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A New Wavelength Shifter for Liquid and Plastic Scintillators

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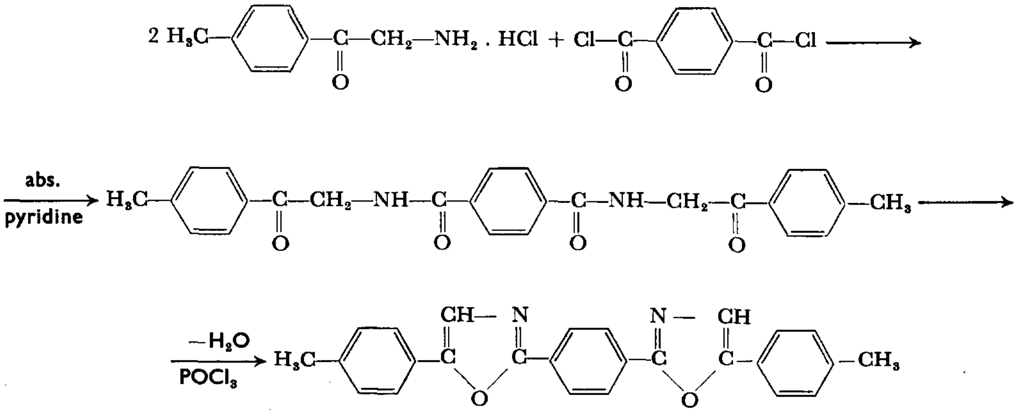
1. Introduction and methods

It is well known, that in modern scintillation counters two scintillator materials, namely the primary and the secondary ones are used for both liquid and plastic scintillators.(1,2) The energy of radioactive radiation is transformed by the primary substance (e.g. PT,PPO) into ultra-violet photons, the secondary substance converts these photons into visible light of a wavelength corresponding to the maximum spectral sensitivity of the photocathode of the photomultiplier. This last-mentioned process determines mainly the light output of the scintillator–photomultiplier system. At the present time among the secondary (wavelength shifting) scintillators POPOP (1,4-di-[2-(5-phenyloxazolyl)]-benzene) is considered most suitable.

Since the S-11 type photomultipliers (spectral maximum at 4500 Å) with $SbCs_3$–Cs photocathodes are generally used, it is quite obvious that maximal light output is attained if the maximum of the luminescent light of the wavelength shifter agrees with the maximum of the spectral sensitivity of the photocathode. This condition is but partly satisfied by POPOP, the maximum of its luminescent light being only about 4300 Å.

On measuring weak β-emitters, especially of H^3 and C^{14}, great difficulties are encountered because the amplitude of useful signals on the output of the photomultiplier scarcely rises above the noise level. An efficient discrimination is thus hardly possible, although this would be of eminent importance when measuring with one tube. The signal–noise ratio on the scintillator side can be improved only by an increase of its light output, which can be brought about by shifting the maximum of the luminescent light near to 4500 Å through convenient modification of the molecular structure of the wavelength shifter. Such efforts have already been mentioned in a monograph(3).

Based on organic chemical theoretical considerations we set ourselves the task of preparing an oxazole derivative which in most respects should be similar to POPOP but would have a luminescent light maximum nearer to 4500 Å. For this purpose starting from the synthesis of POPOP described by Hayes *et al.*(4) we have elaborated the synthesis of 1,4-di-[2-(5-tolyloxazolyl)]-benzene. The new compound was named TOPOT according to international rules of abridgement. The way of the synthesis is the following:



(1)

(2)

Tolacylamine hydrochloride described by Mannich and Hahn(5) served us as starting material. This crystalline white compound melting at 194°C with decomposition, has been converted by terephtalyl chloride in pyridine into similarly white, crystalline N,N′-ditolacylterephtal amide, melting at 282°C. According to our investigations, however, reaction time had to be increased to more than tenfold of the 15 minutes refluxing time mentioned by Hayes(4) for the POPOP synthesis, because otherwise the reaction remaining incomplete, too many by-products arise. In the second, ring-closure step the N,N′-ditolacylterephtalamide is cyclized by phosphorus oxychloride to TOPOT. A very suitable method for the purification of this compound is the crystallization from glacial acetic acid followed by a second crystallization from a mixture of glacial acetic acid/alcohol, because in such a way a substance of analytical purity can be obtained without a chromatographic process.

The TOPOT finally obtained is a yellowish crystalline solid melting at 254–255 C°. Its structure is essentially different from the structure of dimethyl-POPOP*, which had methyl groups in the oxazole ring. TOPOT quite readily dissolves in glacial acetic acid, toluene or in other aromatic solvents. It emits green luminescent light in the first solvent and violet in the other ones. Its luminescent light maximum lies higher than that of the POPOP, by about 80 Å. The decay time of the scintillator produced with TOPOT equals that of stilbene crystals [i.e. 6×10^{-9} sec](6) and its light output surpasses that of POPOP scintillators by about 20 per cent. This fact is supported by Figs. 1 and 2.

The corrected curves of Fig. 1 show the removed maximum in the direction of the higher wavelengths by about 80 Å in the case of TOPOT, but at the same time its quantum efficiency is smaller by about 7 per cent, measured at the maximum, than that of the POPOP. From practical aspects Fig. 2 imparts more information. Figure 2 describes the collective behaviour of the wavelength shifter photomultiplier system. According to this figure both maximums of the TOPOT are also removed towards the higher wavelengths by about 80 Å and its light output is higher by about 20 and 40 per cent respectively, comparing the greater and smaller maximums, than in the case of POPOP. This can be explained only by the fact that the emission maximum of the TOPOT agrees better with the maximum of the spectral sensitivity of the photomultiplier than that of the POPOP.

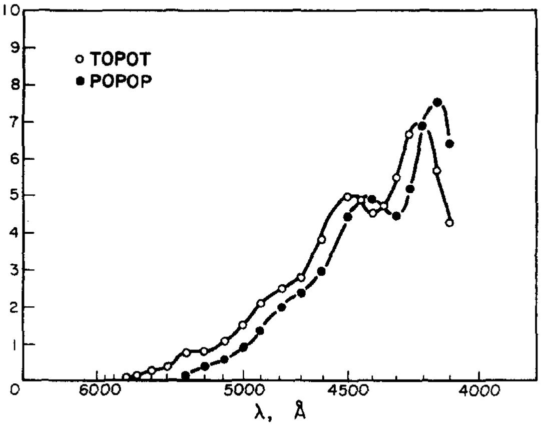


Fig. 1. 0·1 g/l POPOP and TOPOT resp. in toluene. Excitation with the Hg line of 366 mμ. *y*-axis: arbitrary units proportional with the number of photons. Photomultiplier: EMI 9558 with a multi-alkaline photocathode. The curves are corrected for relative photon number /wavenumber.

To establish the counting efficiency, comparative measurements were made using compounds labelled with H^3 and C^{14}, with liquid scintillators containing TOPOT and POPOP. The measurements were performed with a Packard "Tri-Carb" liquid scintillation spectrometer. This is illustrated by Table 1. It appears from the data of Table 1 that the counting efficiency of the scintillator made with TOPOT is not inferior to the efficiency of the other one measuring with an instrument adjusted for the scintillator containing POPOP. Further improvement of the

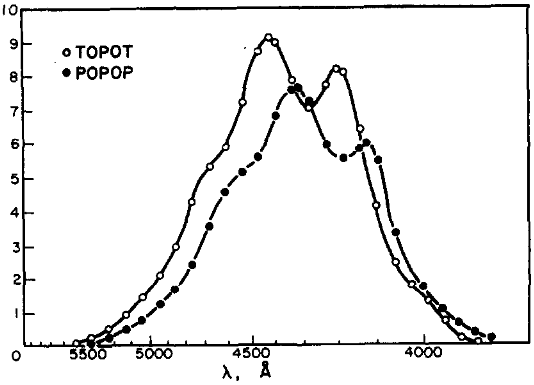


Fig. 2. 0·1 g/l POPOP and TOPOT resp. in toluene. Excitation with the Hg line of 366 mμ. *y*-axis: arbitrary units proportional to the light output of the system. Photomultiplier: EMI 9502 B with a $SbCs_3$–Cs photocathode.

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* Packard Price List, 1 August 1963.

TABLE 1

Isotope	Scintillator	Efficiency (%)
H^3	3 g/l PT + 0·1 g/l POPOP	33·67
C^{14}	in toluene	70·47
H^3	3 g/l PT + 0·1 g/l TOPOT	33·25
C^{14}	in toluene	69·40

signal/noise ratio and the counting efficiency may be expected in the case of an instrument properly adjusted for a scintillator made with TOPOT.

2. Experimental part

(a) *N,N′-ditolacylterephtalamide*

Two grammes of tolacylamine chlorhydrate was gradually added to a stirring solution of 1·2 g terephtalyl chloride in 16 ml anhydrous pyridine. A turbid yellow solution was obtained which had to be refluxed for 3 hr. After cooling the yellowish-brown solution was poured into water and the precipitated product filtered. After drying, the product was crystallized from pyridine. The product is a white solid of 0·6 g, having a melting point of 282 C°.

(b) 1,4-*di*-[2-(5-*tolyloxazolyl*)]-*benzene* (TOPOT)

0·6 g N,N′-ditolacylterephtalamide was refluxed in 25 ml phosphorus oxychloride for 12 hr. Subsequently the superfluous solvent was removed by distillation and the residue was poured cautiously into water under stirring. Stirring was continued until the phosphorus oxychloride was completely decomposed and the product separated as a yellow precipitate. The solid was filtered and recrystallized at first from glacial acetic acid after cleaning with active carbon, then from a mixture of 1:4 alcohol–glacial acetic acid. Finally a crystalline solid of pale yellowish colour was obtained, having a melting point of 254–255 C°. The yield was 0·4 g.

$N_{(Calc)}$7·15%, $N_{(Found)}$7·30%.

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The Preparation of Tritiated Dinitrofluorobenzene of High Specific Activity

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Introduction

DINITROFLUOROBENZENE (DNFB) has been used extensively in the analysis of proteins and amino acids. Tritiated DNFB has found uses in this field, and a quantitative application has been described by BEALE and WHITEHEAD(1). Their method, however, would be very expensive if used for routine analysis employing the commercially available radioactive reagent. We have developed a method (to be described elsewhere) for the estimation of solvent-extractable primary amines, and for this purpose we required tritiated DNFB of high specific activity.

Inactive DNFB is easily prepared by the direct nitration of fluorobenzene(2), but the usual method for the preparation of tritiated DNFB involves generally labelled bromo- or chlorobenzene, which is nitrated, after which the halogen is exchanged with fluorine, using potassium or caesium fluoride in nitrobenzene. This preparation cannot easily be carried out on a small scale, so the specific activity of H^3-DNFB prepared up to now has usually been less than 200 mc/mM. We report the preparation of 2,4-dinitrofluorobenzene-3,5-H^3 having a specific activity of approximately 19 c/mM.

The route employed is