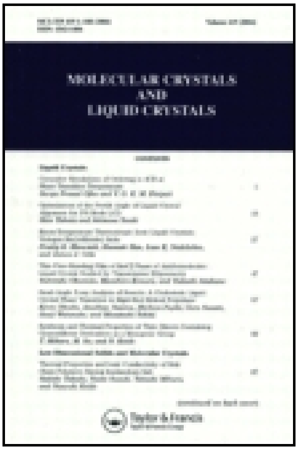

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

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Version of record first published: 21 Mar 2007.

To cite this article: Peter Leggate & Derrek Owen (1968): The Fluorescence and Scintillation Properties of New Oxazoles, Oxadiazoles and Pyrazolines, Molecular Crystals, 4:1-4, 357-373

To link to this article: http://dx.doi.org/10.1080/15421406808082923

Molecular Crystals, 1968. Vol. 4, pp. 357–373
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Printed in Germany

The Fluorescence and Scintillation Properties of New Oxazoles, Oxadiazoles and Pyrazolines

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Received August 22, 1966

Abstract—The advantages of using a secondary solute in plastic and liquid scintillators, and the manner in which such solutes define scintillation performance, are reviewed. Potential secondary solutes of general structure Ar_1-X-Ar_2-X-Ar_1, where X is an oxadiazole, oxazole or 5-phenylpyrazoline group, were synthesized and their spectral and scintillation properties were measured. The relationship between the molecular structure of these compounds and their spectral properties is examined. It is postulated that anomalous spectral displacements which were observed can be explained in terms of the distorting effect of the heterocyclic groups on the conjugated system. A procedure is outlined for the direct measurement of the reabsorption by a solute of its own fluorescence emission. The contribution of reabsorption to light attenuation in practical scintillators is discussed and a model experiment is proposed to determine the extent of this contribution.

1. Introduction

A secondary solute is not an essential component of a liquid or plastic scintillator and its involvement in the mechanism of the scintillation process is of a trivial character when compared to the problems of energy absorption by the solvent and energy transfer from solvent to primary solute. Nevertheless the majority of practical scintillators use a secondary solute to provide a favorable spectral distribution of the scintillation emission, in spite of the longer decay time and reduced energy conversion efficiency of a two solute system. The optimum spectral properties of a scintillator are defined by the following factors:

1. The spectral sensitivity of the photocathode: until recently a wavelength shifter was essential in order to match the emission spectra of the scintillator with the spectral sensitivity of the photocathode. However, increasing use is being made of modern photomultiplier tubes, such as the RCA 8575, in which the range of maximum photocathode sensitivity is extended to shorter wavelengths and corresponds more closely to the emission spectra of the common primary solutes.

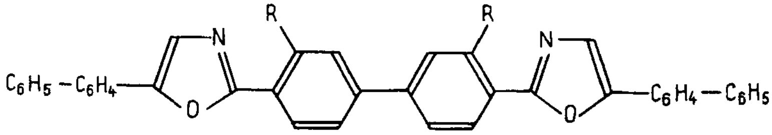
2. The absorption spectra of the solvent: measurements on plastic scintillators by Blincow and Webster[1] suggest that a major reduction in the attenuation of the scintillation light can result from the use of solutes with emission maxima above 400 mμ. To minimise absorption of the scintillation light the emission spectra should be shifted to the longest wavelength consistent with maximum photocathode sensitivity.

3. The absorption spectra of the solute: if self-absorption by a solute of its own fluorescence emission has a significant effect on scintillation performance, then the separation of the absorption and emission spectra (i.e. the Stoke's shift) must be taken into account in selecting the secondary solute. This criteria has not, however, been applied in practice and it is still uncertain to what extent self-absorption contributes to light attenuation.

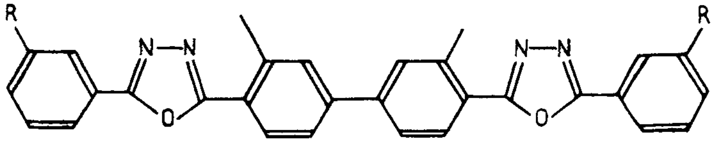
It is in theory possible to incorporate the desired spectral properties into the primary solute. The extensive studies of the *p*-oligophenylenes reported by Wirth[2] illustrate the extent to which modification of the molecular structure of the solute can produce predictable improvements in scintillation performance with respect to decay time, scintillation efficiency, solubility and spectral properties. However, the incorporation into a single solute of all the desired properties poses major problems in molecular design and synthesis. By comparison, in a two solute system, the structural requirements for either component are less rigid. The use of a secondary solute can therefore be considered as a means of reducing synthetic problems. The secondary solute is selected to give a long wavelength of emission and maximum Stoke's shift; these characteristics are then superimposed on a primary solute selected for high scintillation efficiency and adequate solubility.

In the present work an attempt is made to investigate the effect on spectral properties and scintillation performance of systematic variations in the chemical structure of potential secondary solutes. All the compounds investigated consist of linear chains of homocyclic and heterocyclic rings and have the general formula Ar_1-X-Ar_2-X-Ar_1 where X is a heterocyclic ring. Such structures can be formally derived from the *p*-oligophenylenes by replacement of two phenyl groups with two heterocyclic rings. Wirth[2] has shown that, in the *p*-oligophenylene series, an increase in the number of phenyl groups enhances scintillation efficiency and produces a bathochromic shift in the ultraviolet and fluorescence maxima. However, the magnitude of the spectral shift decreases with each additional phenyl group and the maxima tend toward limiting values in the higher members of the series. The compounds synthesized in the present work enable a limited study of the effects on scintillation and, more particularly, spectral properties of systematic increases in the length of the conjugated system in three series of mixed homocyclic-heterocyclic structures. The three series are designated as oxazoles, oxadiazoles, and pyrazolines according to the identity of the heterocyclic ring.

The oxazoles and oxadiazoles are analogues of POPOP and PDPDP[3, 4] and may be derived from these parent compounds by replacement of either the "central" or the "terminal" phenyl groups by other aromatic groups. Examples of these two series of compounds are BOBOB (I, R=H) and dimethyl-PDBDP (II, R=H):



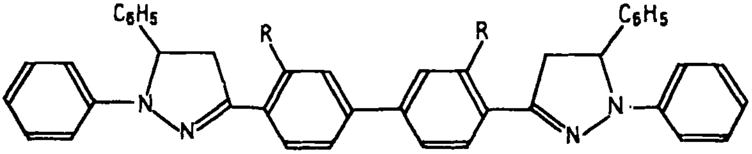
(I)



(II)

The oxazole BOBOB, which is formally analogous to a *p*-octiphenyl, is the most extended conjugated system prepared and, not unexpectedly, it is extremely insoluble. However, the two methyl substituents of dimethyl-BOBOB impart adequate solubility for evaluation as a secondary solute. For reasons of synthetic convenience all the dimethyl substituted compounds which were prepared have the methyl groups in the 3,3′-positions of a 'central' biphenyl group. The positions of the methyl groups in tetramethyl-PDBDP, the only compound containing more than two methyl substituents, are shown in II($R=CH_3$).

To emphasise the common structural features of all the three series of compounds, the conventional nomenclature used in the oxazole and oxadiazole series has been extended to the pyrazoline series by adoption of the letter Y to represent the 5-phenyl-2-pyrazoline group. Thus the abbreviation for the pyrazoline (III, R=CH_3) is dimethyl-PYBYP. Pyrazolines of this type were first reported by Baroni and Kovyrzina[5] who synthesised PYBYP (III, R=H) and PYTYP.[6] In the present work the synthesis of PYBYP was repeated and, in addition, dimethyl-PYBYP and PYPYP were prepared.



(III)

2. Experimental

Synthesis

The oxazoles and oxadiazoles were prepared by the standard procedures described by Hayes.[3] However, in the oxadiazole series, and particularly in those compounds having terminal 1-naphthyl groups, the final cyclisation required a ten-fold or more increase in reaction time. A variety of solvents were evaluated for use in the purification of these compounds. It was found that excellent solvents were dimethylacetamide for the less soluble compounds (e.g. POTOP), and ethylene glycol monomethyl ether (methyl cellosolve) or *iso*propanol for the more soluble solutes (e.g. tetramethyl-PDBDP, dimethyl-POBOP). The three pyrazolines were prepared by the method of Baroni and Kovyrzina.[5] Correct analytical data[7] were obtained for all the new compounds with the exception of NDPDN. Uncorrected melting points are listed in Table 1.

Absorption and Fluorescence Spectra

All spectra were measured in toluene solutions, both for reasons of solubility, and also in order to emulate the composition of a liquid scintillator. Absorption bands below 300 mμ could not therefore be observed. Absorption spectra in the range 300–500 mμ were measured in a Beckman DK-1 spectrophotometer.[8] A fluorescence attachment to the same instrument was used for the measurements of emission spectra. Concentrations of *ca.* 0.1 g/l (1.0–2.0 × 10^{-4} M) were used for the fluorescence measurements wherever solubility permitted. Front face excitation was by a mercury arc source (254 and 314 mμ lines). To provide good resolution of the fluorescence maxima a slit width of 0.2 mm was used for the majority of the spectra. Distortion of the fluorescence spectrum by self-absorption was investigated for each of the solutes by placing the solution under study both in the 1 cm cuvette of the fluorescence attachment and also in a 1 or a 10 cm cuvette which was placed in the compartment normally reserved for absorption samples. This geometry enables the fluorescence emission of a solution to be passed through a 1 or 10 cm length of the same solution before being detected by the photomultiplier tube. Curve A in Figs. 1, 2 and 3 is the fluorescence spectrum after passage through 10 cm of pure toluene. This spectrum showed a slight, wavelength independent, reduction in intensity compared to a spectrum obtained with no cuvette in the absorption compartment. This loss of intensity is attributable to scattering of the light beam as it enters and leaves the cuvette. Curves B and C show the fluorescence spectrum after passage through 1 and 10 cm. lengths of solution respectively.

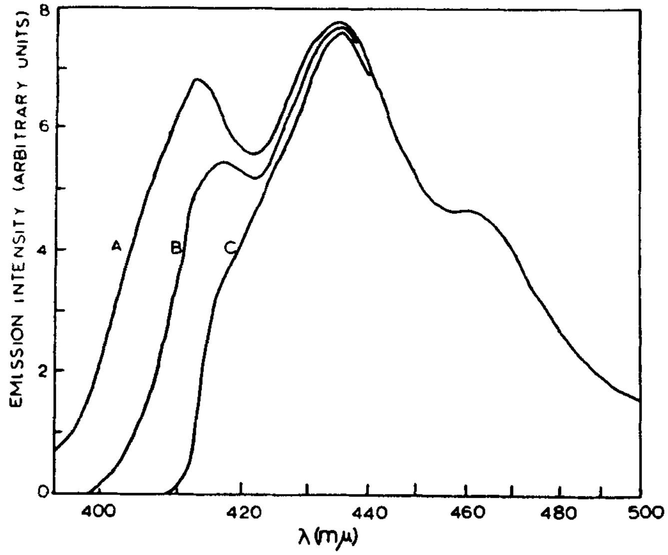
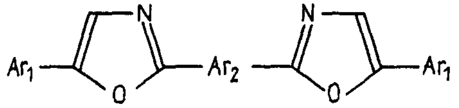
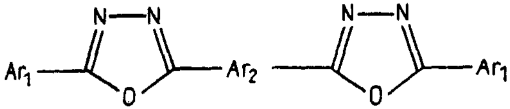
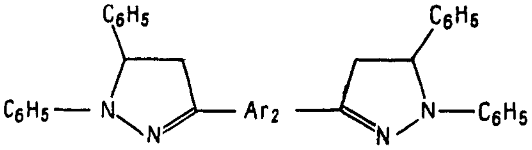


Fig. 1 Fluorescence Spectra of dime-BOBOB (1.3×10^{-4}M, 0.08 g/l)

TABLE 1 Spectral Data

Ar_1	Ar_2	Abbreviation	m.p (°C)	Absorption λ_{max}	Absorption ε_{max}	Fluorescence λ_{max}		
OXAZOLES								
								
phenyl	1,4-phenylene	POPOP	244–245	362^b	4.6	397	418	440
1,4- bis-(2-(4-methyl-5-phenyloxazolyl)-benzene		dimethyl-POPOP^c	231–234	368^b	5.1	408	429	453
phenyl	4,4′-biphenylylene	POBOP	228–231	352	6.1	400	421	444
phenyl	4,4′-(3,3′-dimethylbiphenylylene)	dimethyl-POBOP	202–204	348	5.8	400	422	445
phenyl	4,4″-terphenylylene	POTOP^d	300–302	350	7.8	401	423	447
4-biphenylyl	4,4′-biphenylylene	BOBOB	350 (dec.)	362	—	411	436	460
4-biphenylyl	4,4′-(3,3′-dimethylbiphenylylene)	dimethyl-BOBOB	252–255	359	7.1	413	436	460
4-biphenylyl	1,4-phenylene	BOPOB^e	327–328	376^b	6.6	414	437	464
1-naphthyl	1,4-phenylene	NOPON^e	215–217	363	4.0	421	443	469
OXADIAZOLES								
								
phenyl	1,4-phenylene	PDPDP	302–305^f	328^b	4.4	354	372	392
phenyl	4,4′-(3,3′-dimethylphenylylene)	dimethyl-PDBDP	240–241	325	5.3	371	388	405
3-tolyl	4,4′-(3,3′-dimethylphenylylene)	tetramethyl-PDBDP	227–229	325	5.2	371	389	408

1-naphthyl	1,4-phenylene	NDPDN[g]	—	348	—	378	400	422
1-naphthyl	4,4′-biphenylylene	NDBDN	319–324	342	—	381	404	422
1-naphthyl	4,4′-(3,3′-dimethylbiphenylylene)	dimethyl-NDBDN	280–281	342	6.0	382	404	422
2-(1-naphthyl)-5-(4-biphenylyl)-1,3,4-oxadiazole		α-NBD	121–122	324	3.5	362	382	405



	1,4-phenylene	PYPYP	244–250		420	3.8	472	498
	4,4′-biphenylylene	PYBYP	288–294 (dec.)[h]		408	4.9	465	487
	4,4′-(3,3-dimethylbiphenylylene)	dimethyl-PYBYP	240–244		398	6.2	458	480
	1,3,5-triphenyl-2-pyrazoline	PYP[i]	136–138		363	1.8	439	—

(a) All spectra were measured in toluene solution, wavelengths are in mμ. (b) These compounds showed three absorption maxima. The middle and most intense is listed in the table. (c) Scintillation grade, purchased from Arapahoe Chemicals, Inc., Boulder, Colorado. (d) T = terphenyl, though in a recent paper (11) T is used to represent the 3-tolyl group. An initial few milligrams of POTOP was supplied to us by Kent Chemicals, Ltd., Vancouver, B.C. (e) Scintillation grade, purchased from Pilot Chemicals, Inc., Watertown, Mass. (f) Lit. (3): 308–310°. (g) Was not obtained in an analytically pure form. (h) Lit. (5): 323–325 (i) Synthesised by the method of Sandler *et al.* (12).

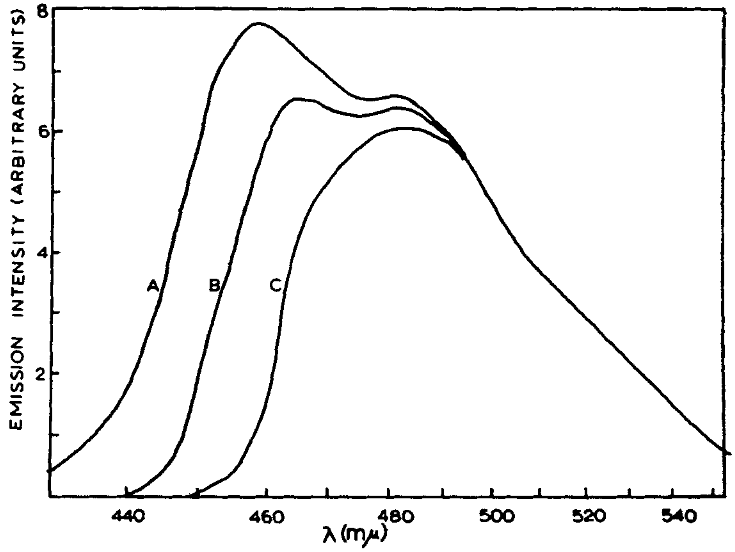


Fig. 2 Fluorescence Spectra of dime-PYBYP (2×10^{-4}M, 0.12 g/l)

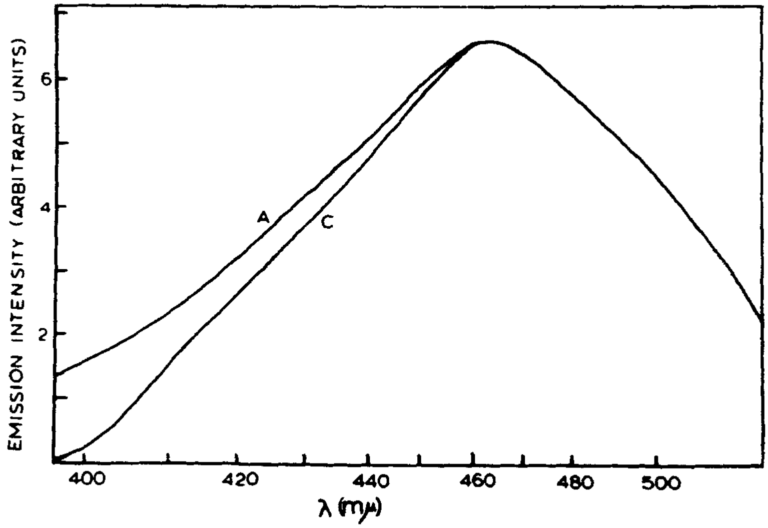


Fig. 3 Fluorescence Spectra of TPB (2×10^{-4}M, 0.12g/l)

No correction was made for variations in the spectral response of the photomultiplier tube. However, for all the compounds the most intense peak is well resolved and, within any one of the three series of compounds, the shape of the peak varies little. Furthermore the fluorescence maxima of POPOP given in Table 1 are almost identical to values read from the corrected spectra of POPOP in benzene which was recently published by Berlman.[9]

Scintillation pulse height measurements

Polyvinyltoluene samples were prepared by polymerisation for 7 days at 125°C in tubes sealed under vacuum. Pulse heights (Cs-137 excitation) of 1 × 1″ polished cylinders cut from these samples were measured relative to a standard plastic (=100) of the same dimensions containing terphenyl (20 g/l) and POPOP (0.5 g/l). Four independently polymerized test samples were prepared for each solute composition and the pulse height data given in Tables 2 and 3 are the mean values for the four samples. Liquid scintillator pulse heights (Cs-137 excitation) were measured with 25 ml. samples contained in a stoppered cell coated externally with a titanium dioxide reflector. The samples were bubbled with nitrogen immediately before testing. A solution of terphenyl (4 g/l) and POPOP (0.1 g/l) in toluene was used as standard (=100). Estimated standard errors of the relative pulse heights were ±2% and ±4% for the liquid and plastic scintillators respectively.

An EMI 7312 photomultiplier tube with an S-11 photocathode was used exclusively for scintillators containing oxazoles or oxadiazoles as wavelength shifters. The relative pulse heights of scintillators containing the pyrazolines were determined both with the EMI tube and with an RCA 'developmental' C70109A tube with an S-20 photocathode. A variety of tubes were evaluated for relative sensitivity to solutes emitting above 460 mμ. The EMI tube was the least sensitive and the RCA tube one of the most sensitive to long wavelength emission.[10]

3. Results and Discussion

Absorption and Fluorescence Spectra

Spectral data for oxazoles, oxadiazoles and pyrazolines are listed in Table 1.

All the oxazoles show three fluorescent maxima though the intensity of the long wavelength peak is in all cases reduced relative to that of POPOP and is particularly weak in compounds having terminal 1-naphthyl or 4-biphenylyl groups. To simplify the following discussion only the shifts in the second and most intense of the three peaks will be quoted. However, a bathochromic shift in this maximum is always associated with similar shifts in the other maxima though the magnitude of the shift is slightly reduced for the short wavelength maximum and slightly increased for the long wavelength maximum.

The expected bathochromic shift in the fluorescence spectra in the series POPOP, POBOP, POTOP is surprisingly small—only 5 mμ for POTOP compared to POPOP. It might appear that the emission maxima are approaching a limiting value analogous to that found in the *p*-oligophenylenes. However the ultraviolet maximum of POBOP shows a hypsochromic shift of 10 mμ relative to POPOP, associated with the disappearance of fine structure and an increase in the extinction coefficient. POTOP shows a further small shift to shorter wavelengths. A more predictable effect is observed in oxazoles in which extension of the conjugated system is achieved by replacing the terminal phenyl rings by 4-biphenylyl (or 1-naphthyl) structures. Both the absorption and emission maxima of BOPOB show strong bathochromic shifts (of 14 and 19 mμ respectively) relative to POPOP. Similar shifts are observed when BOBOB is compared to POBOP. However, the relationship between BOPOB and BOBOB exactly parallels that between POPOP and POBOP --insertion of a second benzene ring between the two oxazole rings shifts the absorption maxima to shorter wavelengths but has almost no influence on the fluorescence spectra. The 1-naphthyl groups of α-NOPON produce the longest emission maximum of the oxazole series but this compound provides a further anomaly in that its absorption maximum is almost the same as that of POPOP. The presence of two methyl substituents on the central biphenyl group has almost no effect on spectral properties. In contrast methyl groups on the oxazole rings in dimethyl-POPOP cause significant bathochromic shifts in both absorption and fluorescence spectra.

The spectral relationships outlined above can be restated in terms of the Stoke's Loss: in all the oxazoles studied, an extension of the conjugated system of POPOP results in an increased Stoke's Loss. The insertion of additional phenyl groups between the oxazole rings increases the

Stoke's loss more than does the replacement of the terminal phenyl groups by 4-biphenylyl or 1-naphthyl groups.

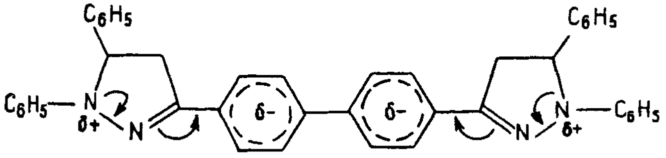
The oxadiazoles exhibit spectral shifts similar to those observed in the oxazoles but the anomalous influence of a central biphenyl group appears somewhat diluted. Thus, replacement of the central benzene ring of PDPDP by a 3,3′-dimethylbiphenyl group produces a larger bathochromic shift (16 mμ) in the fluorescence maximum than that observed with the analogous oxazoles, and a smaller hypsochromic shift (3 mμ) in the absorption maximum. However, the spectra of NDPDN and NDBDN are in the same relationship as the spectra of POPOP and POBOP: extension of the conjugated system causes only a small shift of the fluorescence maximum to longer wavelengths and a somewhat larger shift of the absorption maximum in the opposite direction.

The most dramatic spectral anomalies are reserved for the pyrazoline series. PYBYP exhibits hypsochromic shifts relative to PYPYP in both absorption (12 mμ) *and* emission (7 mμ) maxima. The two methyl substituents of dimethyl-PYBYP induce further spectral shifts to shorter wavelengths. Furthermore, though $\lambda_{\max}$ values are not quoted, the spectral curves given by Baroni and Kovyrzina[5] show the absorption maximum of PYTYP to be at a shorter wavelength than that of PYBYP.

It appears that, in compounds of general structure Ar_1-X-Ar_2-X-Ar_1, an extension of the conjugated system by insertion of additional benzene rings between the heterocyclic groupings results in anomalous spectral shifts which are most marked in the pyrazoline series and least in the oxadiazoles. Thus, extension of the conjugated system in this manner causes hypsochromic shifts of absorption maxima in all three series but the magnitude of these shifts increases in the order: oxadiazoles $<$ oxazoles $<$ pyrazolines. The corresponding fluorescence maxima undergo a hypsochromic shift in the pyrazolines; a small bathochromic shift in the oxazoles and in oxadiazoles having terminal 1-naphthyl groups; and a large bathochromic shift in oxadiazoles having terminal phenyl groups. In contrast, an extension of the conjugated system through replacement of the terminal phenyl groups results in conventional bathochromic shifts in both absorption and emission spectra in the oxazole and oxadiazole series (with the exception of NOPON which has an absorption maximum almost identical to that of POPOP).

In view of the limited number of compounds which have been studied no attempt has been made to develop a theoretical model which could account *in detail* for the observed spectral behaviour. The observed spectral anomalies can however be explained, in general terms at least, as due to distortion of the conjugated system by the heterocyclic groups. Replacement of one or more of the benzene rings of a *p*-oligophenylene with a heterocyclic ring causes the displacement of both absorption and emission maxima to longer wavelengths. The magnitude of this displacement is indicative of the ability of the particular heterocyclic group to distort the conjugated system and increase the contribution made by polar structures to the resonance system. Both the present results and those reported by other workers[3, 13] show that, in compounds represented by the general formulae Ar_1-X-Ar_2 or Ar_1-X-Ar_2-X-Ar_1, the wavelengths of the spectral maxima increase according to the nature of the heterocyclic system in the order: X=benzene < X=oxadiazole < X=oxazole < X=5-phenylpyrazoline. The ability of the heterocyclic groups to distort the conjugated system must therefore follow the same order.

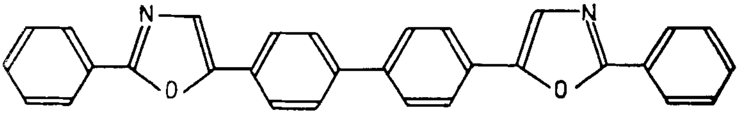
To explain the present results it is postulated that, in compounds of the type Ar_1-X-Ar_2-X-Ar_1, the distorting effect of the heterocyclic system may stabilise polar structures in which conjugation of all the π-electrons is not possible. Specifically the postulated structures would consist, in effect, of two isolated conjugated systems each dominated by one of the two heterocyclic rings. For example, the resonance system of PYBYP may include structures such as (IV) in which a nitrogen atom in each heterocyclic ring acquires a partial positive charge and the residual negative charge is distributed on the adjacent carbocyclic ring. In structure (IV) the electronic character of the molecule is analogous to that of two "isolated" triphenylpyrazoline molecules.[12] The extension of the conjugated system separating the two heterocyclic rings will stabilize such isolated structures and increase their contribution to the resonance system. Contributions to the electronic state of the molecule by isolated structures will tend to displace the spectra to shorter wavelengths.



(IV)

Hence, the overall effect of structures such as (IV) would be to reduce, or even reverse, the bathochromic displacement normally associated with an extension of the conjugated system, when this extension is achieved by the insertion of further benzene rings between the heterocyclic groups. The stability of isolated structures would increase with increasing ability of the heterocyclic ring to distort the conjugated system. Their effect should therefore be most marked in the pyrazoline series in which the most anomalous spectral shifts were in fact observed.

Spectral data on a much wider range of compounds would be desirable in order to provide a more complete picture of the spectral properties of molecules containing two heterocyclic rings. For example, pyrazolines such as BYPYB and BYBYB having terminal biphenyl groups are not represented in the present work. It would also be of interest to know whether the spectral displacements observed in the oxazoles are modified in the isomeric series of oxazoles in which the nitrogen atoms are adjacent to the terminal aryl groups. One compound of this type—1,4-bis-(2-phenyl-5-oxazolyl)-biphenyl (V)—has already been reported.[14]



(V)

Scintillation performance

Tables 2 and 3 give the relative pulse heights of the oxazoles and oxadiazoles, and the pyrazolines, respectively when used as secondary solutes in both plastic and liquid scintillators.

Within experimental error, all the oxazoles give scintillation efficiencies comparable to that of POPOP in both plastics and liquids with the exception of NOPON in plastics and BOPOB in liquids. Pulse height variations among the different oxazoles are too small to indicate any significant correlation of scintillation performance with variations in molecular structure or spectral characteristics. However, measurements of the scintillation performance of larger volume samples may be necessary in order to detect significant variations in the amount of light absorbed by the solvent or self-absorbed by the solute.

The oxadiazoles, dimethyl- and tetramethyl-PDBDP and dimethyl-NDBDN, were found to have efficiencies equivalent to that of POPOP in

TABLE 2 Relative Pulse Heights of Oxazoles and Oxadiazoles as Secondary Solutes in Plastic and Liquid Scintillators

	In polyvinyltoluene with 20 g/l terphenyl		In toluene with 4 g/l terphenyl
Conc. Solute	0.25	0.50	0.1
POPOP		100[a]	100[a]
POBOP	106	101	104
dimethyl-POBOP	92	99	101
POTOP	99[b]	—	—
dimethyl-BOBOB	97	96	97
BOPOB	97	—	82
NOPON	—	88	—
PDPDP	65	71	58
dimethyl-PDBDP	—	97 56[c]	74
tetramethyl-PDBDP[d]	103	105	77, 82[e]
dimethyl-NDBDN	98	100	64, 66[f]

(a) Arbitarily chosen standards (=100). (b) 0.15 g/l, polymerized at 150°C. (c) Contained 0.1 g/l zinc stearate. (d) 5.0 g/l in polyvinyltoluene with POPOP (0.5 g/l) gave a relative pulse height of 98. (e) 0.2 g/l. (f) Saturated solution.

TABLE 3 Relative Pulse Heights[a] of Pyrazolines as Secondary Solutes in Plastic and Liquid Scintillators

	Photocathode[b]	In polyvinyltoluene with 20 g/l terphenyl		In toluene with 4 g/l terphenyl	
Conc. (g/l) Solute		0.25	0.50	0.1	0.2
PYPYP	S-11	58	54	53	56
	S-20	93	89	86	91
PYBYP	S-11	69	59[c]	49[d]	—
	S-20	91	—	—	—
dimethyl-PYBYP	S-11	71	75	68	69
	S-20	—	100	98	94
PYP	S-11	99	93	90	—
	S-20	—	—	90	—

(a) Relative to the same standards as in Table 2 (footnote a). (b) S-11—EMI 7312, S-20—RCA C 70109A developmental tube. Relative pulse height values for each tube are relative to the standard measured *on the same tube.* (c) Undissolved solute in samples. (d) Saturated.

plastic scintillators, in contrast to PDPDP. The poor performance of the latter may be either inherent—due to poor overlap of the absorption spectrum with the emission spectrum of terphenyl, or trivial—due to unfavorable matching with the photocathode sensitivity. However, compared to POPOP, the oxadiazoles are poor secondary solutes in liquid scintillators. Secondary solutes of this type which, relative to POPOP, have a much higher efficiency in plastics than in liquids are a relatively common occurrence. However, as far as is known, no solutes have been reported that give a relatively high performance in liquids, but poor performance in plastics.

Tetramethyl-PDBDP was synthesised in the hope that it would be sufficiently soluble for use as a primary solute. However, the maximum concentration which could be achieved in a plastic scintillator was 5.0 g/l. Even at this low concentration, tetramethyl-PDBDP showed an efficiency equal to that of terphenyl when used as a primary solute in plastic scintillators containing POPOP as the secondary solute.

The fluorescence emission of the three pyrazolines (PYPYP, PYBYP and dimethyl-PYBYP) falls in the spectral range in which photocathode sensitivity is a critical factor in determining scintillator performance. Thus the ratio: (R.P.H. with an S-20 photocathode)/(R.P.H. with an S-11 photocathode) is 1.33 for dimethyl-PYBYP ($\lambda_{\max}$: 458,480 mμ) and 1.60 for PYPYP ($\lambda_{\max}$: 472,498 mμ). However, all these solutes are candidates for use in large volume scintillators providing that specially selected photomultiplier tubes are used and it is probable that all have absolute scintillation efficiencies equivalent to that of POPOP in both liquids and plastics.

Self-absorption measurements

Self-absorption spectra were measured for all of the new solutes which possessed sufficient solubility and also for terphenyl, p,p′-diphenylstilbene, p,p′-diphenyltolan, 1,1,4,4,-tetraphenylbutadiene (TPB), and a variety of oxazoles and oxadiazoles of general formula Ar_1-X-Ar_2. The fluorescence spectra are uncorrected and quantitative comparisons of the percentage photon losses through reabsorption are not possible. However, it was estimated from the spectra shown in Figures 1 and 2 that 25–40% of the light emitted by these two solutes was reabsorbed in a 10 cm light path at a concentration of 0.1 g/l. Furthermore, in qualitative terms, these spectra can be considered typical for all the solutes studied with the exception of TPB. The atypical character of TPB is evident from the spectra shown in Fig. 3. Even qualitative comparisons show that TPB absorbs a very much smaller proportion of its own emission than do any of the other solutes.

If fluorescence spectra are corrected for photocathode sensitivity, the procedure used in the present work provides a direct measurement of the extent of self-absorption by scintillation solutes. It is evident that a large proportion of the total fluorescence emission will be reabsorbed at the concentrations normally used for scintillation solutes, but this is not, in itself, indicative of the contribution made by self-absorption to light attenuation in a practical scintillator. An undetermined, but probably very large, proportion of the reabsorbed light will be re-emitted. Direct measurements of the attenuation of scintillation light are necessary in order to determine the extent of light attenuation resulting from irreversible self-absorption. It has already been observed[15] that light attenuation does not obey a simple exponential law in plastic scintillators containing p,p′-diphenylstilbene or POPOP as secondary solutes. Attenuation is very high in the first few cms. of the light path but decreases as the distance traversed by the scintillation photons increases. This behaviour could be related to preferential self-absorption of the shorter wavelengths of emitted light. The present data suggest that comparative measurements of light attenuation in a scintillator containing TPB as the secondary solute should enable more definite conclusions to be drawn regarding the significance of self-absorption in practical scintillators.

Acknowledgement

This work was made possible by an Industrial Research Assistance grant from the National Research Council of Canada.

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