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Borazarenes and Borazoles. Fluorescence Spectrometry and Quantum Efficiencies in Relation to Slow Neutron Counting

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Some new borazole derivatives and borazarenes for which we predicted luminescent properties, were prepared and fluorescence spectra and quantum yield with u.v. excitation were obtained, as a preliminary study for their use as slow neutron scintillation detectors. Counting experiments with slow neutrons are in progress with satisfactory results.

BORAZARENES ET BORAZOLES. SPECTROMETRIE A FLUORESCENCE ET EFFICACITES DE QUANTUM EN RAPPORT AU COMPTAGE DES NEUTRONS LENTS

On a préparé quelques nouveaux dérivés de borazole et des borazarènes pour lesquels on avait prédit des propriétés luminescentes, et on en a obtenu les spectres de fluorescence et le rendement de quantum sous excitation u.-v. comme étude préliminaire à leur emploi comme détecteurs de scintillation des neutrons lents. On est au cours des expériences de comptage avec les neutrons lents, dont les résultats donnent satisfaction.

БОРАЗАРИНЫ И БОРАЗОЛИ. ФЛЮОРЕСЦИРУЮЩАЯ СПЕКТРОСКОПИЯ И КВАНТОВАЯ ЭФФЕКТИВНОСТЬ В ОТНОШЕНИИ СЧЕТА МЕДЛЕННЫХ НЕЙТРОНОВ

Некоторые новые производные боразолей и боразарины, для которых мы предсказали свойства флюоресценции, были приготовлены и были получены спектры флюоресценции и выход квантов при ультрафиолетовом возбуждении, как предварительный опыт их применения в качестве детекторов сцинтилляции медленных нейтронов. В настоящее время производятся эксперименты по счету медленных нейтронов с получением удовлетворительных результатов.

BOROZARENEN UND BOROZOLEN. FLUORESZENZSPEKTROMETRIE UND QUANTENAUSBEUTE IN ZUSAMMENHANG MIT ZÄHLUNG LANGSAMER NEUTRONEN

Einige neue Borazolderivate und Borazarenen, für die wir Lumineszenzeigenschaften voraussagten, wurden hergestellt und ihre Fluoreszenzspektra sowie Quantenausbeute bei U.V. Anregung festgestellt, als vorausgehendes Studium über ihren Gebrauch als Szintillationsdetktoren für langsame Neutronen. Laufende Zählungsversuche mit langsamen Neutronen liefern befriedigende Ergebnisse.

1. INTRODUCTION

MANY different mixtures and a few solid compounds have been proposed by several authors to be used in scintillation counters for slow neutron detectors. The use of a single compound which may include both a high boron content and the property of fluorescence evidently has many advantages over all other systems, regarding their preparation, purification and efficiency.

Types of compounds for which we predicted and proved these characteristics are borazole derivatives. They are soluble in organic solvents (which allows their use as liquid scintillators) and have relatively low gamma response and small decay time. Several compounds of this type have been prepared[1,2] and some preliminary measurements concerning their fluorescence and slow neutron counting characteristics have been partially reported by the present authors.

When our experiments with borazoles were in progress a series of compounds being prepared[3] were reported. These compounds, named generically borazarenes, also present as borazoles, have a marked aromatic character and an adequate boron content. They are also very chemically stable. However no mention was made of their fluorescence behaviour and as we considered this property highly probable, some typical compounds of this kind were prepared and specially purified to investigate it, with a view to their use as slow neutron scintillators.

The fluorescence study of borazoles and borazarenes reported here includes the determination of emission spectra and quantum yield, following for the latter a simple technique developed in this laboratory, with Dr. Gy. Gergely's collaboration.*

The results obtained suggested that these compounds are suitable as phosphors for slow neutron scintillation counters and the results of preliminary tests are given.

2. EXPERIMENTAL

(i) *Preparations*

(a) N-trimethyl-B-tri-(diphenyl)borazole; N-trimethyl-B-tri-α-naphthylborazole; N-triphenyl-B-tri(diphenyl)borazole and N-trimethyl-B-tri(*p*-terphenyl)borazole, were prepared[1,2] by reaction of the corresponding B-trichloroborazole derivatives with organolithium compounds, in ethyl ether media. Lithium salts were separated by treatment with benzene and the borazoles were crystallized from benzene/petroleum ether solutions. They were identified by elemental analysis, infra-red spectra and by the expected preparative reactions.

(b) The borazarenes, 2,1-borazaronaphtalene; 2-methyl-2,1-borazaronaphtalene and bis-(2,1-borazaro-2-naphthyl) ether, were prepared with the technique of DEWAR *et al.*[4,5] and identified by their melting point, molecular weight and infra-red spectra which had been partially published by them. The results obtained agree with the above-mentioned works.

3. PURIFICATIONS

(i) Bis-2,1-borazaro-2-naphthyl ether was crystallized from light petroleum ether (b.p. 60–80°C), redissolved in the same solvent, treated with activated charcoal, and chromatographed through activated alumina, eluting with a mixture of ethyl ether and light petroleum ether. It was again recrystallized from light petroleum ether (colourless plates m.p. 199–200°C).

(ii) 2-Methyl-2, 1-borazaronaphtalene was chromatographed over activated alumina eluting with light petroleum ether, and it was crystallized from n-pentane. It was sublimated under vacuum (10^{-2} mm Hg) at 70–75°C (colourless plates m.p. 73–74°C).

(iii) 2,1-Borazaronaphtalene: it was chromatographed over activated alumina using light petroleum ether as eluent. It was vacuum sublimed twice (10^{-2} mm Hg) at 75°C (colourless plates m.p. 100–101°C).

(iv) Borazole derivatives were recrystallized from ethyl ether or mixtures of benzene/petroleum ether after treatment with activated alumina or charcoal. All operations were carried out using dry solvents and in a dry closed apparatus. The crystals were heated in a vacuum sublimator to separate any sublimable materials. Finally, white crystals were obtained: N-trimethyl-B-tri(diphenyl)borazole, m.p. 222–223°C; N-trimethyl-B-tri-α-naphthyl borazole, m.p. 291–292°C; N-triphenyl-B-tri(diphenyl) borazole, m.p. 301–302°C and N-trimethyl-B-tri(*p*-ter-phenyl)borazole, m.p. 255–256°C.

4. EMISSION SPECTRA

(i) *Experimental equipment and method of measurement*

From the u.v. absorption spectra of borazole derivatives[2] and borazarenes[4] it was found

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that convenient lines for excitation were the 253·7 mμ and 313·0 mμ from the mercury emission. A Kipp–Zonnen quartz monochromator was used to select the 253·7 mμ line from a low-pressure mercury lamp, which was then used to excite the fluorescence.

The fluorescence was analysed with a Beckman model DU spectrophotometer, with the spectral fluorescence attachment.

When a MgO screen was placed in the sample holder no mercury lines other than that at 253·7 mμ was detected working with maximum sensitivity of the photomultiplier.

The sample crystals were ground in an agate mortar and compressed gently into a hole 3 mm dia. and 2 mm deep bored into a matt black brass block with the same dimensions as a standard Beckman rectangular cell of 1 cm path.

(ii) *Calibrations*

The spectral sensitivity of the instrument was determined by two methods:

(a) A calibrated tungsten lamp (2800°K) was used in the range 340–600 mμ. The emission values for the black body were taken from the tables by Moon[6], and the tungsten emissivity was taken from the DE Vos values[7].

(b) In the second method the spectral sensitivity of the 1P28 photomultiplier was obtained measuring its response to the light from a hydrogen discharge lamp (L). Similar measurements (L_0) were made interposing a fluorescent integrating screen in the beam. The ratio L/L_0 gives the spectral sensitivity of the detector.

1-Dimethyl aminonaphtalene-5-sulphonic acid 2×10^{-2} M solution in NaOH 1N (240–370 mμ);[8–10] anthracene microcrystals 1·6 mg/cm^2 (240–350 mμ)[11]; sodium salicylate microcrystals 2 mg/cm^2 (240–340 mμ);[11] and Rhodamine B 5×10^{-3} molar solution in ethylene glycol (340–590 mμ),[8,9] were used as fluorescent integrating screens.

The data obtained with the different screens agree with each other as well as with those found by other authors for this type of phototubes.[8,12]

These determinations were repeated with the most prominent lines of a mercury lamp in the range 250–550 mμ with consistent results.

The spectral sensitivity curve of the instruments was obtained by multiplying the spectral sensitivity of the detector by the bandwidth of the monochromator, given by the manufacturer. In the overlapping zones, these values agree within 5 per cent or less with those obtained by the tungsten lamp method (Fig. 1).

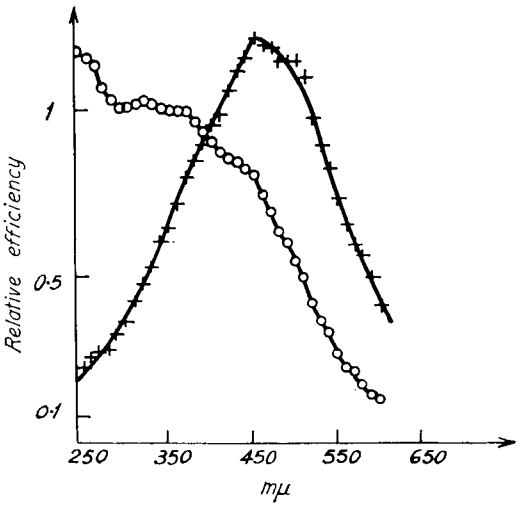

FIG. 1.
Instrument sensitivity: ×–×–×–.
Photomultiplier sensitivity: o–o–o–o–.

(iii) *Fluorescence spectra*

Measurements were made every 5 mμ and the values, corrected point by point with the spectral sensitivity curve of the instrument, are Figs. 2, 3 and 4.

5. ABSOLUTE QUANTUM YIELD

(i) *Experimental equipment*

A Beckman DU spectrophotometer was used as shown in Fig. 5.

The 253·7 mμ and 313·0 mμ lines from a low-pressure mercury lamp, selected with the monochromator, were used as exciting radiation. The exit slit beam was collimated to obtain an illuminated area of about 5 mm^2 on the sample, prepared as before.

(ii) *Principles of the method*

The absolute quantum yield was calculated from the ratio between the sample response and the MgO screen response, taking account of: (a) spectral sensitivity of the detector, (b) reflection coefficient of the sample for the exciting radiation, (c) absolute reflection of

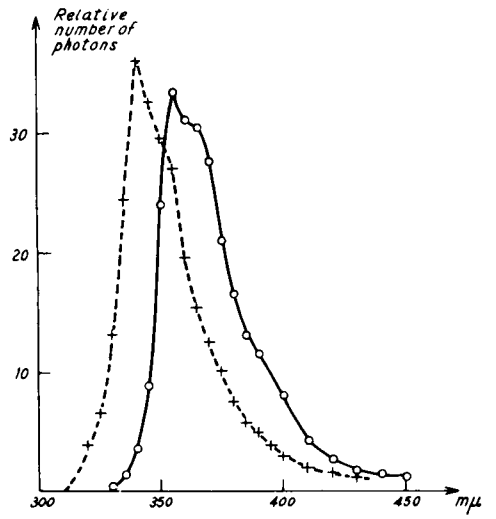

FIG. 2. Fluorescence emission spectra.
Excitation: 253·7 mμ.
Half bandwidth: 2 mμ at 350 mμ.
Naphtalene: – – – – –.
Bis-2,1-borazaro-2-naphthyl ether ———.

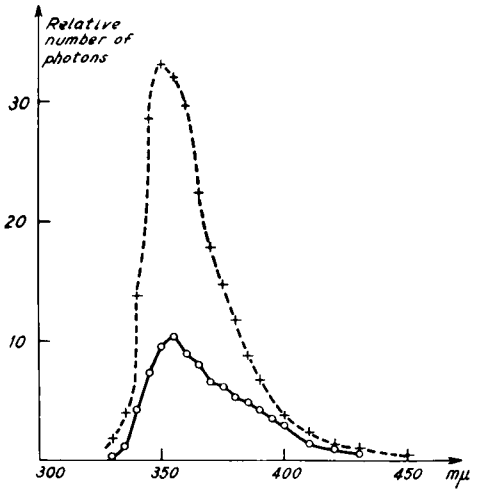

FIG. 3. Fluorescence emission spectra.
Excitation: 253·7 mμ.
Half bandwidth: 2 mμ at 350 mμ.
2-Methyl-2,1-borazaronaphtalene – – – – –.
2,1 Borazaronaphtalene ———.

the MgO and (d) angular distribution of the emitted radiation.

(a) *Spectral sensitivity.* The correction for spectral sensitivity of the detector is negligible because that of the photomultiplier is nearly constant in the range of spectral emission of the substances, and differs little from the spectral sensitivity of the exciting radiation (see Fig. 1).

(b) *Reflection of exciting radiation.* The reflection coefficient of the samples for the exciting radiation was obtained from the

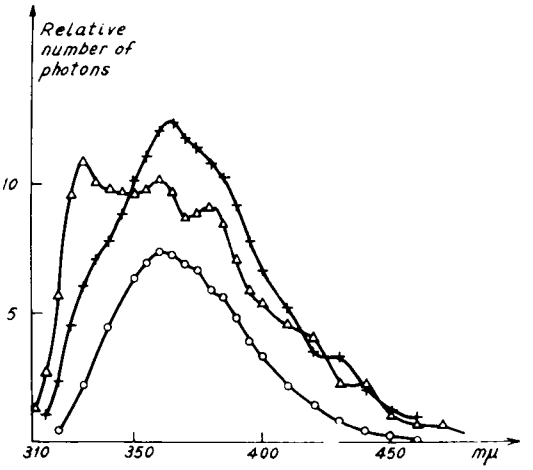

FIG. 4. Fluorescence emission spectra.
Excitation: 253·7 mμ.
Half bandwidth: 2 mμ at 350 mμ.
B-tri-(diphenyl)-N-trimethylborazole: ×–×–×–×–.
B-tri-(α-naphthyl)-N-trimethylborazole: o–o–o–o–.
B-tri-(diphenyl)-N-phenylborazole: – – – –.

detector responses with a MgO screen (L_m), with a sample (L_a) and with a common glass filter interposed between sample and detector to cut off the exciting radiation (L_b).

This procedure requires knowledge of the transmission of the glass filter T since it stopped some of the emitted fluorescence. The thickness of this filter was 1·5 mm for 253·7 mμ and 6 mm for 313·0 mμ.

Let ρ be the absolute reflection coefficient of the MgO and q the relative number of emitted

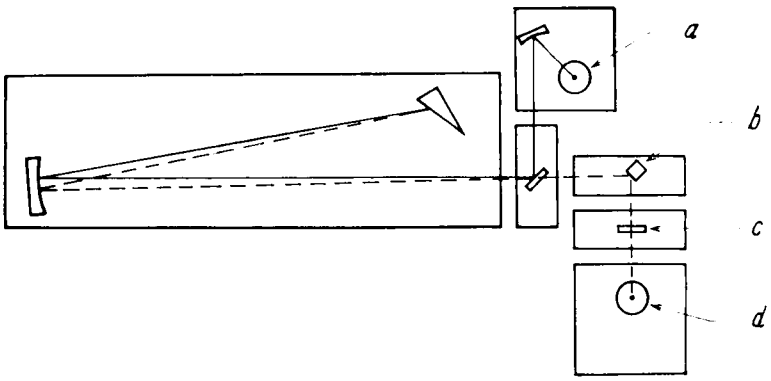

FIG. 5. Equipment used in quantum yield determinations.
(a) Mercury lamp.
(b) Sample.
(c) Filter.
(d) Photomultiplier.

TABLE 1

	Excitation 253·7 mμ	Excitation 313 mμ
2,1-Borazaronaphtalene	0·15	—
2-Methyl-2,1-borazaronaphtalene	0·31	0·33
Bis 2,1-borazaro-2-naphthyl ether	0·30	0·32
B-tri-(diphenyl)-N-trimethylborazole	0·50	0·47
B-tri-(diphenyl)-N-triphenylborazole	0·33	0·32
B-tri-α-naphthyl-N-trimethylborazole	0·33	0·34
Willemite	0·69	—

photons for each wavelength, then the reflection coefficient of the sample will be:

$$r = \frac{\rho}{L_m}\left[L_a - L_b \frac{\int q(\lambda)\,\mathrm{d}\lambda}{\int q(\lambda)\tau(\lambda)\,\mathrm{d}\lambda}\right].$$

(c) *Reflection by* MgO. The absolute reflection coefficient of the MgO screen at the excitating wavelength was determined by comparing the photomultiplier responses to some different mercury lines before and after reflection using the value of 0·97 for the 435·8 mμ line[13]. We found reflection coefficients of 0·80 at 253·7 mμ and 0·94 at 313·0 mμ for the MgO used.

(d) *Angular distribution.* We assume an angular fluorescence distribution similar to that of the exciting radiation dispersed by the MgO. This condition was shown for many fluorescent substances.

From the above data we can calculate the absolute quantum yield with the following formula

$$\mu = \frac{\rho}{1-r} \frac{L_b \int \frac{q(\lambda)\tau(\lambda)\,\mathrm{d}\lambda}{q(\lambda)\tau(\lambda)S_a(\lambda)\,\mathrm{d}\lambda}}{\frac{L_m}{Sq_0}} \int \frac{q(\lambda)\,\mathrm{d}(\lambda)}{q(\lambda)\tau(\lambda)\,\mathrm{d}\lambda}.$$

In order to check this procedure, the quantum yield of a willemite sample was obtained. The results agreed with those obtained by other authors.[14,15] The standard deviation was 1·2 per cent for a series of 10 determinations. The errors in the determinations was estimated as 10 per cent main sources of uncertainty in the calibration of the spectral response of the photomultiplier and the MgO reflection coefficient.

The results are shown in Table 1.

6. COUNTING EXPERIMENTS

Some of the borazole derivatives were tested in solution[2] and in solid state (thin film) as

phosphors in a conventional counting equipment with slow neutrons from a moderated Ra Be source, and from a nuclear critical facility (enriched uranium/natural water and graphite).

The preliminary results[1,2] confirmed that these compounds have fast fluorescence decay, similar to common organic scintillators and are satisfactory as well for slow as for fast counting rates and further experiments with the borazoles and borazarenes are in progress.

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