

A COMPARATIVE SCINTILLATION STUDY OF SOME SELECTED  
BIS-BENZOXAZOLE SOLUTES. BENZOXAZOLES III.\*

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Summary

Some tentative proof of a hypothesis is presented concerning the energy absorption and emission mechanism of conjugated bis-benzoxazole solutes. Based on the initial assumption, two series of bis-benzoxazoles were prepared and tested as primary and/or secondary scintillators. A few of the compounds yielded favorable light outputs comparable to that of PPO and POPOP. Furthermore, in certain cases, the scintillation performance can be directly correlated with corresponding molecular structures.

Introduction

A favorable relative light output is under report from this Laboratory (1) as the scintillation performance of 2,2'-o-phenylene bis-benzoxazole and trans-1,2-bis(2'-benzoxazolyl)-ethylene. The two compounds can be considered as representative members of a new class, the bis-benzoxazoles. The former substance being a potential primary solute, and the latter a wavelength shifter, yield pulse height values comparable to that of PPO and POPOP (2,3), respectively.

The interest in a comparative scintillation study of bis-benzoxazoles arose when, based on the correlation of light

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absorption and emission properties of analogous substances, it appeared that a tentative interpretation of the relationship between corresponding molecular structures and the mechanism of scintillation can be presented.

In addition, the relative ease of the synthesis of bis-benzoxazoles, as reported earlier (4), facilitated the accessibility of several structurally related compounds to be prepared for spectroscopical investigations.

### Development of Theory

A hypothesis was put forward (4) that certain bis-benzoxazoles, having a conjugated double bond system, would acquire quinoid type structures in their lowest excited electronic states, as illustrated in Fig. 1 by the 2,2'-o-phenylene bis-benzoxazole. These structures are, among several others, possible resonant forms of the respective molecular species\*, and may contribute in a lesser extent to the ground state.

As the absorption of electromagnetic energy results in the population of various vibrational levels of an upper electronic state(s), according to the Frank-Condon principle, thermal equilibrium will be rapidly established (in ca.  $10^{-12}$  sec.) due to collisional deactivation (5). Thus, prior to radiational deactivation, the lowest vibrational level of the lowest excited electronic state will be occupied by the activated molecules. As the condition of fluorescence of conjugated bis-benzoxazoles, however, it was assumed that their corresponding quinoid structures will be the predominant contributors to this lowest excited electronic state (4), which is then usually involved in the emission of fluorescent photons.

Consequently, the establishment of quinoid structures in the electronically lowest activated state would first effect a single separation of charge accompanied by a transient polarization of the molecules, as seen from Fig. 1. Secondly, it would result in the formation of a more or less

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\* for example, about eight resonant forms of 2,2'-o-phenylene bis-benzoxazole can be written which have comparable energies.

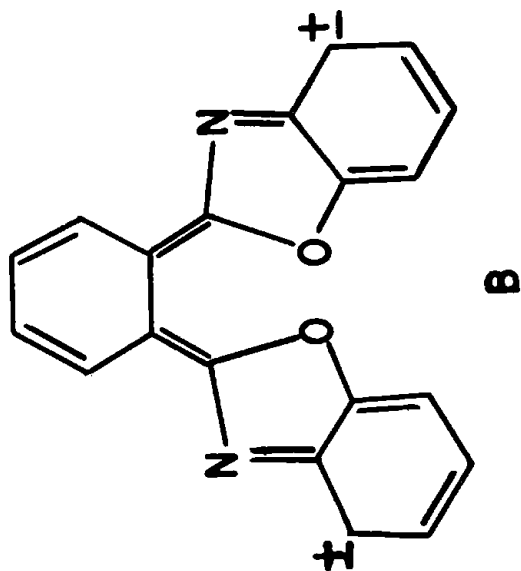
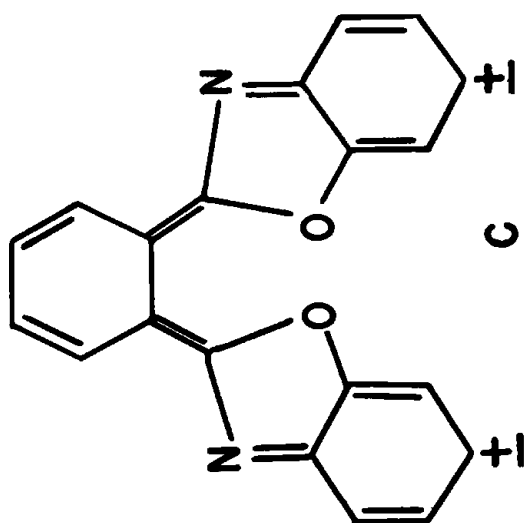
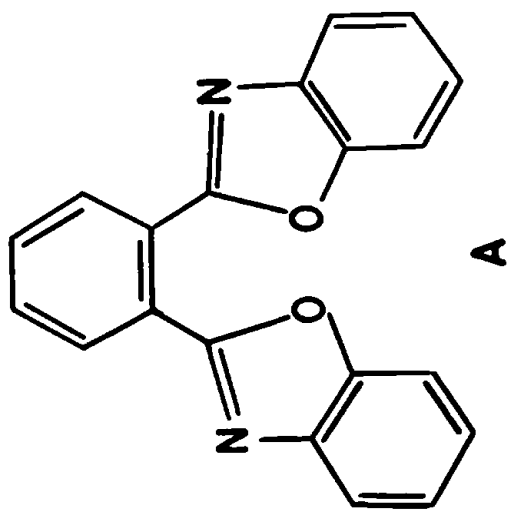


Fig. 1. Kekule (A) and quinoidal type structures (B, C) of 2,2'-o-phenylene bisbenzoxazole.

planar type configuration because of the conjugated double bond system of the molecule, which will not only be retained, but altered to a form negating the normal twisting motion of the benzoxazole nuclei. Hence, the arrangement of double bonds in the postulated quinoid structure, as it can be conceived from Fig. 1, might prevent a considerable amount of the absorbed energy to be utilized for internal rotation, viz., to be consumed in processes defined as internal quenching.

As a possible consequence of the latter postulation, it may also be concluded that the persistence of the assumed planar type configuration will then better enhance the re-emission of absorbed energy than favor a radiationless transition of the excited molecule to the ground state. Accordingly, the introduction of inert substituents into positions where they do not electronically interfere with the displacement of double bonds, but might sterically hinder the establishment of the postulated planar structures, is expected to decrease the capability of fluorescence and/or scintillation.

In view of the assumed structural mechanism of energy absorption and emission outlined above, there seem to be two independent prerequisites to efficient scintillation : a) the capability of the formation of polarized quinoid forms in the excited state, and b) that of acquiring a sterically planar structure in the same state. Both of them are also inherent molecular properties. Thus, the  $1/\tau_i$  factor which denotes the probability of internal quenching of the scintillation solute in the Kallmann-equation (6), and which has been referred to as being "inherent to the solute molecule", could be defined more precisely. Besides the already suggested solvation effect, there are two other structure dependent parameters to which the constant could be related. It could measure the solute molecule's ability of quinoid structure formation (polarization) and also, the degree of planarity of the configuration present in the lowest excited electronic state. By this interpretation, both of the former parameters would separately contribute to the final value of  $1/\tau_i$ . References supporting the outlined suggestion will be made in discussing the scintillation efficiency of sterically hindered bis-benzoxazoles.

Finally, it should be pointed out that the hypothesis outlined above appears to be in agreement with the electromagnetic theory of energy absorption, and with previous

concepts relating the property of fluorescence to the compactness of certain molecular structures, rigidity of the molecule in the activated state, etc. (5,7,8,9,10).

## Discussion

### Ultraviolet Absorption Spectra and the Quinoid Structure

Concerning some tentative proof of the presence of transient quinoid structures in the lowest excited electronic state, it is suggested to consider the first member of the alkenyl bis-benzoxazole series, trans-1,2-bis(2'-benzoxazolyl)-ethylene, as a model. The outlined single separation of charge in this symmetrical molecule might be expected to occur, for example, between either the 6'-6'-positions or the 4'-4'-positions of the two benzoxazole nuclei, as seen from Fig. 2. The diagram depicts the front and the top views of a few approximate patterns of bis-benzoxazolyl ethylene in the ground state. Construction of the molecular patterns was performed with the utilization of known bond lengths and bond angles of analogous heterocyclic compounds, which data is available in the literature (11, 12, 13). The thick solid line illustrates the contours of one of the possible vibrational-rotational forms of the molecule. Two also perceivable structures (out of several others) are shown by thin solid lines. Broken lines represent the oxygen-bridges of the benzoxazole nuclei, which are presumed not to be participating in electronic transitions. Thus, the motion of  $\pi$ -electrons would be restricted to the two benzene rings and to the connecting conjugated double bond system including the two nitrogen atoms of the oxazole rings as well.

Let us allow the first electronic transition to occur with the formation of charge on the 6'-6'-carbon atoms of trans-1,2-bis(2'-benzoxazolyl)-ethylene. The components of the resulting dipole vector,  $a_x$ ,  $a_y$ ,  $a_z$ , can be calculated from the pattern and will assume values of 2.81, 11.69 and 1.23 Angstrom units, respectively, as noted in the diagram. By considering the data as the dimensions of a box in which the potential has been set equal to zero, the solution of the appropriate free electron Schrödinger equation (14) yields the wavelength of the corresponding transition which is about 371 m $\mu$ . The dimensions of another box can be ob-

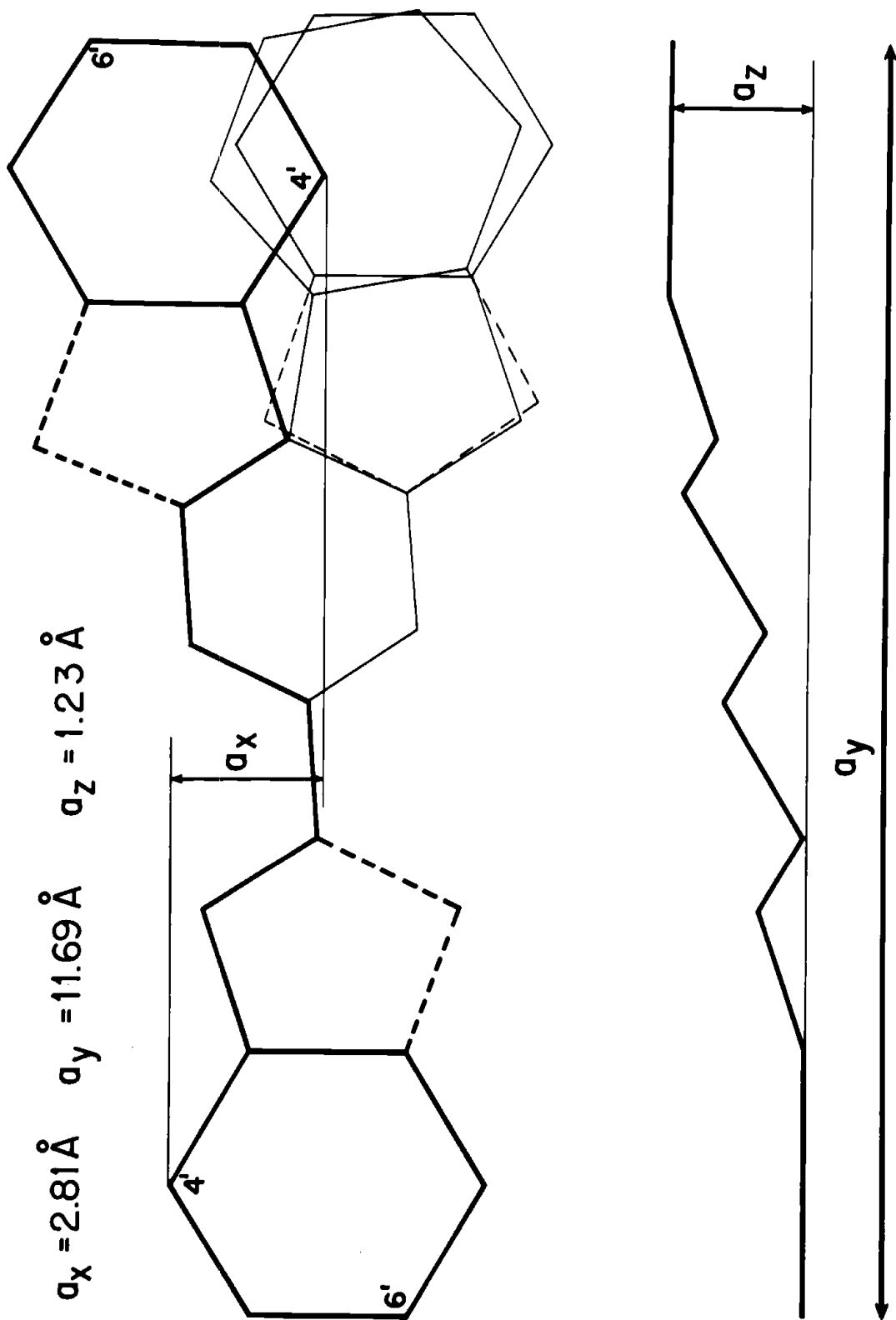


Fig. 2. Trans-1,2-Bis(2'-benzoxazolyl)-ethylene.

tained from the same pattern, when an electronic transition is allowed inducing a transient separation of charge between the 4'-4'-positions of the bis-benzoxazole skeleton. The vector extending between the latter pair of carbon atoms has components of 1.33, 10.45 and 1.23 Angstroms, respectively. Again, by inserting these values into the proper Schrödinger equation, the wavelength of this so-called 4'-4'-transition will be 338  $\mu$ .

As seen from Fig. 3, the ultraviolet absorption spectrum of trans-1,2-bis (2'-benzoxazolyl)-ethylene exhibits a broad K-band\* of considerable intensity in the range of 320 and 380  $\mu$ . The above calculated wavelengths of electronic transitions, which were assumed to be associated with the formation of 4',4'- and 6',6'-quinoidal structures, lay well within the band. As also seen from this curve, there are two distinctive shoulders, displayed by the fine structure of the spectrum, which are located between 336-343  $\mu$  and at 367-373  $\mu$ . The range of these shoulders is then comparable to the calculated single wavelength values of 338 and 371  $\mu$ , respectively.

The fact that calculated and observed wavelengths are in somewhat satisfactory agreement does not necessarily prove the first assumption of this treatment, viz., the exclusion of oxygen atoms from the  $\pi$ -electron transport within the molecule. The approximation of restricting the motion of  $\pi$ -electrons to the two benzo-groups which are conjugated through the connecting unit, including the two nitrogen atoms only of the oxazole rings, appears to be less severe because the free movement of electrons was allowed in a box having a volume almost equivalent to that of the entire molecule. Consequently, the volume of this box includes the formerly excluded oxygen atoms as well. It should be noted, however, that in the solution of the wave-equations another approximation has been made by setting the potential inside the box equal to zero. In fact, the potential inside the box cannot be zero, since the electronegativity values of the carbon and nitrogen atoms are quite different.

Recently, Passerini and co-workers offered an interpretation of the ultraviolet spectra of several benzoxazoles (15). It is based on the assumption that only the benzo-ring should be regarded as the basic chromophore in the compounds

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\* K-bands in general, have been ascribed to N-V transitions leading to polarized structures.

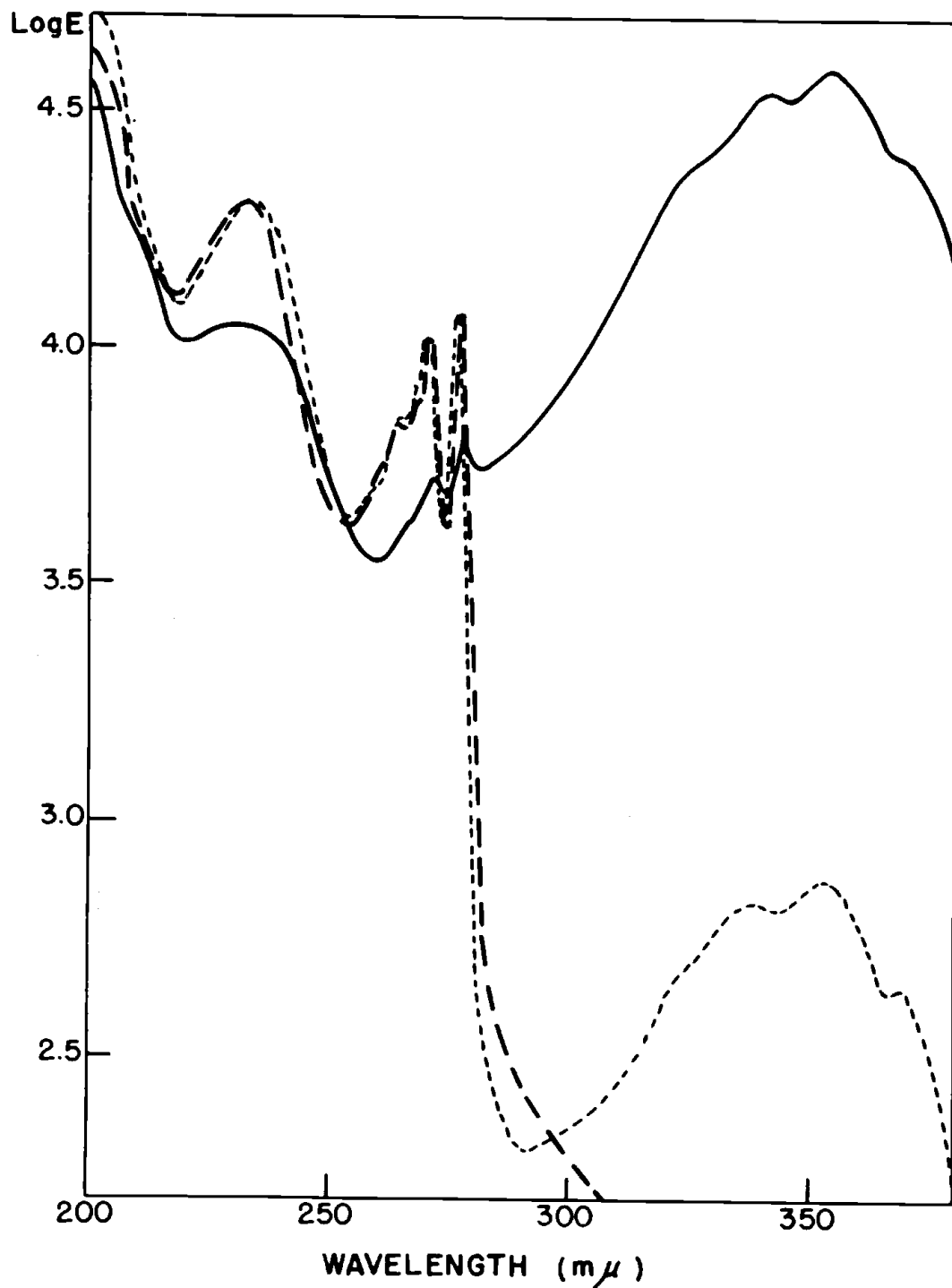


Fig. 3. Ultraviolet absorption spectra of *trans*-1,2-Bis(2'-benzoxazolyl)-ethylene (solid line), 1,2-Bis(2'-benzoxazolyl)-ethane (dotted line), and 1,2-Bis(2'-benzoxazolyl)-propane (broken line).

investigated. The aromatic  $\pi$ -shell of the hetero nucleus, particularly the nitrogen atom is stereo-electronically restricted from conjugation with the benzo-ring.

In view of the location and intensity of K-bands, being present in the absorption spectra of alkenyl bis-benzoxazoles, it can be concluded that there is some resonance interaction between the two benzoxazole nuclei necessarily involving the electron shells of the two nitrogen atoms. It can be easily shown that such resonance occurring between the different parts of a molecule would contribute to the formation of polarized quinoid structures and would facilitate the establishment of a planar type configuration.

Furthermore, as shown by a dotted line in Fig. 3, even the formally non-conjugated analog, 1,2-bis-(2'-benzoxazolyl)-ethane exhibits a K-band in the same region, but which is perhaps less intense. In addition, this saturated substance was found to be scintillating to a small extent. The maximum of its relative pulse height is 0.1 at about 2.5 g/l concentration. These two phenomena could be attributed to hyperconjugation extending over the relatively short aliphatic connecting unit and bridging the gap between the two benzoxazole rings.

By increasing the connecting unit with one more methylene group, the resulting 1,3-bis(2'-benzoxazolyl)-propane no longer possesses scintillation properties. Its ultraviolet absorption curve, as seen from the broken line in Fig. 3, does not indicate any resonance interaction between the two heterocyclic nuclei but resembles very much the spectrum of a single benzoxazole molecule.

### The Planar Type Configuration and Steric Hindrance

Outlined in the precedings, the establishment of a more or less planar type configuration in the lowest excited state was also assumed besides the formation of quinoidal structures discussed earlier, as an independent prerequisite to efficient scintillation of the bis-benzoxazoles. The introduction of inert substituents which do not electronically interfere with the displacement of double bonds but, due to their relative positions, might distort the planarity of the activated molecule, was accordingly expected to decrease the capability of scintillation. Some experimental proof which can be furnished supporting this postulated condition of light emission,

involves the comparison of light output data of sterically non-hindered bis-benzoxazoles with that of analogous, but sterically hindered ones.

In Fig. 4 the top view of three-dimensional patterns of the trans-1,2-bis(2'-benzoxazolyl)-ethylene, trans-2,3-bis(2'-benzoxazolyl)-propene(-2) and trans-2,3-bis(2'-benzoxazolyl)-butene(-2) molecules are illustrated in the ground state. As pointed out in the preceding chapter, the figures depict only one of the several possible vibrational-rotational forms, however, they can be useful in studying the effect of steric hindrance. Construction of these approximate molecular diagrams was performed as described before and the framework of the 2-propene and 2-butene derivatives was considered to be identical with that of the bis-benzoxazolyl ethylene. Small and big circles in the diagrams indicate areas occupied by the hydrogen atoms and methyl groups, respectively, which are attached to the connecting unit.

Together with the patterns listed are the corresponding scintillation efficiencies. In this respect  $RPH_{\max}^*$  refers to a relative pulse height yielded as a primary solute at optimum concentration which is 2.00 g/l (saturated solution) for the first two scintillating substances. The symbol  $RPH_{\max}^*$  denotes the relative pulse height as a secondary solute (0.1 g/l) to p-terphenyl (4.00 g/l).

As seen from Fig. 4, a considerably decreased efficiency of scintillation or, even no scintillation, is found for trans-2,3-bis(2'-benzoxazolyl)-propene(-2) and trans-2,3-bis(2'-benzoxazolyl)-butene(-2).

Another pair of compounds having comparable structures but quite different light output values, is presented by the 2,2'-o-phenylene bis-benzoxazole and 2,2'-o-(p-xylene) bis-benzoxazole. Relative pulse heights of the latter substances are listed in Table 1.

Structurally, these bis-benzoxazoles are some methylated analogs of the corresponding unsubstituted parent molecules, the latter of which were found to be more or less efficient scintillators. The sharp loss in the light output of the 2-propene and 2-butene derivatives, as compared to that of the trans-ethylene compound, does not seem to be singularly ascribable to the presence of methyl groups.

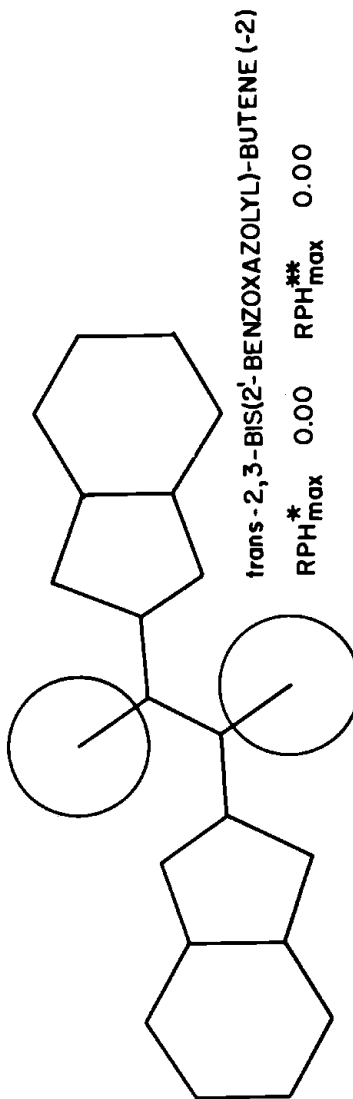
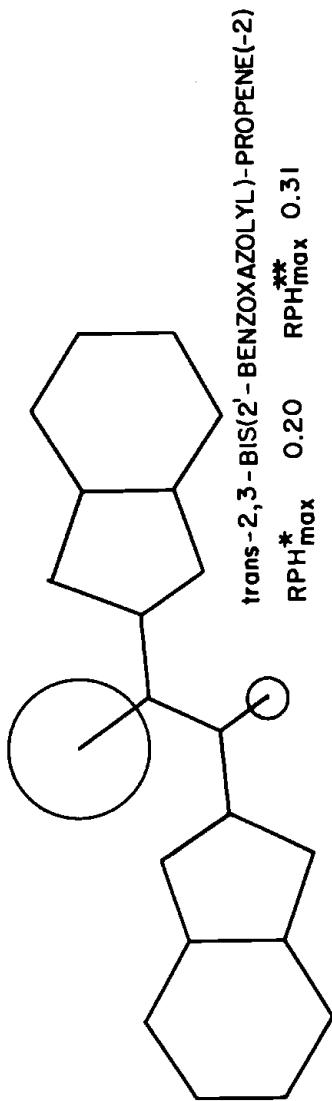
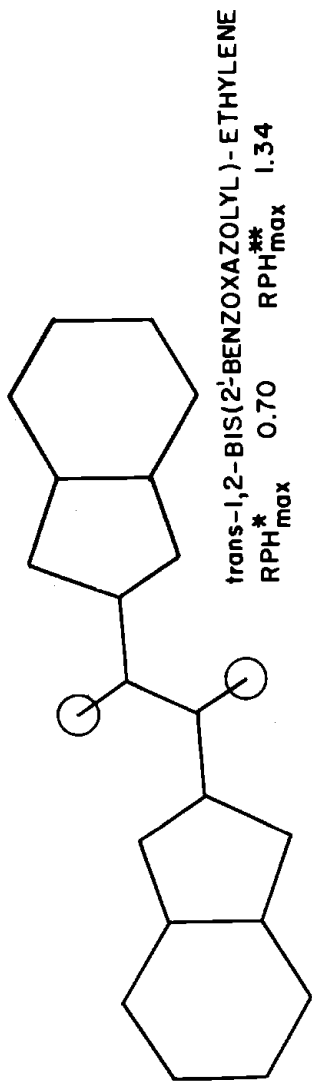


Fig. 4. Approximate molecular patterns of trans-1,2-Bis(2'-Benzoxazolyl)-ethylene, trans-2,3-Bis(2'-Benzoxazolyl)-propene(-2), and trans-2,3-Bis(2'-Benzoxazolyl)-butene(-2).

Secondly, it appears very improbable that the decreased scintillation efficiency of the methylated analogs would be due to enhanced concentration quenching. It seems unlikely that the relative size of the methyl group(s) would basically alter the collision of activated and unexcited molecules of the same species. Furthermore, this argument could be also disclosed in view of the fact that both the methylated and their unsubstituted parent compounds exhibit optimum scintillation at almost identical concentrations.

But the essential loss in light output might be explained by considering the relative positions of these methyl groups in respect to the establishment of a planar type configuration, which was assumed to be also acquired in the excited state. Such type of substitution does neither interfere substantially with the postulated formation of polarized quinoid structures in the lowest excited state, nor can it be attributed to interference with the displacement of double bonds.

Ultraviolet absorption spectra of both of the methylated analogs of ethylene bis-benzoxazole exhibit a strong K-band in about the same region as that of the parent molecule, as seen from Fig. 5. The presence of the band indicates resonance interaction between the two benzoxazole nuclei and presumably the formation of polarized structures contributing to the lowest excited state. However, by increasing the number of methyl groups substituted into the connecting unit, the main peak of the K-band shifts moderately towards shorter wavelengths. This hypochromic effect could be attributed to the steric hindrance of resonance present to a certain extent even in the ground state. The above interpretation could also be supported by the fact that no fine structure is displayed in the K-band of the 2-butene compound which is sterically a more hindered one than the 2-propene derivative.

In view of the experimental facts presented, it can be easily realized that substitution of inert groups into positions adjacent to the benzoxazole nuclei, in general, would sterically interfere with the suggested establishment of a planar type configuration of the excited molecule. As it can be perceived from the relative position and size of the methyl groups - (big circles) in Fig. 4, forcing one or both benzoxazole nuclei out of plane results in enhanced self-quenching, or in other words, decreased scintillation efficiency. The introduction of the same groups, as seen from Table 2, into electronically significant but sterically non-critical positions, induces only a small alteration in the relative pulse

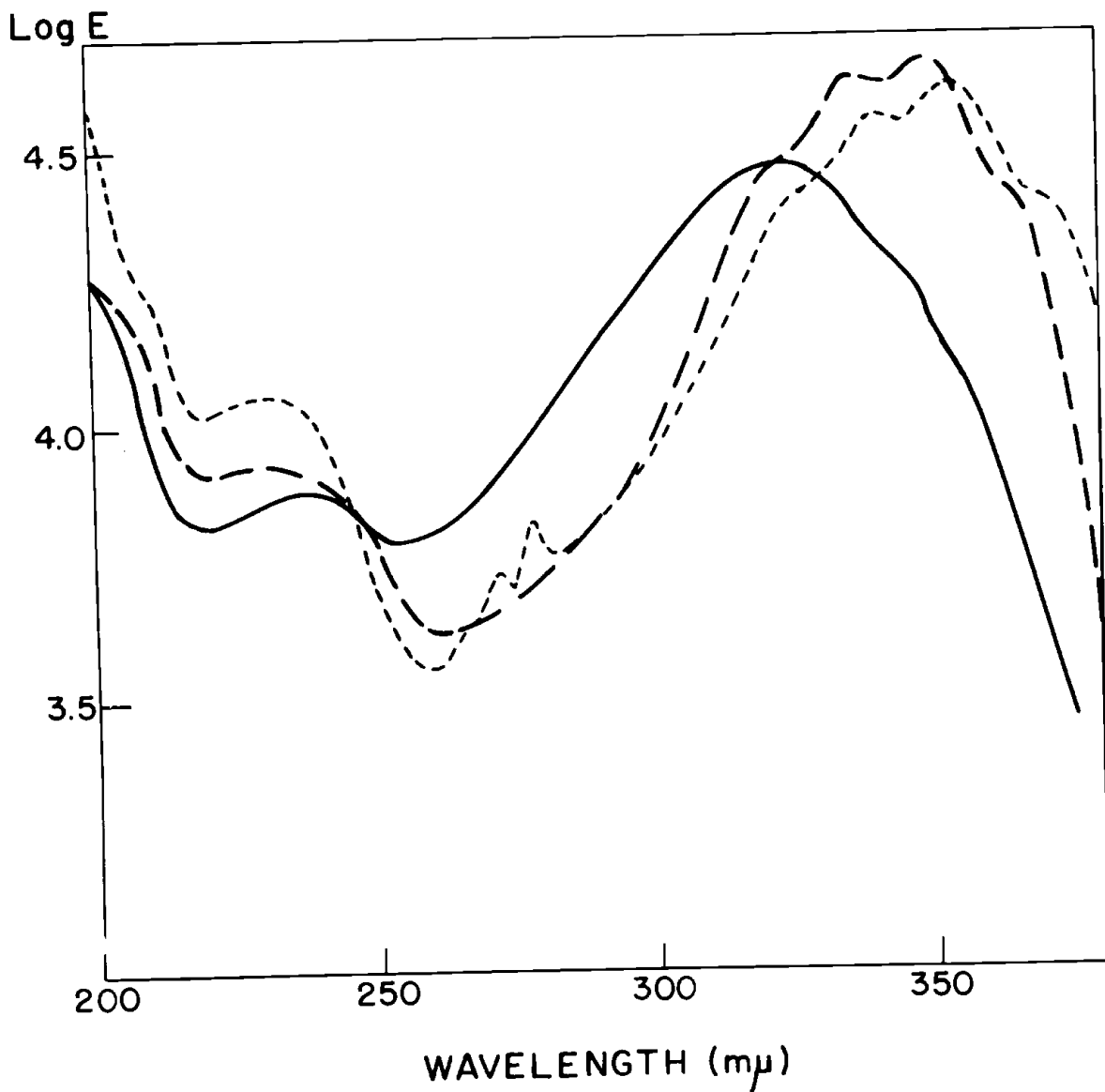


Fig. 5. Ultraviolet absorption spectra of *trans*-2,3-Bis(2'-benzoxazolyl)-butene (solid line), *trans*-2,3-Bis(2'-benzoxazolyl)-propene (broken line), and *trans*-1,2-Bis(2'-benzoxazolyl)-ethylene (dotted line).

height as compared to that discussed heretofore. Thus, steric hindrance of the activated state could be observed as an argument supporting the assumption described earlier.

However, the initial phases of scintillation and fluorescence are known to be different; it seems that the final stages of the light emission mechanism of conjugated bis-benzoxazoles could be interpreted by the hypothesis outlined in the precedings. This mechanism is pictured in Fig. 6.

### Chemical Structure and Scintillation Efficiency

Based on the initial postulation and also on the fact that favorable relative pulse heights were obtained from 2,2'-o-phenylene bis-benzoxazole as a primary solute and from trans-1,2-bis(2'-benzoxazolyl)-ethylene used as a wavelength-shifter, a number of bis-benzoxazoles were prepared and screened for scintillation efficiency.

Our experiments were directed to the replacement of the linkage between the two benzoxazole nuclei by conjugated connecting units varying in structure and in the length of the chain. Also, modification of spectral characteristics by the introduction of various substituents into suitable positions in the benzoxazole nuclei of certain compounds which were found to be already efficient scintillation solutes, appeared to be important as well. The comparison of spectral properties and, in particular, comparison of the relative light output data of members of these two series was expected to yield some information about the relationship between the chemical structure and the scintillation efficiency of bis-benzoxazoles.

The variation of relative light output is reflected in Table I when the connecting unit linking the two benzoxazole nuclei has been varied from simple alkene chains to some heterocyclic systems. Typical members of the already available series of bis-benzoxazoles have been selected and classified according to their connecting units.

The relative efficiency of these substances was determined as being primary scintillators which data is tabulated under the heading of  $RPH_{max}$ , or as being secondary solutes

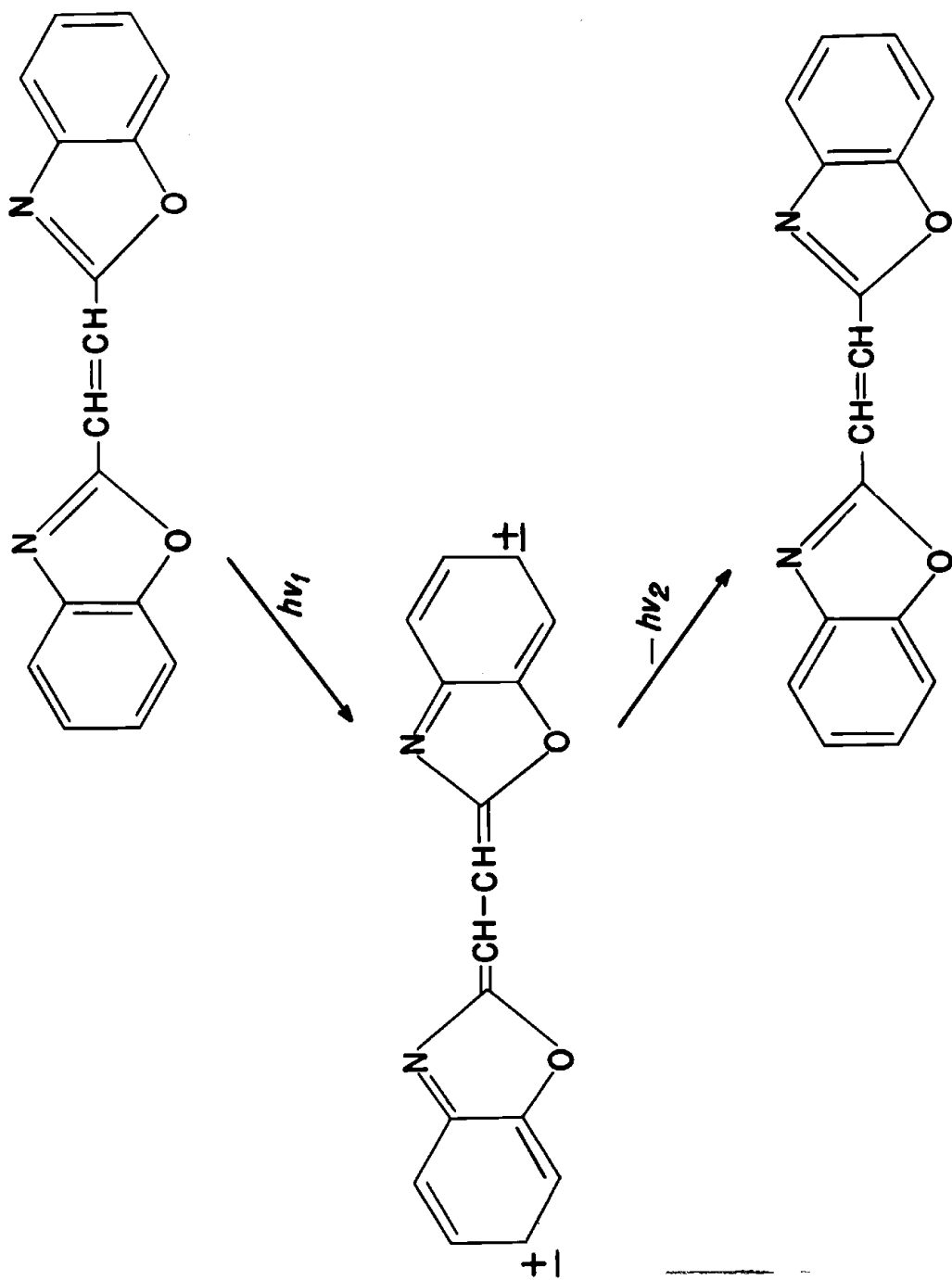


Fig. 6. Assumed structural mechanism of the energy absorption and emission process.

in 0.1 g/l concentration to 4. g/l p-terphenyl, values listed in the third column under  $RPM_{max}$  were obtained. Corresponding primary solute optimum concentrations are compiled in the table's first column. The benzoxazole nucleus which can be referred to either as benzoxazole or benzoxazoly, has been denoted as BOX.

As seen from Table 1, in general, compounds having a straight alkene chain as connecting unit furnish primary solute pulse heights of moderate values only and the respective optimum concentrations indicate limited solubilities in toluene. However, their performance will be increased when used as wavelength-shifters. Solutions containing 0.1 g/l quantities of trans-1,2-bis(2'-benzoxazoly)-ethylene or trans, trans-1,4-bis(2'-benzoxazoly)-butadiene as secondary scintillators to p-terphenyl yield pulse heights of 1.34 and 1.18, respectively with an average grade DuMont 6363 tube. These light outputs are comparable to that of the same amount of POPOP (1.23) which data has been found as the performance of the latter substance in connection with the use of average grade photomultiplier tubes (3).

Replacement of the connecting unit by different aromatic nuclei results in an increase in the light output when the corresponding compounds are tested as primary solutes. In this respect, however, the efficiency of 2,2'-o-phenylene bis-benzoxazole is less than that of PPO, viz., 0.95 versus 1.00.

Regarding the approximate patterns of the o-phenylene bis-benzoxazole, it seems to be likely that due to their mutual ortho-positions, the two benzoxazole nuclei might sterically hinder each other to a certain extent in attaining the previously postulated establishment of a planar type configuration in the lowest excited state.

The cause of steric hindrance referred to was expected to be eliminated by introducing the benzoxazole nuclei into para-positions of an aromatic system, like it is in 2,2'-p-phenylene bis-benzoxazole or in the 2,2'-(4,4'-biphenylene) bis-benzoxazole. These two compounds then can be considered as heterocyclic analogs of p-terphenyl and p-quaterphenyl respectively, and would also be potential primary scintillators. The relative light output versus the concentration curve of both aromatic bis-benzoxazoles has a steep slope, and considerable pulse heights are found for even relatively low concentrations. Unfortunately, the solubility in toluene of both substances is a very limited one.

Table 1.

EFFECT of the VARIATION in the CONNECTING UNIT (R) on  
SCINTILLATION EFFICIENCY

	Conc. (g/l)	RPH <sub>max</sub> *	RPH <sub>max</sub> **
1.1. R = ALKENE CHAIN			
trans-1,2-Bis(2'-BOX)-ethylene	2.00 (s)	0.70	1.34
trans-2,3-Bis(2'-BOX)-propene(-2)	2.00 (s)	0.20	0.31
trans-2,3-Bis(2'-BOX)-butene(-2)	---	0.00	0.00
trans,trans-1,4-Bis(2'-BOX)-butadiene	0.86 (s)	0.80	1.18
1.2. R = AROMATIC NUCLEUS			
2,2'- <i>o</i> -Phenylene BisBOX	6.00	0.95	0.97
2,2'- <i>o</i> -( <i>p</i> -Xylenyl)BisBOX	5.00	0.55	0.93
2,2'- <i>p</i> -Phenylene BisBOX	0.17 (s)	0.30	1.01
2,2'-(4,4'-Biphenylene)BisBOX	0.10 (s)	0.27	1.24
1.3. R = HETEROCYCLIC NUCLEUS			
2,3-Bis(2'-BOX)-pyridine	5.00	0.04	0.75
3,4-Bis(2'-BOX)-pyridine	5.00	0.30	0.54
2,5-Bis(2'-BOX)-pyridine	0.35 (s)	0.35	0.98

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RPH<sub>max</sub>\*, Relative Pulse Height as primary solute

RPH<sub>max</sub>\*\*, Relative Pulse Height as secondary solute  
(0.1 g/l) to *p*-terphenyl (4.0 g/l)

(s) saturated solution

The biphenylene bis-benzoxazole, however, appears to be an efficient secondary scintillator to the primary solute p-terphenyl by yielding a relative light output of 1.24 in this respect.

The decreased scintillation efficiency of 2,2'-o-(p-xylyl) bis-benzoxazole, a sterically hindered dimethyl analog of the parent 2,2'-o-phenylene derivative, has already been discussed in the preceding chapter.

Substitution of benzoxazole nuclei into a heteroaromatic system, such as pyridine, decreases the scintillation efficiency, as compared to that of the corresponding aromatic isomers. In agreement with other available data (16), this effect can be attributed to a transition of an electron of the unshared pair in the pyridine nitrogen atom to an antibonding  $\pi$ -molecular orbital.

In a second approach to the modification of spectral properties of certain bis-benzoxazoles having an established scintillation efficiency, a series of symmetrically substituted bis-benzoxazolyl ethylenes as well as o-phenylene bis-benzoxazole derivatives was prepared and tested. Relative pulse height values of some selected members of these two series are presented in Table 2. The arrangement of data compiled is the same as in the preceding table.

As seen from this table, the introduction of methyl groups into sterically non-critical but electronically significant positions, viz., positions in the benzoxazole rings, results only in a less pronounced modification of the relative light output. As a result of an inductive effect on the displacement of double bonds, substitution of an electron-donating group(s), slightly decreased the scintillation efficiency of the corresponding 5,5'-dimethyl derivatives as compared to that of the parent trans-ethylene and o-phenylene compounds. For the same reason, introduction of the same groups into 6,6'-positions effects a slight increase in the pulse height when the respective 6,6'-dimethyl derivatives are tested as primary solutes.

Electron withdrawing groups, as expected, decrease the efficiency of scintillation in general, like it is found for the 5,5'-dichloro- and 5,5'-dinitro members of both series. The presence of the same substituents in 6,6'-positions cancels the fluorescence and/or scintillation ability of such substances.

Table 2.

EFFECT of SUBSTITUTION in the BENZOXAZOLE NUCLEI on  
SCINTILLATION EFFICIENCY

SUBSTITUENTS ( $R_1=R_2$ )	Conc. (g/l)	RPH* max	RPH** max
<u>2.1. SYMMETRICALLY SUBSTITUTED BIS-BENZOXAZOLYL</u>			
<u>ETHYLENES</u>			
$R_1 = R_2 = H, H$	2.00	0.70	1.34
,5,5'- Dimethyl	4.00	0.57	0.95
,6,6'- Dimethyl	2.50	0.81	1.10
,5,5'- Dichloro	0.80 (s)	0.22	0.68
,5,5'- Dinitro	0.75 (s)	0.18	0.55
,6,6'- Dinitro		insignificant	
<u>2.2. SYMMETRICALLY SUBSTITUTED 2,2' -o- PHENYLENE</u>			
<u>BIS-BENZOXAZOLES</u>			
$R_1 = R_2 = H, H$	6.00	0.95	0.97
,5,5'- Dimethyl	7.00	0.83	1.16
,6,6'- Dimethyl	8.00	0.98	1.05
,5,5'- Dichloro	3.50	0.66	0.85
,5,5'- Dinitro	2.80	0.23	0.65
,6,6'- Dinitro		insignificant	

RPH\*<sub>max</sub>, Relative Pulse Height as primary solute

RPH\*\*<sub>max</sub>, Relative Pulse Height as secondary solute  
(0.1 g/l) to p-terphenyl (4 g/l)

(s) saturated solution

In summarizing, based on the relative pulse height data presented of this selected series of bis-benzoxazoles, it appears that members of this molecular species having a straight alkene chain as connecting unit might have also some practical value as being secondary solutes to p-terphenyl. In addition, it could be concluded that certain bis-benzoxazoles having an aromatic connecting unit might be useful as primary scintillators.

### Method of Evaluation

All of the phosphors prepared were evaluated with the use of a detecting system containing no specific components.

Accordingly, an average grade 3" DuMont 6363 photomultiplier tube was utilized as light detector. The 90% sensitivity of this type of tube occurs in the range of 390 and 490 m $\mu$  which corresponds to S-11 characteristics (17).

Samples for testing were covered only with an aluminum reflector having a highly polished inner surface, and then were excited with 662 KeV  $\gamma$ -rays from a Cesium-137 source built into the top of the reflector.

In contrast to the simple detecting system, the unit analyzing and recording the resulting line spectra was a RCL 256-channel pulse-analyzer.

Since there are many critical variables involved in the quantitative evaluation of liquid scintillation solutes, a standardized procedure was followed. To obtain reliable results, which would be also comparable to that of other scintillators published, the calculation of pulse height values was based on a reference curve. The curve which was determined both before and after the measurement of each set of new samples, is a plotting of pulse height versus the width in millimeters of the registered spectra, and is defined by two calibration points each having a fixed value. These fixed points were the actual widths of spectra registered by two arbitrary standards in presence of the aluminum type reflector. Used as standards were a) a 3 g/l PPO solution in toluene, and b) a 4 g/l p-terphenyl solution containing 0.1 g/l of

POPOP as secondary solute. The spectrum width of the former solution was regarded equivalent to a pulse height of 1.00. That of the latter reference standard was considered to be 1.23 under the experimental conditions described and in agreement with the value recorded as the performance of PPO under similar conditions (3).

#### REFERENCES

1. E. Nyilas and J. L. Pinter, J. Org. Chem., in press.
2. F.N. Hayes, D.G. Ott, V.N. Kerr and B.S. Rogers, Nucleonics, 13, No. 12, 38 (1955).
3. F.N. Hayes, D.G. Ott and V.N. Kerr, ibid., 14, No. 1, 42 (1956).
4. E. Nyilas and J.L. Pinter, J. Am. Chem. Soc., 82, 609 (1960).
5. W. West, "Fluorescence and Phosphorescence" in "Chemical Applications of Spectroscopy", pp. 711-714, W. West, ed., Interscience Publishers, Inc., New York, N.Y., 1956.
6. H. Kallmann and M. Furst, Phys. Rev., 79, 857 (1950).
7. G.N. Lewis and M. Calvin, Chem. Revs., 25, 273 (1939).
8. T. Förster, Naturwiss., 33, 220 (1946).
9. T. Förster, "Fluoreszenz organischer Verbindungen", pp. 120-122, Vandenhoeck and Ruprecht, Göttingen, 1951.
10. L. J. E. Hofer, R. J. Grabenstetter and E. O. Wiig, J. Am. Chem. Soc., 72, 203 (1950).
11. G. W. Wheland, "Resonance in Organic Chemistry", pp. 695-784, John Wiley and Sons, Inc., New York, N. Y., 1955.
12. L. E. Sutton scientific ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions", Special Publication No. 11, The Chemical Society, London, 1958.
13. A. Lofthus, Mol. Physics, 2, 367 (1959).
14. Reference 11, pp. 550-557.
15. R. Passerini, J. Chem. Soc., 2256 (1954).

16. Reference 5, p. 731.
17. Technical Sales Dept., Allen B. DuMont Laboratories, Inc., ed., "DuMont Multiplier Photo Tubes", p. 43, Allen B. DuMont Laboratories, Inc., Clifton, N. J., 1958.