Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Scintillation Measurements at Very High Solute Concentrations; Self Quenching-Structure Correlatios

Donald L. Horrocks [a] & Hermann O. Wirth [a b]
[a] Chemistry Division, Argonne National Laboratory, Argonne, Illinois, 60439
[b] Johannes Gutenberg-Universität, Mainz, Germany
Version of record first published: 21 Mar 2007.

To cite this article: Donald L. Horrocks & Hermann O. Wirth (1968): Scintillation Measurements at Very High Solute Concentrations; Self Quenching-Structure Correlatios, Molecular Crystals, 4:1-4, 375-383

To link to this article: http://dx.doi.org/10.1080/15421406808082924

Molecular Crystals, 1968. Vol. 4, pp. 375–383

Printed in Germany

Scintillation Measurements at Very High Solute Concentrations; Self Quenching-Structure Correlations†

DONALD L. HORROCKS AND HERMANN O. WIRTH‡

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

Abstract—Measurements of the relative scintillation yields of some liquid organic systems were carried out with several highly soluble scintillator solutes. Self quenching was observed at high concentrations with some of the solutes, but not with others. The results were correlated with the ability of the solute molecules to come together, in a special configuration, close enough to form an association. A study of the atomic models of the solute molecules showed that those molecules with chromophor systems which were non-coplanar, or co-planar but shielded by substituent groups, did not produce self quenching. However, those solute molecules with unprotected co-planar chromophor systems did produce self quenching at high solute concentrations.

1. Introduction

The scintillation properties of liquid organic systems at very high solute concentrations had not previously been investigated in detail because most efficient scintillator solutes (except PPO) have limited solubility in the commonly used organic solvents. The recent development of highly soluble scintillator solutes,[1] which are derivatives of basic molecules previously used as solutes, has now made such studies possible. The solubility of the solutes is greatly increased by the substitution of alkyl and alkyloxy groups onto a basic solute molecule. This technique does not appreciably alter the scintillation properties of the solute molecule.[1]

From this study information was obtained about scintillation properties at very high solute concentrations and about the nature of the self quenching process. Also some information was obtained about the ability of the substituent group to shield the solute molecule from self quenching.

† Based on work performed under the auspices of the U.S. Atomic Energy Commission.

‡ Formerly of the Johannes Gutenberg-Universität, Mainz, Germany.

2. Experimental

Equipment

A simple single multiplier phototube scintillation detector was used in this work. This has been previously described.[2]

Chemicals

The solvent for all samples was research grade toluene from Phillips Petroleum, Bartlesville, Oklahoma. Table 1 shows the formulas and other important information for the scintillator solutes used in this work. The 1,1′-binaphthyl* (BN) and the $1^1,4^4$-di(2-butyloctyloxy)-p-quaterphenyl† (QP-G12) were obtained commercially. The other compounds were specially synthesized‡ The solutes were specially purified whenever necessary.[1]

Sample Preparation

The samples were prepared by accurately weighing both the solute and solvent. This required the use of a micro balance since the sample size was only 0.25 ml. The samples were prepared in thin walled quartz sample containers as described elsewhere.[2] Due to the very high solute concentrations of some samples, the concentrations were expressed as the mole fraction, γ;

$$\gamma = \frac{n_1}{n_1 + n_2}$$

n_1 = moles of solute

n_2 = moles of solvent

Counting Procedure

The samples were excited with an external Cs-137 γ-ray source. The Cs-137 γ-rays produced Compton electrons in the scintillator solution and these excited the sample. The Compton electrons give a very characteristic spectrum (Fig. 1). The relative light yield was proportional to the relative pulse height (RPH) value of the Compton edge.

3. Results

Figure 2 shows the comparison of the relative scintillation yields of PPO and the two *p*-quaterphenyl derivatives, QP-G12 and QP-G16, as a

* K and K Laboratories, Inc., Jamaica, New York.

† Supplied by the courtesy of E. Merck AG, Darmstadt, Germany.

‡ Work partly performed under the auspices of the Bundesministerium für Wissenschaftliche Forschung, Bad Godesberg, Germany.

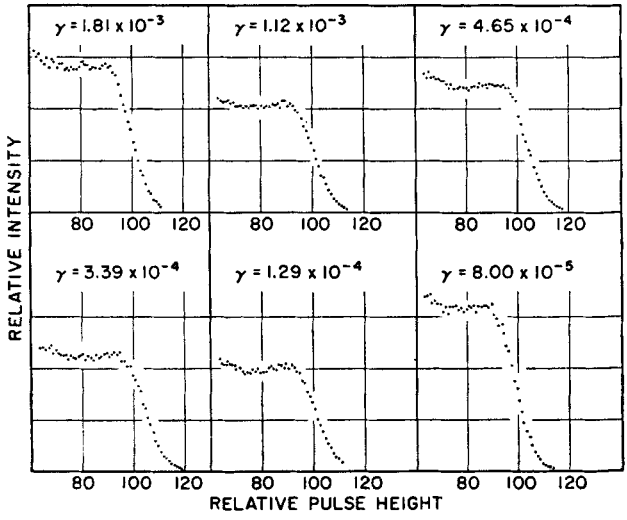


Figure 1. Typical Compton electron spectra for Cs-137 gamma ray excitation of solutions of BN-11.

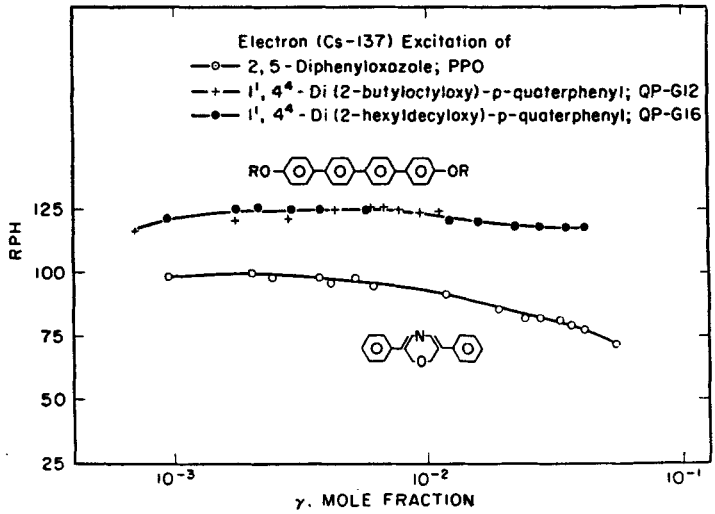


Figure 2. Scintillation yield as a function of concentration for PPO and two dialkyloxy-*p*-quaterphenyl derivatives.

function of their concentration, γ. There is self quenching at the higher concentrations of PPO. The amount of self quenching is less than reported in another study.[3] This is partly due to the experimental techniques employed in this study which eliminated self absorption and oxygen quenching. The measurement of the excimer emission also contributes to this apparent higher light production at the higher concentrations.

Both of the *p*-quaterphenyl derivatives showed no self quenching. An effect due to the different size of the two alkyloxy groups was not observed. Further work will be necessary to determine the effect of the size of the substituent group on self quenching. The slight decline in the RPH *vs* concentration curve at high concentrations might be explained as a "solvent dilution"† effect.

The results of a study of a series of binaphthyl derivatives; BN, BN-4, and BN-11; are shown in Fig. 3. This series is interesting because of the large difference in the size of the substituent and the similar solubilities of these compounds (Table 1). However, the results show no difference which can be attributed to a difference in the size of the alkyloxy groups.

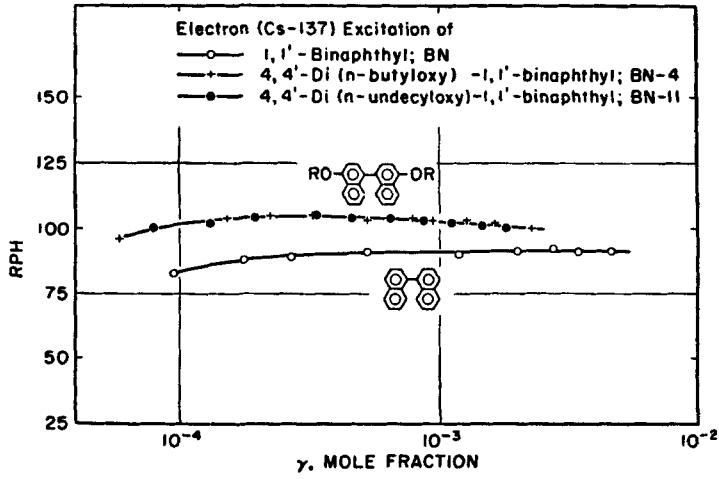
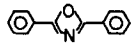
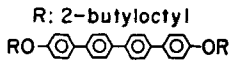
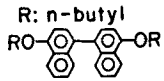
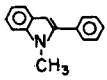
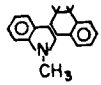


Figure 3. Scintillation yields as a function of concentration for a series of 1,1′-binaphthyl derivatives.

† Hayes *et al.*[4] observed that the addition of aliphatic hydrocarbon solvents to liquid scintillator solutions produced a decrease in the scintillation yield.

TABLE 1

Structural Formula	Symbol	Solubility (toluene 20°C) [g/l]	Optical Data λ max (Absorpt.) [Å]	Optical Data λ mean (Fluoresc.) [Å]
	PPO	250	3060	3760
 R: 2-butyloctyl R: 2-hexyldecyl	QP-G12	63	3090	3855
	QP-G16	370	3090	3855
 R: n-butyl R: n-undecyl	BN-4	79	3080	3910
	BN-11	94	3080	3910
	BN	100	2860 2960	3700
	PI-NI	200	3010	3810
	EPI-NI	250		3940

Even with the completely unshielded 1,1′-binaphthyl (BN) no self quenching is observed.

The 1,1′-binaphthyl (BN) does not show the slight decline in the RPH *vs* concentration curve at high concentrations. This is further evidence that the slight decline observed at high concentrations of the dialkyloxy binaphthyls (BN-4 and BN-11) is most likely due to the "solvent dilution" effect. In fact the data indicate a slightly greater "solvent dilution" effect with BN-11 than BN-4.

The higher RPH values obtained with the dialkyloxy binaphthyl compounds compared to BN are due to the fact that alkyloxy groups which are in a position of conjugation with the chromophor system of the basic molecule result in a higher scintillation efficiency.[1]

Self quenching is also observed for N-methyl-2-phenylindole (PI-N1) which increasing concentration (Fig. 4). The decrease in RPH values with increasing concentration of PI-N1 is even greater than that observed for PPO. The ethylene bridged N-methyl-2-phenylindole (EPI-N1), which has the same chromophor as PI-N1, showed no self quenching with increasing concentration (Fig. 4).

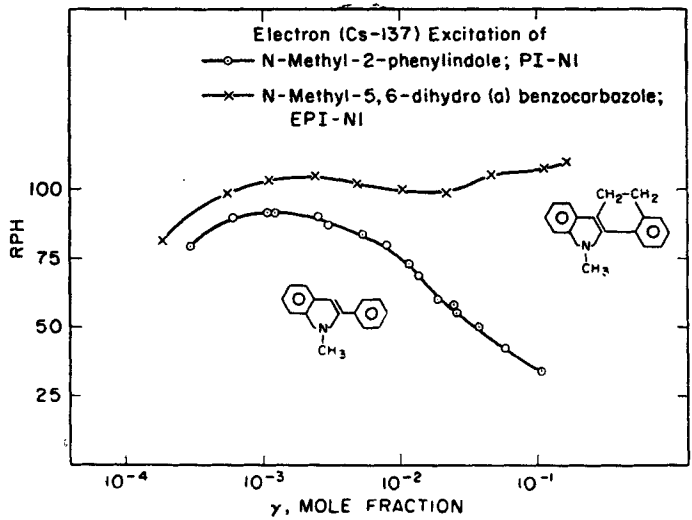


Figure 4. Scintillation yields as a function of concentration for two phenylindole derivatives, PI-NI and EPU-Nl.

4. Discussion

It is concluded from this work that the presence or absence of self quenching with solute molecules can be correlated with the stereochemical structure of the molecules. The atomic models of the solute molecules are used to explain the results. Self quenching seems to occur only when two solute molecules (one in an excited state) are able to come very close together in a manner such that there is a complete overlap of the whole chromophor system.[5]

For the dialkyloxy substituted compounds; QP-G12, QP-G16, BN-4 and BN-11; the bulkiness of the substituents shields the chromophor system from self quenching by preventing the close approach of two solute molecules in the proper orientation for overlap of the whole

chromophor system. The atomic model of QP-G12 (Fig. 5) shows the shielding of the large substituents.

The atomic model of 1,1′-binaphthyl (BN) (Fig. 6) shows that this molecule is not co-planar. This non-co-planarity prevents two molecules from coming together in such a manner as to have a complete overlap of the whole chromophor systems. Therefore, even the completely unprotected BN does not produce self quenching.

The atomic models of PPO (Fig. 7) and PI-N1 show that the co-planar configuration of the chromophor systems of these molecules is very propable and that they are completely unshielded. Thus two solute molecules of PPO or PI-N1 can come very close together in the special orientation required for the complete overlap and matching of the chromophor systems and produce self quenching.

There was no self quenching observed with increasing concentration of EPI-N1, this is just the opposite of the results for PI-N1. The ethyleno bridge produces a non-co-planar chromophor systems by rotating the

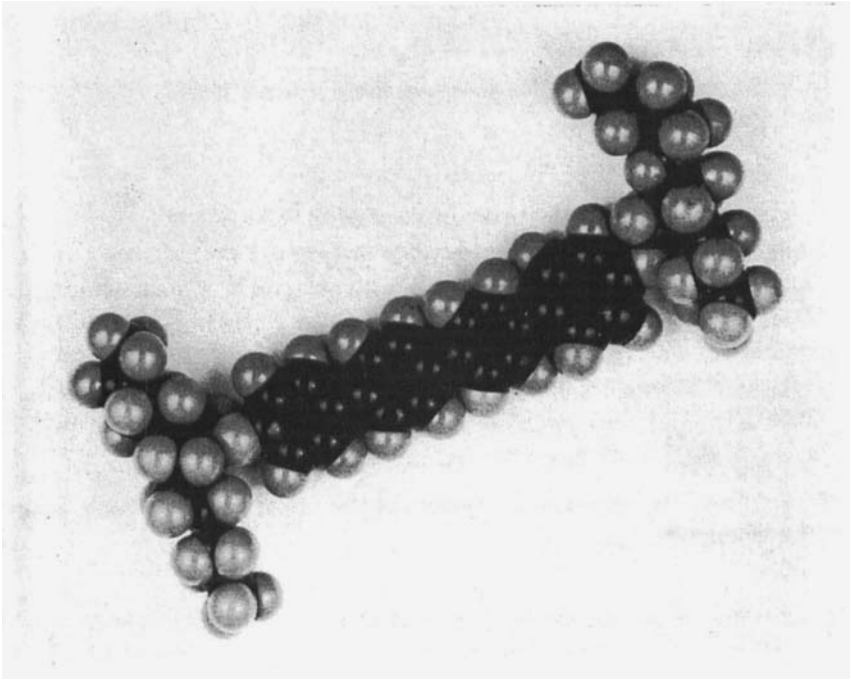


Figure 5. Atomic model of $1^1,4^4$-di(2-butyloctyloxy)-*p*-quaterphenyl (QP-G12).

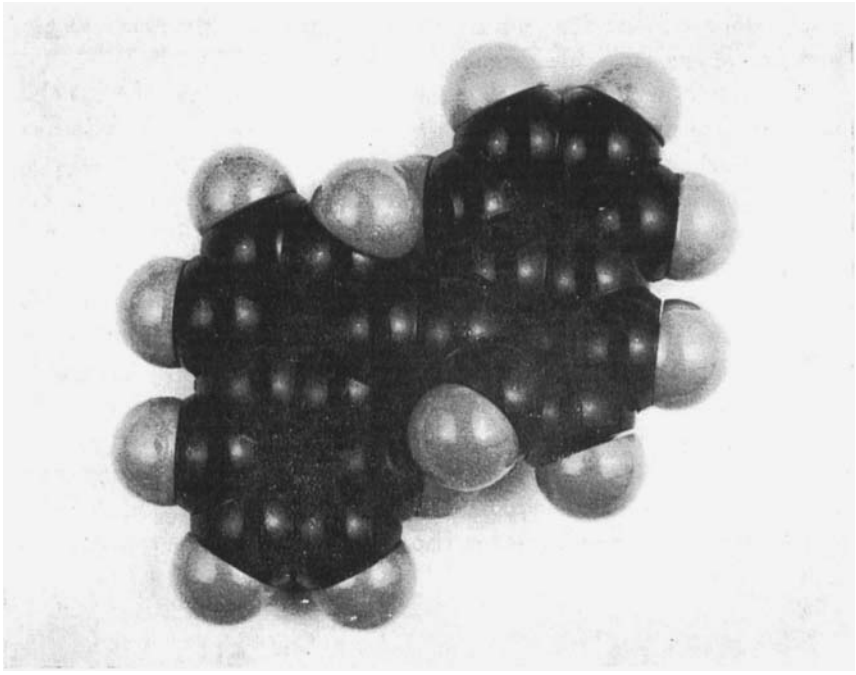


Figure 6. Atomic model of 1,1′-binaphthyl (BN).

2-phenyl ring out of the plane of the rest of the molecule. However, the optical properties of the chromophor system are not affected (Table 1). Again this demonstrates that with a non-co-planar chromophor system it is impossible to have overlap in the manner necessary for association which will lead to self quenching.

It is concluded that two types of steric situations will prevent the close approach and complete matching and overlap of the chromophor systems that is necessary for self quenching:

1. Where the chromophor system of the solute molecule has a non-co-planar configuration

and

2. where a solute molecule, which has a chromophor system with a co-planar configuration, is shielded by the substitution of a bulky group.

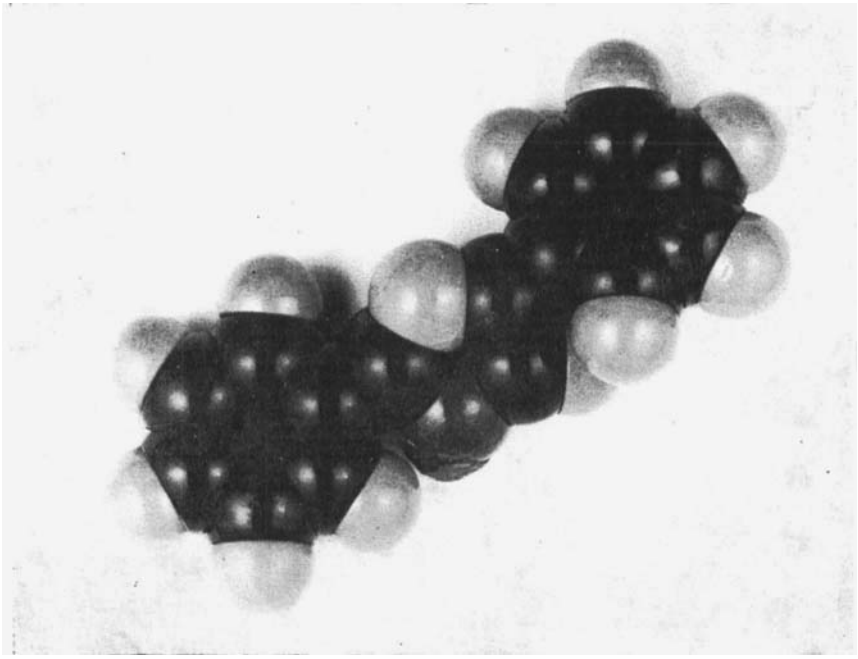


Figure 7. Atomic model of PPO.

REFERENCES

1. Wirth, H. O., Herrmann, F. U., Herrman, G. and Kern, W., International Symposium on Organic Scintillators, Argonne National Laboratory, June 20–22, 1966; Wirth, H. O., International Symposium on Luminescence, Munich, September 5–9, 1965; Wirth, H. O., *Chemiker Ztg.* **89**, 517 (1965); Wirth, H. O., Waese, G. and Kern, W., *Makromolekulare Chem.* **86**, 139 (1965).
2. Horrocks, D. L., International Symposium on Organic Scintillators, Argonne National Laboratory, June 20–22, 1966.
3. Kallmann, H. and Furst, M., *Liquid Scintillation Counting*, Ed. Bell, C. G. and Hayes, F. N. (London: Pergamon Press) p. 3 (1958).
4. Hayes, F. N., Rogers, B. S. and Sanders, P. S. *Nucleonics* **13**, No. 1, 46 (1955).
5. Stevens, B., *Spectrochim. Acta.* **18**, 439 (1962).