[CONTRIBUTION FROM THE BIOMEDICAL RESEARCH GROUP, LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA]

Liquid Scintillators. V. Absorption and Fluorescence Spectra of 2,5-Diaryloxazoles and Related Compounds[1]

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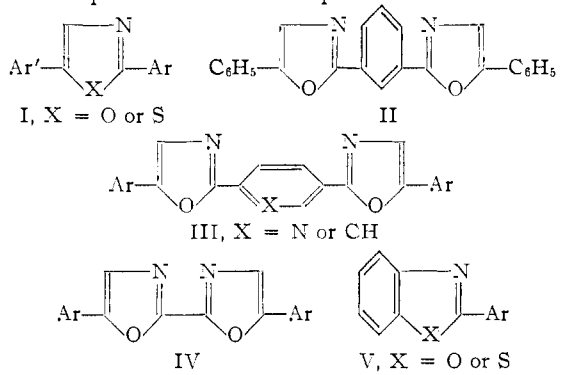
Ultraviolet absorption data and wave lengths of maximum emission and mean wave lengths of fluorescence are presented. The synthesis and evaluation as scintillator solutes of previously unreported compounds are given.

The spectral properties of scintillators are of fundamental importance in the study of organic compounds as solutes in scintillation detector systems. Scintillators are usually evaluated by relative pulse height or relative current measurements.[2,3] The result obtained depends, among other things, on how well the wave length distribution of the light emitted by the scintillator matches the response of the detector. A scintillator with a high light yield (number of photons emitted with respect to the energy deposited by the ionizing radiation) might be classed as a relatively poor scintillator if the photomultiplier sensitivity or the optical path of the detector system is not favorable for the light emitted. Knowledge of the emission and absorption spectra of the compounds under investigation should not only yield information of immediate practical value but should also allow better interpretation of the effects of molecular structure on scintillation ability.

The availability in this Laboratory of a number of oxazole derivatives and related compounds (I–V) has afforded the opportunity to compile the absorption and emission spectra of a rather com-



plete series within a heterocyclic system which has found extensive application in scintillation detectors.

Earlier investigations[4] have indicated that under certain conditions scintillation (radioactive-source excited) and fluorescence (ultraviolet-light excited) spectra have the same shape although the relative interspectral intensities may differ. Since fluorescence spectra are more conveniently obtained than scintillation spectra, ultraviolet-light excitation was used in the present study. The spectrum obtained is not that of the fundamental emission ("molecular" spectrum)[5] which may be observed with very dilute solutions but rather the wave length distribution of the emitted light after encountering the modifying effects of absorption, quenching and scattering present in liquid scintillator solutions ("technical" spectrum).[5] An arbitrary concentration was employed which would provide fluorescence spectra of essentially the same shape as those obtained from the commonly used scintillator solutions.

Fluorescence was excited by a portion of the mercury arc spectrum isolated by means of a monochromator, and the spectrum of the light emitted from the side of the sample cell opposite to that receiving the excitation was obtained as a recorder tracing with a suitably modified recording spectrophotometer.[6] The tracings were corrected for instrument dispersion (effective band width) and sensitivity to give spectra in terms of relative number of photons *vs.* wave length. The slit widths employed were sufficiently wide for good signal-to-noise ratio, yet narrow enough to reveal band structure if present. The resolution was not noticeably improved by using narrower slits and appeared to be as good as that produced in the photographic method in which considerably narrower slits were used. Comparison of corrected spectra obtained by the two methods using identical solutions showed excellent agreement except that the photographic method failed to reveal the presence of low-intensity light extending into the longer wave length region (above *ca.* 500 mμ) where the emulsion sensitivity was very low and correction factors became questionable.

Some of the compounds involved have not been reported previously and additional data are reported in Table I. Preparations of oxazoles or intermediates by procedures different from previous methods[7,8] are given in the Experimental Part.

Experimental Part[9]

m-(**5-Phenyl-2-oxazolyl**)-phenol (I-al).—A solution of 4.5 g. (0.014 mole) of 2-(*m*-methoxyphenyl)-5-phenyloxazole[7] and a crystal of phenol in 110 ml. of 58% hydriodic acid

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(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) D. G. Ott, F. N. Hayes, V. N. Kerr and R. W. Benz, *Science*, **123** 1071 (1956).

(5) J. B. Birks, *Phys. Rev.*, **94**, 1567 (1954).

(6) Similar instruments for this purpose have been described; for leading refs. see C. C. Gemmill, *Anal. Chem.*, **28**, 1061 (1956).

(7) F. N. Hayes, B. S. Rogers and D. G. Ott, THIS JOURNAL, **77**, 1850 (1955).

(8) D. G. Ott, F. N. Hayes and V. N. Kerr, *ibid.*, **78**, 1941 (1956).

(9) Melting points are uncorrected. Microanalyses are by Micro-Tech Laboratories, Skokie, Ill. The fluorescence spectra have been deposited as Document number 5195 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress,

TABLE I: OXAZOLES

Cmpd.[a]	Ar	Ar′	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Corresponding phenacylamide M.p., °C.	Corresponding phenacylamide Nitrogen, % Calcd.	Corresponding phenacylamide Nitrogen, % Found	I_{max} (concn., g./l.)[b]	TiO_2/Al reflector ratio
I-ae[c]	C_6H_5	2,5-$(CH_3)_2C_6H_3$	80–81	$C_{17}H_{15}NO$	81.90	82.05	6.07	5.98	5.62	5.62	107–108	5.23	5.07	99(6.0)	1.00
I-af[c]	2,5-$(CH_3)_2C_6H_3$	C_6H_5	88–89	$C_{17}H_{15}NO$	81.90	81.80	6.07	6.25	5.62	5.60	123–125	5.23	4.95	97(4.5)	1.00
I-ag[c]	2,4,6-$(CH_3)_3C_6H_2$	C_6H_5	70–72	$C_{18}H_{17}NO$	82.10	82.39	6.51	6.49	5.32	5.45	.....	...	...	103(7.0)	0.97
I-ak	*o*-HOC_6H_4	C_6H_5	107–108	$C_{15}H_{11}NO_2$	75.94	76.03	4.67	4.81	5.90	6.02	.....	...	...	28(7.0)	1.24
I-al	*m*-HOC_6H_4	C_6H_5	214–215	$C_{15}H_{11}NO_2$	75.94	75.60	4.67	4.67	5.90	5.95	.....	...	...	66(1.0)[d]	1.02[d]
I-am	*p*-HOC_6H_4	C_6H_5	255–256	$C_{15}H_{11}NO_2$	75.94	75.46	4.67	4.52	5.90	6.33	.....	...	...	31(0.23)	1.04
I-be	*m*-$H_2NC_6H_4$	C_6H_5	144–145	$C_{15}H_{12}N_2O$	76.25	75.71	5.12	5.21	11.86	11.85	.....	...	...	40(0.90)	1.10
I-bf	*p*-$H_2NC_6H_4$	C_6H_5	173–175	$C_{15}H_{12}N_2O$	76.25	76.40	5.12	5.17	11.86	11.87	.....	...	...	80(1.7)	1.11
I-bg[e]	*p*-$(CH_3)_2NC_6H_4$	C_6H_5	117–118	$C_{17}H_{16}N_2O$	77.25	77.47	6.10	6.03	10.60	10.68	172–174	9.92	9.95	95(3.2)	1.14
I-bh[e]	*p*-$(C_2H_5)_2NC_6H_4$	C_6H_5	78–79	$C_{19}H_{20}N_2O$	78.05	78.04	6.90	7.08	9.58	9.76	157–159	9.03	8.86	85(3.3)	1.13
I-ce	(1-CH_3-4-C_5H_9N)	C_6H_5	56–57	$C_{15}H_{18}N_2O$	74.35	74.42	7.49	7.49	11.56	11.46	.....	...	...	10(4.5)	..
I-cd	(5-HO_2C-2-C_5H_3N)	C_6H_5	258–259	$C_{15}H_{10}N_2O_3$	67.66	67.80	3.79	4.04	10.52	10.27	.....	...	...	<7	..
I-cf	2-Quinolyl	C_6H_5	137–138	$C_{18}H_{12}N_2O$	74.47	74.70	4.86	4.98	9.65	9.76	149–151	9.65	9.76	74(3.2)	1.17
I-cg	6-Quinolyl	C_6H_5	147–148	$C_{18}H_{12}N_2O$	74.47	74.32	4.86	4.79	9.65	9.57	155–157	9.65	9.57	84(3.2)	1.16
I-ch	(2-Phenyl-4-quinolyl)	C_6H_5	157–158	$C_{24}H_{16}N_2O$	82.73	82.93	4.63	4.64	8.04	8.22	178–180	7.65	7.79	37(20)[d]	1.22
II[c]	C_6H_5	..	174–175	$C_{24}H_{16}N_2O_2$	79.10	79.11	4.43	4.56	7.69	7.56	168–169	7.00	7.14	89(3.7)	1.05
III-c[c]	2-$C_{10}H_7$ (X = CH)	..	293–295	$C_{32}H_{20}N_2O_2$	82.74	82.98	4.34	4.53	6.03	6.18	.....	...	...	22(0.15)[g]	1.18
III-d[e]	C_6H_5 (X = N)	..	216[f]	$C_{23}H_{15}N_3O_2$	75.60	75.89	4.14	4.62	11.50	11.32	226–229	10.47	10.28	63(1.1)	1.15
IV-b[c]	2-$C_{10}H_7$	..	255–257	$C_{26}H_{16}N_2O_2$	80.40	80.49	4.15	4.49	7.21	7.12	250–252	6.60	6.72	22(0.7)[c,g]	0.93[g]
V-b	4-$C_6H_5C_6H_4$ (X = O)	..	138–139	$C_{19}H_{13}NO$	84.11	84.36	4.83	4.95	5.16	5.20	.....	...	...	96(6)[g]	1.11[g]

[a] Designation of compound as given in Table II. [b] Relative pulse height in toluene solution, PPO = 100; *cf.* ref. 2. [c] Prepared by method in ref. 7. [d] Saturated solution. [e] Prepared by method in ref. 8. [f] Solidifies and remelts at 224–225°. [g] Previously reported in ref. 2.

was refluxed for 4 hr. An additional 15 ml. of 47% hydriodic acid (containing 1.5% hypophosphorous acid) and 50 ml. of acetic acid was added, and the solution was refluxed 3.5 hr., cooled and poured into water. The precipitate was filtered and dissolved in dilute potassium hydroxide and the solution was filtered. The filtrate was treated with solid carbon dioxide and the resulting precipitate was filtered, washed with water and dried; m.p. 210–212°, yield 3.4 g. (81%). Recrystallization from toluene containing a small amount of absolute ethanol gave white crystals, m.p. 215°.

The *o*- and *p*-analogs (I-ak and I-am) were prepared similarly in 40 and 88% yields, respectively.

2-(*p*-Aminophenyl)-5-phenyloxazole (I-bf).—A solution of 500 mg. (1.88 mmoles) of 2-(*p*-nitrophenyl)-5-phenyloxazole[7] in 19 ml. of ethanol was hydrogenated in the presence of 50 mg. of 5% palladium-on-carbon catalyst at room temperature. After 5.6 mmoles of hydrogen had been absorbed, the mixture was filtered and the filtrate was treated with 100 ml. of dilute hydrochloric acid, washed with ether, made basic with sodium hydroxide and extracted with ether. Evaporation of the ether and recrystallization of the residue from toluene–hexane gave 195 mg. (46%) of product.

2-(*m*-Aminophenyl)-5-phenyloxazole (I-bg).—A solution of 170 mg. (0.64 mmole) of 2-(*m*-nitrophenyl)-5-phenyloxazole[7] in 40 ml. of concentrated hydrochloric acid was heated on a steam-bath for 15 minutes with 3.84 g. of granulated tin. The solution was diluted with 65 ml. of water, heated 45 minutes, cooled and filtered. The filtrate was diluted with 100 ml. of water, washed with toluene, made strongly basic with sodium hydroxide to dissolve the tin salts and extracted with three 200-ml. portions of toluene. The toluene was evaporated and the residue was recrystallized from toluene–hexane; yield 70 mg. (46%).

2-(1-Methyl-4-piperidyl)-5-phenyloxazole (I-ce).—A solution of 816 mg. (2.0 mmoles) of 1-methyl-4-(5-phenyl-2-oxazolyl)-pyridinium *p*-toluenesulfonate[8] in a few ml. of water was hydrogenated in the presence of 0.20 g. of 5% palladium-on-charcoal catalyst at room temperature. The brilliant yellow-green fluorescence of the quaternary salt gradually disappeared and the hydrogen uptake stopped after about 6 mmoles had been absorbed. Alcohol was added and the mixture was filtered and evaporated to dryness at diminished pressure. The white solid was dissolved in dilute hydrochloric acid and the solution was washed with ether, made basic with sodium hydroxide and extracted with ether. On evaporation the ether extract gave a colorless oil which readily crystallized; yield 426 mg. (97.5%) of long white needles from petroleum ether (b.p. 30–60°).

By treating a chlorobenzene solution of the product at 80° with the stoichiometric amount of methyl *p*-toluenesulfonate, 1,1-**dimethyl-4-(5-phenyl-2-oxazolyl)-piperidinium *p*-toluenesulfonate** was formed in 75% yield, m.p. 182° after recrystallization from methanol–ether.

Anal. Calcd. for $C_{23}H_{28}N_2O_4S$: S, 7.48. Found: S, 7.57.

By heating the free amine or the piperidinium salt at about 125° with excess methyl tosylate, both nitrogen atoms in the molecule were alkylated to give 1,1-**dimethyl-4-(3-methyl-5-phenyl-2-oxazoliumyl)-piperidinium di-*p*-toluenesulfonate**, m.p. 208–210°.

Anal. Calcd. for $C_{31}H_{38}N_2O_7S_2$: S, 10.43. Found: 10.13.

6-(5-Phenyl-2-oxazolyl)-nicotinic Acid (I-cd).—The crude acid chloride prepared from 18.5 g. (0.1 mole) of isocinchomeronic acid and thionyl chloride was dissolved in 1.5 l. of acetic acid and maintained at 60° while 14.6 g. (0.08 mole) of phenacylammonium chloride was added with rapid stirring, followed by 150 g. of anhydrous sodium acetate. The solution was heated at 80° for 25 minutes and poured into water. The volume was reduced to 0.5 l., an equal volume of ethanol was added, and the solid material was filtered, washed with ethanol and discarded. The filtrate

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was evaporated to dryness and the residue was extracted with ethanol. The solution was filtered and evaporated and the residue of crude **6-(phenacylcarbamoyl)-nicotinic acid** was refluxed for 2 hr. with 100 ml. of phosphorus oxychloride. The reaction mixture was poured onto ice and the resulting dark, gummy precipitate was filtered, dried and dissolved in hot sodium hydroxide solution. Acidification with hydrochloric acid to *p*H 3 precipitated a gelatinous solid which was filtered and extracted with boiling toluene. The solid which precipitated on cooling was filtered, dissolved in sodium hydroxide solution, treated with a small amount of hydrogen peroxide to remove the dark color, acidified, filtered and recrystallized successively from ethanol, methanol and methanol–water to yield 890 mg. (4%) of pale yellow product. A small amount of this material had been isolated previously as a by-product in the preparation of 2,5-bis-(5-phenyl-2-oxazolyl)-pyridine (III-d). The infrared absorption spectrum exhibited bands, in addition to those expected for a phenyloxazolylpyridine, which are characteristic of carboxyl groups and amine salts: 3.50, 3.65, 3.90, 4.10, 5.30, 5.85 (strong) and 7.90 μ (strong). The product was shown to be the nicotinic acid and not the other possible isomer—a picolinic acid, by its resistance to decarboxylation and by its failure to give a color reaction with ferrous sulfate.[10]

2-(4-Biphenylyl)-benzoxazole (V-b).—The acid chloride prepared from 10.0 g. (0.10 mole) of 4-biphenylcarboxylic acid was dissolved in 75 ml. of pyridine and added dropwise to a stirred pyridine solution of 4.9 g. (0.045 mole) of *o*-aminophenol. The mixture was allowed to stand overnight and poured into water to precipitate the crude amide which was washed with dilute hydrochloric acid and water. The solid was heated for 45 minutes at 220° and the product was recrystallized from toluene to yield 9.0 g. (70.5%) of tan solid which gave small white crystals from hexane–toluene.

N,N'-Diphenacylisocinchomeronamide.—A mixture of 9.0 g. (0.044 mole) of isocinchomeronoyl chloride and 16.2 g. (0.1 mole) of phenacylammonium chloride was added in small portions to 200 ml. of rapidly stirred pyridine. The solution was heated on a water-bath for 30 minutes and then poured into ice-water. The crude product was filtered, washed with water and dried; yield 10.9 g. Recrystallization from *o*-dichlorobenzene and again from wet dimethylformamide gave slightly brown crystals, m.p. 232–235°.

***p*-Dimethylaminobenzoic Acid.**[11]—On a mixture of 24 g. of potassium hydroxide and 16 g. of sodium hydroxide in a porcelain evaporating dish was placed 15.0 g. (0.10 mole) of *p*-dimethylaminobenzaldehyde. The mixture was heated on a hot-plate and stirred until all of the aldehyde had melted, cooled, dissolved in water and acidified to *p*H 4 with concentrated hydrochloric acid. The flocculent precipitate was filtered, washed with water and dried; yield 10.6 g., m.p. 239–241° (reported[12] m.p. 235–236°) after recrystallization from ethanol.

***p*-Diethylaminobenzoic acid** was prepared similarly, m.p. 193° (reported[12] m.p. 191–193°).

Fluorescence Spectra.—The solutions were contained in a 1-cm. rectangular quartz cuvette supported in a cuvette holder which was positioned at the rear of the source housing of a Beckman DK-1 recording spectrophotometer. Fluorescence was excited by a portion of the spectrum from a Hanovia type-SH mercury arc which was isolated by passage (in the opposite direction from the usual light path) through a Beckman DU monochromator unit from which the sample and receiver compartments and source housing had been removed. The exciting radiation leaving the monochromator was condensed by a quartz lens, 2.5-cm. diameter, 7.5-cm. focal length, onto the rear face of the sample cell. The light path was shielded to prevent entrance of stray light into the spectrophotometer unit. The instrumental settings generally employed were as follows: monochromator (DU) slit width, 2.00 mm.; spectrophotometer slit widths, 0.40 mm. with 314-mμ excitation or 1.50 mm. with 254-mμ excitation; detector, photomultiplier 20X; energy operation, scale 0–10; time constant, 0.1 sec.; sensitivity control, *ca.* 40; 100% adjustment, completely open. "Standard conditions" were maintained and instrumental drift was checked by adjusting the sensitivity control so that a standard reading was obtained at the emission maximum of a cuvette-shaped sample of plastic scintillator; a change in the sensitivity control also necessitated a change in the zero adjustment. With no sample present, or with pure solvent in the sample cell, or with the shutter at the detector closed, a zero tracing was recorded from 700 mμ down to the appearance of the exciting radiation (if the shutter was open) in the case 314 mμ excitation; with 254-mμ excitation and the cell (containing toluene, ethanol or water) in place, considerable deviation from zero was present in the region around 400 mμ.

For conversion of the recorder tracings to spectra of relative number of photons *vs.* wave length, the intensities at various wave lengths were tabulated (subtraction of the background around 400 mμ was made for spectra excited with 254-mμ radiation), each was multiplied by the correction factor for the particular wave length involved and the resulting data were replotted. The correction-factor curve was obtained by comparing recorded intensities against the known emission spectrum of a tungsten filament.[13] Essentially the same correction-factor curve was obtained by calculation based on the expected detector sensitivity (RCA 1P28 photomultiplier, S-5 response)[14] and tabulated values for effective band width.[15]

The areas under the corrected spectral curves were measured with a polar planimeter; by trial and error, the mean wave length was determined by finding the line perpendicular to the wave length axis which bisected this area. Independent observations with a given solution indicate a probable error of about $\pm 3\%$ in a relative area determination and about ± 2 mμ in a mean wave length assignment; the emission maxima in the replotted spectra are reproducible to within ± 1 mμ.

Absorption Spectra.—A Beckman DK-1 recording spectrophotometer was used for determination of ultraviolet absorption spectra of solutions at concentrations of *ca.* 2.5×10^{-5} *M* in 1-cm. silica cells. Cyclohexane was used as solvent except where insolubility in this solvent necessitated the use of ethanol or chloroform.

Discussion

General and theoretical discussions regarding the measurements and interpretations of fluorescence of solutions have been presented by many authors.[16] Briefly, it may be stated that the simplest type of dissipation of electronic excitation energy is the emission of light. Absorption of energy excites the luminescent molecules from the ground electronic state to various vibrational levels of an upper electronic state. Thermal equilibrium is rapidly (*ca.* 10^{-12} sec.) established and the molecules return from the lowest vibrational level of the first excited electronic state within about 10^{-8} sec. to various vibrational levels of the ground state (in accordance with the Franck–Condon principle) with the emission of fluorescent light.

The appearance of a representative spectrophotofluorometer tracing is shown in Fig. 1 along with the composite correction curve which is ap-

(10) H. Ley, C. Schwarte and O. Münnich, *Ber.*, **57**, 349 (1924).

(11) This method [suggested by a procedure of C. D. Hurd, A. R. Goldsby and E. N. Osborne, THIS JOURNAL, **54**, 2532 (1932)] is a convenient synthesis of the product from readily available starting material.

(12) C. C. Price and W. J. Belanger, *ibid.*, **76**, 2682 (1954).

(13) H. H. Willard, L. L. Merritt and J. A. Dean, "Instrumental Methods of Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1951, p. 16.

(14) Phototube Section, "R.C.A. Tube Handbook," Commercial Engineering, Tube Dept., Radio Corporation of America, Harrison, N. J.

(15) Reference 13, p. 64.

(16) (a) W. West, "Fluorescence and Phosphorescence," in "Chemical Applications of Spectroscopy," W. West, ed., Interscience Publishers, Inc., New York, N. Y., 1956; (b) E. J. Bowen and F. Wokes, "Fluorescence of Solutions," Longmans, Green, London, 1953; (c) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, Inc., New York, N. Y., 1949; (d) T. Förster, "Fluoreszenz organischer Verbindungen," Vandenhoeck und Ruprecht, Göttingen, 1951; (e) J. L. Rosenberg, "Photochemistry and Luminescence," in "Physical Techniques in Biological Research," G. Oster and A. W. Pollister, ed., Academic Press, Inc., New York, N. Y., 1955.

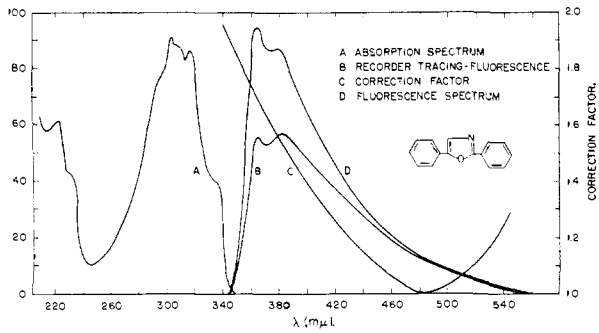

Fig. 1.—A, Absorption spectrum in cyclohexane (left-hand ordinate, $\epsilon/(3 \times 10^{-5})$); B, plot of spectrophotofluorometer recorder tracing of fluorescence, 1 g./l. in toluene; C, instrumental correction factor (right-hand ordinate); D, fluorescence spectrum (corrected).

plied to the tracing in order to produce the spectrum showing the distribution of photons emitted from the solution of 2,5-diphenyloxazole (PPO). In Table II are given the values for the fluorescence maxima (λ^{fl}_{max}), the mean wave length ($\bar{\lambda}$) and the relative areas under the fluorescence spectra of a number of oxazole derivatives which have been evaluated[2,3] as solutes for liquid solution scintillators. In Fig. 2 are shown fluorescence spectra

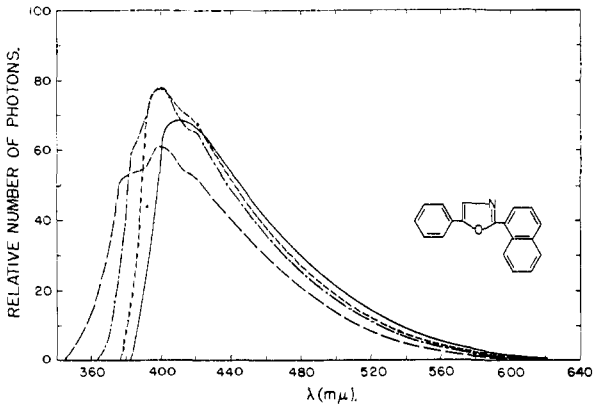

Fig. 2.—Fluorescence spectra of α-NPO at various concentrations in toluene; from left to right: 0.01 g./l., 0.1 g./l., 1.0 g./l. and 10 g./l.

of 2-(1-naphthyl)-5-phenyloxazole (αNPO) at various concentrations. As the concentration becomes greater, self-absorption of the shorter-wavelength portion of the spectrum increases. In very dilute solution or with reflection (front-face excitation) spectra,[4] the shortest wave length band frequently is well resolved and quite prominent. The effects of concentration on $\bar{\lambda}$ and relative area are shown in Fig. 3; with increasing concentration, $\bar{\lambda}$ is progressively shifted to longer wave length and the relative area goes through a maximum; also given is the relative pulse height curve. The fact that the maxima of the two curves appear at different concentrations is attributed to a difference in the mechanism of excitation of the solute. In radioactive-source excitation, the solute is excited as a result of various degradative and energy-transfer steps involving the solvent; with ultraviolet-light excitation, the solute is excited di-

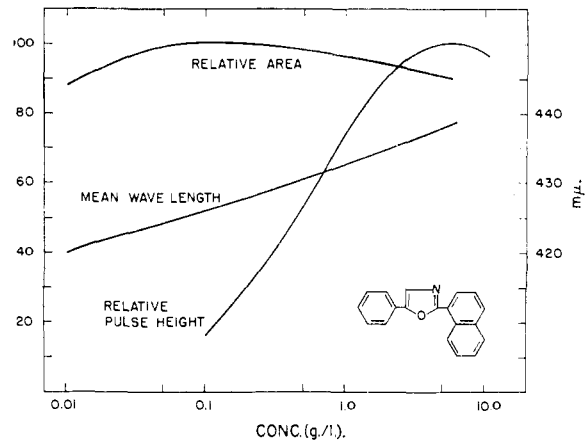

Fig. 3.—Concentration curves for α-NPO in toluene: relative areas of fluorescence spectra, mean wave lengths of fluorescence and scintillation relative pulse heights.

rectly. The fluorescence spectra are generally similar in appearance to that shown for PPO in Fig. 1. The maximum toward longer wave length, $\lambda^{fl}_{max_2}$, is frequently well resolved; its relative intensity with respect to $\lambda^{fl}_{max_1}$ increases with increasing concentration.

The absorption spectra of the various oxazole derivatives are usually quite similar in structure to that of 2,5-diphenyloxazole (Fig. 1). The main band consists of three peaks of about equal intensity with another peak or shoulder of about one-third to two-thirds this intensity toward longer wave length. The shorter wave length peak (303 mμ for PPO) has been recorded as $\lambda^{abs}_{max_1}$ in Table II. In a few instances, the shape of the fine structure in this band has the same character, but the longer wave length peak is of greater intensity—both peaks are recorded in these cases. An absorption maximum at shorter wave length (sometimes not well resolved) also is presented. In general, the changes in absorption spectra caused by simple substitution are similar to those observed in other conjugated aromatic systems, *e.g.*, the biphenyls,[17] benzoxazoles,[18] benzothiazoles,[19] pyrroles and furans.[20]

A comparison among absorption maxima of a series of related compounds is made in Table III. When a CH group in a six-membered ring aromatic hydrocarbon is replaced by nitrogen, there is only a small change in the absorption spectrum[21]; replacement in a five-membered heterocyclic ring, however, has considerable effect. The furan, oxazole and oxadiazole (to a lesser extent) exhibit fine structure, whereas spectra of the other compounds listed are smooth. The pyrrole, furan and thiophene systems have been likened to 1,4-diphenyl-1,3-butadiene—the contribution of the positive forms of the hetero-atom to the resonance of the

(17) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951.
(18) R. Passerini, *J. Chem. Soc.*, 2256 (1954).
(19) A. Cermani and R. Passerini, *ibid.*, 2261 (1954).
(20) S. M. King, C. R. Bauer and R. E. Lutz, THIS JOURNAL, **73**, 2253 (1951).
(21) F. A. Matsen, "Electronic Spectra in the Visible and Ultraviolet," in "Chemical Applications of Spectroscopy," W. West, ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 687.

TABLE II

ABSORPTION AND FLUORESCENCE SPECTRAL DATA[a]

	Compound	Absorption λ_{max1}^{abs}	$\epsilon_1 \times 10^{-4}$	λ_{max2}^{abs}	$\epsilon_2 \times 10^{-4}$	Fluorescence λ_{max1}^{fl}	λ_{max2}^{fl}	$\bar{\lambda}$	Area
	Oxazole, substituents								
I-aa	2,5-Diphenyl	303	3.04	223	2.04	365	381	394	100
ab	5-Phenyl-2-*o*-tolyl	303	2.67	223	1.74	364	380	392	105
ac	5-Phenyl-2-*m*-tolyl	303	2.55	224	1.58	365	382	384	107
ad	5-Phenyl-2-*p*-tolyl	304	3.11	225	1.76	365	381	392	104
ae	2-Phenyl-5-(2,5-xylyl)	306	2.24	225s	1.45	368	386	396	94
af	5-Phenyl-2-(2,5-xylyl)	307	2.73	..	..	365	380s	392	95
ag	2-Mesityl-5-phenyl	281	2.33	..	..	363	380s	388	101
ah	2-(*o*-Methoxyphenyl)-5-phenyl	314	2.42	240	0.95	376	392	396	98
ai	2-(*m*-Methoxyphenyl)-5-phenyl	303	2.86	231s	1.30	366	381s	392	95
aj	2-(*p*-Methoxyphenyl)-5-phenyl	308	3.19	223	1.40	370	388	398	104
ak	2-(*o*-Hydroxyphenyl)-5-phenyl[b]	327[c]	2.86	..	..	485	..	512	59
al	2-(*m*-Hydroxyphenyl)-5-phenyl[b]	305[c]	2.80	..	..	364	382	384	101
am	2-(*p*-Hydroxyphenyl)-5-phenyl[b]	313[c]	3.28	222s	1.58	366	384s	396	97
an	2-(3,4-Methylenedioxyphenyl)-5-phenyl	328	1.73	218	1.34	375	391s	402	103
		320	1.68						
ao	2-(*o*-Fluorophenyl)-5-phenyl	303	2.68	223	1.70	366	381s	392	100
ap	2-(*m*-Fluorophenyl)-5-phenyl	304	2.61	224	1.55	369	386	396	112
aq	2-(*p*-Fluorophenyl)-5-phenyl	303	2.90	223	1.65	362	380s	390	112
ar	2-(*o*-Chlorophenyl)-5-phenyl	306	2.26	226	1.56	374	386s	394	98
as	2-(*m*-Chlorophenyl)-5-phenyl	306	3.06	226	1.80	370	385s	396	105
at	2-(*p*-Chlorophenyl)-5-phenyl	309	4.10	226	1.98	374	389	394	81
au	2-(2,4-Dichlorophenyl)-5-phenyl	312	2.82	229	1.77	383	395s	404	96
av	2-(3,4-Dichlorophenyl)-5-phenyl	311	2.86	226	1.50	377	388s	404	107
aw	2-(*o*-Bromophenyl)-5-phenyl	306	2.48	234s	1.48	372	..	394	24
ax	2-(*m*-Bromophenyl)-5-phenyl	306	1.96	242	0.90	372	388	396	75
ay	2-(*p*-Bromophenyl)-5-phenyl	307	3.52	226	1.58	374	390s	400	59
az	2-(*o*-Iodophenyl)-5-phenyl	310	1.92	220	1.84	370	..	390	4[d]
ba	2-(*m*-Iodophenyl)-5-phenyl	306	2.88	223	2.50	404	..	442	29
bb	2-(*p*-Iodophenyl)-5-phenyl	312	3.94	221	1.58	376	..	396	11
bc	2-(*m*-Nitrophenyl)-5-phenyl	310	2.46	215s	1.20	..	..	..	0
bd	2-(*p*-Nitrophenyl)-5-phenyl	347	2.52	218	1.54	..	..	..	0
be	2-(*m*-Aminophenyl)-5-phenyl	303	2.20	222	2.22	384	..	404	75
bf	2-(*p*-Aminophenyl)-5-phenyl	323	3.28	258	0.88	391	..	416	93
bg	2-(*p*-Dimethylaminophenyl)-5-phenyl	345	4.08	227	1.45	403	..	428	90
bh	2-(*p*-Diethylaminophenyl)-5-phenyl	350	4.06	227	1.32	409	..	432	82
bi	5-(4-Biphenylyl)-2-phenyl	323	3.90	260s	0.67	386	402	412	112
bj	5-(4-Biphenylyl)-2-(*p*-methoxyphenyl)	333	4.17	263	1.07	394	412s	420	104
bk	2-(4-Biphenylyl)-5-phenyl	320	3.86	260	0.98	392	412s	420	114
bl	2,5-Di-(4-biphenylyl)	335	4.76	274	1.35	410	428s	434	109
bm	2-(1-Naphthyl)-5-phenyl	330	2.28	235	3.42	402	416s	432	99
bn	5-(1-Naphthyl)-2-phenyl	323	[e]	229	[e]	395	420s	[f]	[f]
bo	2-(2-Naphthyl)-5-phenyl	332	3.20	230*s*	3.20	386	398s	414	107
bp	5-(2-Naphthyl)-2-phenyl	330	3.11	233s	2.70	382	400	408	102
bq	2-(*p*-Methoxyphenyl)-5-(2-naphthyl)	337	3.54	243	2.42	390	404	416	104
br	5-(4-Biphenylyl)-2-(1-naphthyl)	339	3.42	238	3.50	419	434s	446	108
bs	2,5-Di-(1-naphthyl)	339	2.34	234	5.35	424	445s	452	106
bt	2-(1-Naphthyl)-5-(2-naphthyl)	341	2.74	232	5.38	414	432s	444	110
bu	2,5-Di-(2-naphthyl)	343	3.65	265s	2.66	401	416	436	118
bv	2-Cyclohexyl-5-phenyl	277	2.14	..	..	316	..	332	52[g]
bw	5-Methyl-2-(1-naphthyl)	320	1.43	233	4.44	368	382s	392	77
bx	5-Phenyl-2-styryl	334	3.19	241	1.26	410	..	448	87
by	2-(2-Furyl)-5-phenyl	305	3.84	240s	0.77	368	380s	396	97
bz	5-Phenyl-2-(2-thienyl)	318	2.54	245	0.70	391	402s	428	76
ca	5-Phenyl-2-(2-pyridyl)[b]	322	2.90	224s	1.10	378	..	396	94
		310	2.64						
cb	5-Phenyl-2-(3-pyridyl)[b]	320	2.42	221	1.36	370	385s	396	92
		307	2.54						
cc	5-Phenyl-2-(4-pyridyl)[b]	322	2.62	224s	1.35	380	..	400	86
		307	2.52						
cd	2-(5-Carboxy-2-pyridyl)-5-phenyl[b]	331[c]	2.94	225	1.17	414	..	428	105[h]
ce	2-(1-Methyl-4-piperidyl)-5-phenyl[b]	277	2.03	..	..	320	..	332	48[g]

cf	5-Phenyl-2-(2-quinolyl)[b]	346	2.58	237	2.39	401	..	420	85
cg	5-Phenyl-2-(6-quinolyl)[b]	325	2.85	235	2.28	400	416s	420	94
ch	5-Phenyl-2-(2-phenyl-4-quinolyl)[b]	351	2.60	270	3.84	412	..	436	49
ci	2,4,5-Triphenyl	310	2.26	234	2.53	378	..	400	69
cj	2,5-Diphenylthiazole	322	1.36	..	..	396	412s	420	48
II	2,2′-*m*-Phenylenebis-(5-phenyloxazole)	307	5.31	224s	2.38	374	390s	394	98
III-a	2,2′-*p*-Phenylenebis-(5-phenyloxazole)	358	5.52	230s	2.06	420	440	444	105
b	2,2′-*p*-Phenylenebis-[5-(4-biphenylyl)-oxazole]	373[i]	6.14	..	..	440	462s	462	95[j]
c	2,2′-*p*-Phenylenebis-[5-(2-naphthyl)-oxazole]	375[i]	5.60	243	4.70	438	460	464	102[k]
d	2,5-Bis-(5-phenyl-2-oxazolyl)-pyridine	370[e]	4.70	234	1.40	432	450s	456	101
IV-a	5,5′-Diphenyl-2,2′-bioxazole	337[e]	2.75	223s	1.00	401	420	428	102
b	5,5′-Di-(2-naphthyl)-2,2′-bioxazole	367[c]	4.27	230	6.50	428	450	456	111[l]
V-a	2-Phenylbenzoxazole	299	3.06	225	1.08	339	354	364	93
b	2-(4-Biphenylyl)-benzoxazole	313	4.05	..	..	374	386	400	102
c	2-(1-Naphthyl)-benzoxazole	336	2.09	232	3.40	380	398	408	82
d	2-(*o*-Hydroxyphenyl)-benzoxazole[b]	322	1.75	231s	1.14	500	..	512	21
e	2-Phenylphenanthr[9,10]oxazole	330	2.50	236	3.00	385	403	404	69
f	2-Phenylbenzothiazole	299	2.00	227	2.32	362	..	376	8
g	2-(*p*-Dimethylaminophenyl)-benzothiazole	348	3.90	227	2.37	412	..	432	95

[a] Wave lengths are in mμ; the solvent was cyclohexane for absorption and toluene with 314-mμ excitation for fluorescence unless otherwise indicated; an s following a wave length signifies a shoulder (inflection). [b] Name does not conform to *Chemical Abstracts*. [c] 95% ethanol as solvent. [d] Approximate values. [e] Insufficient compound available, $\epsilon_1/\epsilon_2 = 0.51$. [f] Non-comparable photographic method used. [g] 254-mμ excitation. [h] Concn. 0.1 g./l. [i] Chloroform as solvent. [j] Concn. 0.3 g./l. [k] Concn. 0.15 g./l. [l] Concn. 0.5 g./l.

system being of secondary importance.[20] The strong absorption of 2-arylbenzoxazoles and 2-arylbenzothiazoles has been attributed to the benzylidine-imine type chromophore.[18,19]

TABLE III

ABSORPTION OF 2,5-DIPHENYL-SUBSTITUTED FIVE-MEMBERED RING HETEROCYCLIC SYSTEMS IN CYCLOHEXANE

System	λ_{max}, mμ	$\epsilon_{max} \times 10^{-4}$
1,3,4-Oxadiazole	282	2.61
Oxazole	303	3.04
1,3,4-Thiadiazole	305	2.16
Thiazole	321	4.13
Thiophene	323	2.62
Pyrrole	324	2.98
Furan	325	3.40
(*p*-Terphenyl	276	3.02)

The value of the molecular extinction coefficient (ϵ_1) of the first absorption band was found for several compounds in Table II to be unaffected by changes in concentration or path length over a ten-fold range. At shorter wave lengths, however, the fluorescence excited in the solution does have a small effect on the extinction coefficient and consequently the Beer–Lambert law does not apply in this region.

In general, the shifts observed in λ^{fl}_{max} parallel those in λ^{abs}_{max}. A notable exception to this statement can be found with 2-(*m*-aminophenyl)-5-phenyloxazole (I-be). Substitution of the amino group has no effect on λ^{abs}_{max}, although λ^{fl}_{max} is considerably increased; both absorption and fluorescence intensities are decreased and fine structure is lost in both spectra.

Methyl substitution effects little change (I-ab, ac, ad). Steric hindrance by the *o*-methyl group is not as severe as in the polyphenyl series—2-methylbiphenyl exhibits a hypsochromic shift of about 10 mμ,[22] whereas the analogous 5-phenyl-2-*o*-tolyloxazole (I-ab) shows no change in λ^{abs}_{max}; ϵ is decreased, however, and the absorption spectrum (although not the fluorescence spectrum) has less fine structure. 2-Mesityl-5-phenyloxazole (I-ag) shows the extreme effect of substitution at both *o*-positions of PPO— λ^{abs}_{max} decreases almost to that of the compound having no aromatic substituent in the 2-position, 2-cyclohexyl-5-phenyloxazole (I-bv), and, in addition, all fine structure is lost. Surprisingly, the fluorescence spectrum is hardly affected.

Halogen substitution produces changes in λ^{abs}_{max} commonly observed in other aromatic systems. The heavier halogen substituents strongly quench fluorescence—the effect is less pronounced with *m*-substitution. Fluorescence has been completely quenched in the nitro compounds, I-bc and I-bd. Introduction of amino and dialkylamino groups into the *p*-position produces a pronounced bathochromic shift in both λ^{abs}_{max} and λ^{fl}_{max}; fine structure is lost in both cases.

When the 2- and/or 5-phenyl groups in PPO are replaced with naphthyl or 4-biphenylyl radicals, the extension of conjugation produces the expected bathochromic shift in both absorption and fluorescence. The effectivensss for increasing λ^{abs}_{max} follows the order 4-biphenylyl $\leq$ 1-naphthyl $<$ 2-naphthyl. However, for λ^{fl}_{max} the order is 2-naphthyl $<$ 4-biphenylyl $<$ 1-naphthyl. The inclusion of a 4-biphenylyl group results in loss of structure in absorption but not fluorescence spectra.

The absorption maxima of the *p*-polyphenyls move to longer wave lengths in a regular manner as the number of benzene rings is increased.[23] A similar effect may be observed in the oxazole series for both λ^{abs}_{max} and λ^{fl}_{max} and is illustrated in Fig. 4.

Replacement of the 2-phenyl of PPO with the heterocyclic groups 2-furyl and 2-thienyl does not produce as great a change as might be expected

(22) R. A. Friedel, M. Orchin and L. Reggel, THIS JOURNAL, **70**, 202 (1948).

(23) G. M. Badger, "The Structures and Reactions of the Aromatic Compounds," Cambridge University Press, Cambridge, 1954, p. 391; A. E. Gillam and E. S. Stern, "Electron Absorption Spectroscopy," Edward Arnold (Publishers) Ltd., London, 1954, pp. 208–210.

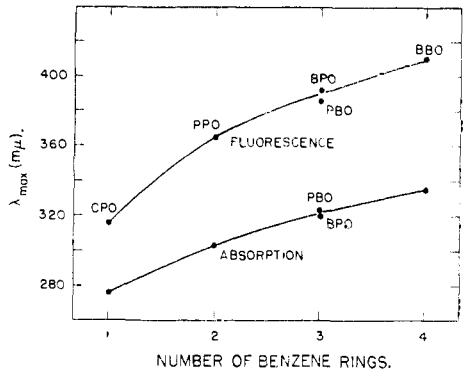

Fig. 4.—Absorption and emission maxima of compounds I-bv, I-aa; I-bi; I-bk; and I-bl as a function of the number of benzene rings in phenyl- or 4-biphenylyl-substituents.

from consideration of their effect when replacing the central ring of *p*-terphenyl (Table III). The thienyl group again causes loss of fine structure. Replacement of 2-phenyl with a pyridyl group produces a slight shift of λ^{abs}_{max} and λ^{fl}_{max} to longer wave length. The analogous compounds in the polyphenyl series, 2-, 3- and 4-(4-biphenylyl)-pyridine, have λ^{abs}_{max} 292, 279 and 279 mμ, respectively[24] (*p*-terphenyl, 276 mμ). Pyridine, itself, does not fluoresce and, in fact, quenches the fluorescence of other compounds.[25] The near-ultraviolet absorption of such N-heterocyclic molecules involves a transition of an electron of the lone pair on the nitrogen atom to an antibonding π-molecular orbital. This excited state rapidly undergoes a radiationless transition to a lower triplet state with few molecules remaining in the excited state long enough to fluoresce.[26] Since the lifetime of the excited state varies inversely with the intensity of absorption,[27] the substitution of the pyridine nucleus with a phenyloxazolyl group, which increases the intensity of absorption, allows a decrease in the lifetime of the excited state and fluorescence can occur before self-quenching.

The addition of a carboxyl group to the 5-position of the 2-pyridyl isomer results in a compound (I-cd) whose properties indicate that inner-salt formation is responsible for the observed spectral changes.

Introduction of a phenyl group into the 4-position of the oxazole ring, a position not conjugated with the major system, to give 2,4,5-triphenyloxazole (I-ci) produces a slight bathochromic shift and lowered intensities for both absorption and fluorescence. The similar structure, 2-phenylphenanthr[9,10]oxazole (V-e), differing by the presence of an additional bond joining the 4- and 5-phenyl groups, shows a further bathochromic shift and inclusion of fine structure. The effect of increased rigidity with respect to more open molecular structures in which the various parts may vibrate independently has long been recognized.[28] Replacement of the terminal phenyl groups in III-a (POPOP) by 4-biphenylyl or 2-naphthyl groups (III-b and III-c) increases λ^{abs}_{max} and λ^{fl}_{max} in the same order as given previously for analogous changes in the PPO series; *i.e.*, 2-naphthyl has more effect than 4-biphenyl for increasing λ^{abs}_{max} and the converse is found for λ^{fl}_{max}. The differences are not so pronounced as with the simpler series. Introduction of a pyridine ring in place of the central benzene ring (III-d) produces a bathochromic shift.

The inclusion of another oxazole nucleus to form the bis-compounds III or the bioxazoles IV, causes a large displacement to longer wave lengths—the addition of the hetero-ring has much greater effect than the corresponding substitution of a benzene ring.

In the 2-arylbenzoxazoles (V, X = O), the shifts caused by replacement of 2-phenyl with 4-biphenylyl or 1-naphthyl are similar to those produced in the 2,5-diphenyloxazole series but of greater magnitude. Substitution in the 2-phenyl group to give *o*-2-benzoxazolylphenol (V-d) produces a splitting into two sets of bands (λ^{abs}_{max} 293 mμ, ε 23,000, and λ^{abs}_{max} 323 mμ, ε 17,500), which has been attributed[18] to the perturbation produced by hydrogen bonding of the hydroxyl group with the ring nitrogen which reduces the benzylidine-imine conjugation and allows the benzo ring to appear separately. Displacement of λ^{fl}_{max} to much longer wave length is accompanied by greatly decreased intensity and loss of band structure. A very similar affect was found with *o*-(5-phenyl-2-oxazolyl)-phenol (I-ak)—λ^{abs}_{max} 297 mμ, ε 17,700, and λ^{abs}_{max} 326 mμ, ε 27,100, in cyclohexane.

2-Phenylbenzothiazole (V-f) with respect to 2-phenylbenzoxazole has the same λ^{abs}_{max} but with no fine structure and decreased intensity; λ^{fl}_{max} is shifted considerably to longer wave length and the intensity is greatly lowered. Introduction of a *p*-dimethylamino group produces a striking bathochromic shift and increased intensity for both absorption and fluorescence; the latter may be attributed to the decreased lifetime of the excited state and consequent diminution of internal quenching. Such a substitution into a compound which already has high fluorescence efficiency may be expected to be detrimental, rather than beneficial (compare I-aa with I-bg, for example). The 2,5-diaryloxazoles have high fluorescence efficiencies; several members of the series, *e.g.*, 2,5-di-(4-biphenylyl)-oxazole (BBO), 2-(4-biphenylyl)-5-phenyloxazole (BPO) or 2,2′-*p*-phenylenebis-(5-phenyloxazole) (POPOP), are known to have fluorescence yields approaching 100%.[29]

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(24) A. E. Gillam, D. H. Hey and A. Lambert, *J. Chem. Soc.*, 364 (1941).

(25) V. N. Kerr, F. N. Hayes and D. G. Ott, *Intern. J. Appl. Radiation and Isotopes*, 1, 284 (1957).

(26) Reference 16a, p. 731.

(27) Reference 16a, p. 709.

(28) Reference 16a, p. 726.

(29) R. K. Swank, Argonne National Laboratory, private communication.