochemical products are in close proximity to excited molecules, and their influence as quenchers or as energy acceptors can be readily felt. In dilute solutions the concentrations and therefore the respective distances are very much larger.

The alkyl-substituted *p*-terphenyls were also investigated in benzene solutions under various concentrations and with β particle excitation. The scintillation light yield was found to increase as a function of concentration up to about 20 g/L. At higher concentrations, this maximum value remained essentially constant until and including the neat condition. There was not sufficient material of the other types of compounds to make similar investigations.

The quenching by oxygen is a diffusion-controlled process with each encounter leading to quenching,⁴ so that the value of L/L_0 generally is inversely proportional to the lifetime of the excited state. Since the values of this ratio

and the decay times remain essentially unchanged with substitution, it may be concluded that the substituents do not appear to offer any protection or hindrance to the quenching process. The slightly larger values of L/L_0 for the substituted anthracenes are mainly related to an increase in decay time and less so to any protection mechanism.

In the case of heavy atom quenching, it is noticed that there is an appreciable reduction in the value of L_B/L_{B_0} for the substituted compounds. Here the substituents do offer some steric hindrance to the quenching process. This result is in agreement with previous observations⁹ that a close approach between the heavy atom and a chromophore is necessary for the increased rate of intersystem crossing and for effective quenching of the fluorescence state. The substituents act as "bumpers" and hinder a close approach.

Conclusions

Straight and branched alkyl groups are effective substituents in reducing the melting point of a chromophore. In fact, the melting points of many compounds can be reduced to below room temperature without interfering with the favorable fluorescence characteristics of the parent chromophore. In all cases some ingenuity is required in knowing where to position the substituents and then in effecting an efficient synthesis procedure.

As expected, there is a dramatic increase in the solubility as the melting point is decreased. In particular, those substituted compounds that are liquid at room temperature have almost unlimited solubility in aromatic solvents.

Unfortunately almost all of the substituted anthracenes and anthracene itself are photochemically unstable. The compound 9,10-diphenylanthracene appears to be more stable than the others.

The encouraging results from the *p*-oligophenylenes and other linear chromophores, such as BBD, however, open up new experimental vistas. New types of scintillators with high solubilities are now available as components of new types of scintillation cocktails and scintillation plastics. Our present work is continuing along the lines of this report and is directed toward producing scintillation detectors that have more favorable characteristics than those presently available commercially.

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Appendix: Code for the Compounds

| | |
|--------|--|
| SG-15 | <i>p,p'</i> -dihexadecyl- <i>p</i> -terphenyl |
| SG-52 | 4-[6-(5-ethylundec-6-enyl)]-4''-(6-undec-6-enyl)- <i>p</i> -terphenyl |
| SG-53 | 4-[6-(5-ethylundecyl)]-4''-(6-undecyl)- <i>p</i> -terphenyl |
| SG-56 | 4-(6-dodec-6-enyl)-4''-[6-(5-ethyldodec-6-enyl)]- <i>p</i> -terphenyl |
| SG-57 | 4-[4-(3-methyl-5-ethylnon-4-enyl)]-4''-[4-(3-methylnon-4-enyl)]- <i>p</i> -terphenyl |
| SG-58 | 4-(6-dodecyl)-4''-[6-(5-ethyldodecyl)]- <i>p</i> -terphenyl |
| SG-59 | 4-[4-(3-methyl-5-ethylnonyl)]-4''-[4-(3-methylnonyl)]- <i>p</i> -terphenyl |
| SG-63 | 4-[6-(5-ethyldodecyl)]- <i>p</i> -terphenyl |
| SG-80 | 4,4''''-bis[5-(2-methyldodecyl)]- <i>p</i> -sexiphenyl |
| SG-87 | 4,4''''-bis(5-eicosyl)- <i>p</i> -quaterphenyl |
| SG-136 | 4,4''-bis(8-hexadec-8-enyl)- <i>p</i> -terphenyl |
| BBD | 2,5-bis(4-biphenyl)-1,3,4-oxadiazole |
| SG-122 | 2,5-bis[4-(9-heptadecyl)-4'-biphenyl]-1,3,4-oxadiazole |
| SG-35 | 2-(1-anthryl)-2-octene |
| SG-37 | 9,10-dibutylanthracene |
| SG-38 | 2-(1-anthryl)-2-decene |
| SG-40 | 9-butyl-10-isopentylanthracene |
| SG-41 | 9-butyl-10-(4-octyl)anthracene |
| SG-44 | 9-butyl-10-(2-ethylbutyl)anthracene |
| SG-45 | 9-butyl-10-(2-butyl)anthracene |
| SG-46 | 9-butylanthracene |

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