

Fluorescence and Liquid Scintillation Properties of 1,3,4-Oxadiazoles. II.
5,5'-Bis(*p-t*-butylphenyl)-2,2'-bi(1,3,4-oxadiazole) (I)

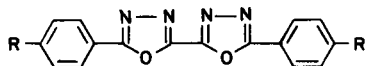
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Early investigations of 1,3,4-oxadiazole derivatives as primary liquid scintillation solutes by the Biomedical Research Group at Los Alamos uncovered many compounds that were found to be excellent fluors. One derivative of the 1,3,4-oxadiazole system, 5,5'-diphenyl-2,2'-bi(1,3,4-oxadiazole) (Ia) was reported to be a poor primary solute, exhibiting a maximum relative pulse-height of only 0.22 at a concentration of 0.7 g./l. (2). The poor scintillation performance of Ia was likely due to the relative insolubility of that compound. We wish to report the synthesis of the soluble compound 5,5'-bis(*p-t*-butylphenyl)-2,2'-bi(1,3,4-oxadiazole) (Ib), which we found to be an excellent liquid scintillation solute.

The synthesis of Ib was accomplished by first allowing *p-t*-butylbenzoyl chloride to react with oxalyl dihydrazide and cyclization of the subsequent amide with phosphoryl chloride.



Ia, R = H
b, R = C(CH₃)₃

Scintillation measurements were carried out by Donald L. Horrocks of Argonne National Laboratories on gas-free solutions in thin-walled 5 mm i.d. quartz tubes using the Compton-edge technique with a single photomultiplier tube as previously described (3-5). Fluorescence measurements were made using a Farrand MK-1 spectrofluorometer with a triangular quartz cuvette using slits with a 5 nm bandpass. Relative fluorescence data were obtained by measuring the area under the curve for a corrected spectrum relative to the area for a 3.0 g./l. solution of 2,5-diphenyloxazole (PPO).

As can be seen from Figure 1, compound Ib is an excellent primary liquid scintillation solute, having a relative pulse-height of 1.06 at a concentration of about 8 g./l. in toluene. The maximum relative fluorescence intensity was found to be 1.03. Compound Ib, as an excellent liquid scintillator, compares in performance with 2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole (PBD) which

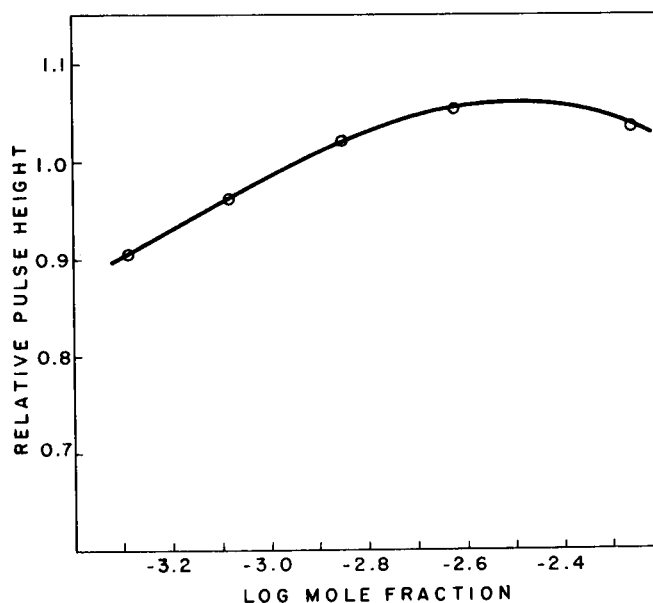


Figure 1. Relative pulse-height curve for 5,5'-di(*p-t*-butylphenyl)-2,2'-bi(1,3,4-oxadiazole) (I). Data relative to a 3.0 g./l. solution of 2,5-diphenyloxazole (PPO) in toluene.

has a reported relative pulse-height of 1.28 (2) at similar concentrations.

A study of the fluorescence properties of Ib was undertaken since many investigators have shown a particular interest in the possibility of excimer formation in 1,3,4-oxadiazole derivatives. Lami (6) reported that 2,5-diphenyl-1,3,4-oxadiazole (PPD) and PBD do not form excimers whereas Horrocks (7) has reported that PBD derivatives do form excimers to a slight extent. Our investigations indicate that at concentrations as high as 25 g./l. at 0° in toluene Ib does not form excimers since no long wavelength components were found at high concentration. In addition, the fluorescence spectrum of Ib was identical at 0° and 90° with no long wavelength component being present at the lower temperature, again indicating that no excimers are present.

EXPERIMENTAL (8)

5,5'-Bis(*p-t*-butylphenyl)-2,2'-bi(1,3,4-oxadiazole) (Ib).

To 4.08 g. (0.0346 mole) of oxalyl dihydrazide in 75 ml. of dry pyridine was added 14.75 g. of *p-t*-butylbenzoyl chloride. The reaction mixture was refluxed for one hour, 100 ml. of water was added, and refluxing continued for an additional hour. The precipitate was collected on a Buchner funnel and dried in a vacuum oven to give 12.22 g. of crude *N,N'*-di(*p-t*-butylbenzoyl) oxamide, which decomposed at 265-280°. The crude amide, which was not purified further, was refluxed with 60 ml. of phosphoryl chloride for 12 hours, and the reaction mixture was then poured into water. The precipitate was collected and dried in the air to give 10.4 g. (75%) of Ib, m.p. 216-218°. Purification was accomplished by recrystallization from cyclohexane and chromatography through an alumina column to give an analytical sample, m.p. 218-219°. The analytical sample and all samples used for scintillation and fluorescence studies were found to be homogeneous by thin-layer chromatography on silica gel plates developed in 90% methylene chloride-10% diethyl ether. Maximum and log ϵ values for the ultraviolet absorption spectrum are 304 nm (4.60). The fluorescence spectrum of Ib was determined using an activating wavelength of 315 nm and exhibited a maximum at 360 nm with a second peak at 374 nm of 93% intensity of the maximum.

Anal. Calcd. for $C_{24}H_{26}N_4O_2$: C, 71.62; H, 6.51. Found: C, 71.72; H, 6.52.

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- (8) Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Ultraviolet absorption spectra were obtained in cyclohexane solution at about 10^{-5} molar concentration using a 1 cm. quartz cuvette in a Beckman DU-2 spectrophotometer. Carbon-hydrogen analysis was performed by Huffman Laboratories, Inc., Wheat Ridge, Colorado.