material, however, deposited traces of zinc oxide on brief standing in an anhydrous atmosphere which interfered with molecular weight determinations. That the product was probably polymeric, however, was indicated by the formation of viscous solutions upon concentration of dimethyl sulfoxide solutions of the reaction product under reduced pressure.

Repeated extraction of the reaction product with boiling benzene eventually gave 9.2 g. of hexaphenyltrisiloxane-1,5-diol and left 10.2 g. of zinc oxide contaminated with traces of a silicon-containing compound.

Evaporation of the original filtrate from the reaction mixture and reprecipitating the residue from benzene–petroleum ether gave 9.0 g. of a white powder which was soluble in ethanol and from which no pure compounds could be separated by repeated fractional reprecipitation. The analysis of this material (13.04% Si; 1.09% Zn) indicated that it might be a mixture of metallosiloxane polymer and hexaphenyltrisiloxane-1,5-diol (or other siloxanes).

Decomposition of polymers for analysis. The polymers were decomposed for analysis by the conventional wet-ashing technique using concentrated sulfuric and nitric acids.

Acknowledgment. The authors are indebted to Dr. W. E. Foster, who suggested this problem, to Dr. P. E. Koenig for many helpful discussions, to Dr. R. P. Curry for the infrared spectra and their interpretation and to Mr. G. Z. Smith for the emission spectra. Thanks are due also to the members of the Analytical Group who performed the analyses reported.

BATON ROUGE, LA.

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

Liquid Scintillators. VII. 2,5-Diaryl Substituted Thiazoles as Liquid Scintillator Solutes[1]

V. N. KERR, F. N. HAYES, D. G. OTT, AND E. HANSBURY

Received March 30, 1959

A number of 2,5-diaryl substituted thiazoles have been evaluated as liquid scintillator solutes. A comparison of the effect of substituent groups upon the pulse height of the thiazoles has shown a marked improvement only with the 4-pyridyl and the *p*-dimethylaminophenyl groups. The thiazole pulse heights, fluorescence spectra, and ultraviolet absorption spectra have been compared with the analogous oxazoles.

In an effort to improve upon the existing liquid scintillator counting solutions and to provide data which would help to correlate chemical structure with the ability of various solutes to scintillate, a large number of organic compounds have been investigated.[2–4]

By and large, those solutes which contain sulfur are generally thought to scintillate with a low efficiency, if at all. Thus when Arnold[5] tested a substituted phenylbenzothiazole, it gave a wholly unexpected result. This compound, 2-(*p*-dimethylaminophenyl)benzothiazole, gave a pulse height which was 75% of that of the best solute which had been tested, whereas 2-phenylbenzothiazole was "dead."[6]

There were available in this laboratory a number of oxazole intermediates which could be readily converted to thiazoles. The products of these syntheses would give thiazoles which would have directly comparable oxazoles and thus could provide a comparison of the effects of substituent groups.

Table I contains the data for evaluation of the thiazoles; the maximum relative pulse height (I_{max}); the concentration of solute at I_{max} (c_{max}); the wave length of maximum emission and the mean wave length of the fluorescence spectra (λ_{max}^{fl} and $\bar{\lambda}$, respectively); and the ultraviolet absorption data (λ_{max}^{abs} and ϵ_{max}).

A comparison of the thiazole pulse heights with those of the corresponding oxazoles (in parentheses) shows that in no case does the thiazole equal or excel the oxazole. The highest pulse height obtained is only 80% of that of the analogous oxazole.

The importance of the effects produced by substitution has been noted by several authors.[6,7]

The effect of substitution can be measured relative to 2,5-diphenylthiazole, which can be regarded as the parent member of this series. Several groups produce very little change in the ability of the solute to scintillate. These are the *p*-chlorophenyl, *p*-fluorophenyl, 1-naphthyl, 3-pyridyl, and styryl groups. The 2-naphthyl and 4-biphenylyl groups

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(1) (a) Work performed under the auspices of the U. S. Atomic Energy Commission. (b) Paper VI: M. D. Barnett, G. H. Daub, F. N. Hayes, and D. G. Ott, *J. Am. Chem. Soc.*, **81**, 4583 (1959).

(2) F. N. Hayes, V. N. Kerr, D. G. Ott, E. Hansbury, and B. S. Rogers, Los Alamos Scientific Laboratory Report **LA-2176**, Office of Technical Services, U. S. Dept. Commerce, Washington 25, D. C. (1958).

(3) H. Kallman and M. Furst, *Phys. Rev.*, **79**, 857 (1950).

(4) H. Kallman and M. Furst, *Nucleonics*, **13**, No. 3, 32 (1951).

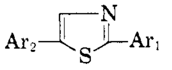
(5) J. R. Arnold, *Science*, **122**, 1139 (1955).

(6) F. N. Hayes, D. G. Ott, V. N. Kerr, and B. S. Rogers, *Nucleonics*, **13**, No. 12, 38 (1955).

(7) H. Gilman, E. A. Weipert, T. Soddy, and F. N. Hayes, *J. Org. Chem.*, **22**, 1169 (1957).

TABLE I

PULSE-HEIGHT AND SPECTRAL DATA



Ar_1	Ar_2	I_{max}[a]	c_{max}	λ^{fl}_{max}	$\bar{\lambda}$	$\lambda^{abs}_{max_1}$	$\epsilon_1 \times 10^{-4}$	$\lambda^{abs}_{max_2}$	$\epsilon_2 \times 10^{-4}$
p-FC_6H_4	C_6H_5	0.23 (*0.96*)	7.5	392	424	323	2.35	221s[b]	1.08
p-ClC_6H_4	C_6H_5	0.26 (*0.94*)	6.0	400	428	330	2.69	228	1.02
o-IC_6H_4	C_6H_5	0.10 (*>0.10*)	...	403	436	315	1.76	247s	1.08
m-IC_6H_4	C_6H_5	0.10 (*>0.10*)	...	394	424	330	2.54	224	1.94
p-$(CH_3)_2NC_6H_4$	C_6H_5	0.72 (*0.95*)	2.3	434	444	365	3.40	232	1.52
4-C_6H_5-C_6H_4	C_6H_5	0.39 (*1.18*)	6.0	414	440	339	3.48	220s	1.76
1-$C_{10}H_7$	C_6H_5	0.22 (*0.93*)	4.4	425	456	337	1.80	288	1.12
C_6H_5	2-$C_{10}H_7$	0.42 (*1.02*)	5.0	410	440	339	2.84	221[c]	5.60
Styryl	C_6H_5	0.21 (*0.71*)	10.0	430	470	352	3.20	222	1.40
2-Thienyl	C_6H_5	0.10 (*>0.41*)	...	424	456	343	2.63	...	...
3-Pyridyl	C_6H_5	0.26 (*0.93*)	5.2	396	424	324	2.26	226s	0.92
4-Pyridyl	C_6H_5	0.70 (*0.79*)	2.9	400	422	333	2.16	225s	0.80
2-(5-Phenyl-thiazolyl)	C_6H_5	0.13 (*0.76*)	3.2	454	484	370	3.58	223s	1.64
C_6H_5	C_6H_5	*0.23*[d]	*5*	*396*	*428*	*337*	*2.75*	*223s*	*1.00*

[a] Pulse heights are relative to 2,5-diphenyloxazole at 3 g./l. = 1.00. Italicized figures in parentheses for corresponding oxazoles.[6,8] [b] s following a wave length signifies a shoulder. [c] Other maxima occur at 295, 284, 254, and 246 mμ. [d] Refs. (6) and (8).

produced a doubling of the pulse height. These results are quite in line with those found in the oxazole series.

The most striking change is wrought by the p-dimethylaminophenyl and the 4-pyridyl groups. In both instances, the pulse height has been raised by a factor of three. While this effect has been noted before in connection with the p-dimethylamino group,[5,7] this is the first instance where the same effect can be attributed to the 4-pyridyl substituent. It is interesting to compare the effect of the pyridyl substituents upon the oxazole and the thiazole. With the former, the 4-pyridyl substituted compound has a smaller pulse height than the 3-pyridyl substituted one. Here, with the thiazoles, the effect is reversed and the differences in pulse height are much greater.

This increase in pulse height with dimethylamino substitution has been attributed to the increase in extinction coefficient of the ultraviolet absorption spectrum with a consequent diminution of the lifetime of the excited state, thereby eliminating some internal quenching.[8] Such an explanation would not apply in the case of 4-(5-phenyl-2-thiazolyl)-pyridine, since its extinction coefficient is lower even than that of 2,5-diphenylthiazole.

A further introduction of sulfur into the scintillator molecule proved to be quite detrimental. Thienyl substitution rendered the molecule inactive, and phenylthiazolyl substitution lowered the pulse height by one half.

Though the lighter halogens produced no large objectionable effect, the heavier halogens did. A solution of 2-(m-iodophenyl)-5-phenylthiazole in toluene was exposed to light for a period of several days and soon produced a color characteristic of free iodine. Thus, in addition to other modes of quenching, these halo compounds are inherently unstable and could decompose to give nonscintillating materials.

The replacement of an oxygen atom by a sulfur atom produced a bathochromic shift both in fluorescence and absorption spectra, with one exception. Although the absorption spectrum of 2-(m-iodophenyl)-5-phenylthiazole had shifted to longer wave lengths, the fluorescence spectrum showed a hypsochromic shift. The ultraviolet absorption spectra were quite similar to those of the oxazoles. In general, there were three bands present, though only the first was well resolved. The other bands were represented by shoulders. The shoulder which represented the second absorption band occurred in the same place (225 ± 5 mμ) as $\lambda^{abs}_{max_2}$ of the oxazole,[7] and thus this band seemed to be a characteristic shared in common.

Structure in the thiazole fluorescence spectra was much less well defined. The long wave-length shoulder was missing in some of the spectra and the relative intensities were lower, which was in agreement with the decreased pulse heights. The mean wavelength is important, since the detector system is discriminatory with regard to wave length of the light. Though thiazoles produce light which is more favorably treated in the detector system, their inherent low efficiency for scintillation makes them less preferred in general for application as liquid scintillator solutes.

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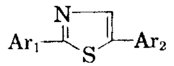
(8) D. G. Ott, F. N. Hayes, E. Hansbury, and V. N. Kerr, *J. Am. Chem. Soc.*, **79**, 5448 (1957).

TABLE II

THIAZOLES



Ar_1	Ar_2	Formula	M.P., °C.[a]	Carbon, %		Hydrogen, %		Nitrogen, %		Sulfur, %		Yield, %	Amide Ref.
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found		
p-FC_6H_4	C_6H_5	$C_{15}H_{10}FNS$	137–138.5	70.57	70.65	3.95	4.22	5.49	5.56	...	...	62	[b]
p-ClC_6H_4	C_6H_5	$C_{15}H_{10}ClNS$	144.5–145	66.29	66.50	3.71	3.75	5.15	5.17	11.80	11.85	56	[b]
o-IC_6H_4	C_6H_5	$C_{15}H_{10}INS$	77–78	49.60	49.89	2.78	2.98	3.86	3.79	8.83	8.73	12	[b]
m-IC_6H_4	C_6H_5	$C_{15}H_{10}INS$	117–117.5	49.60	49.80	2.78	2.78	3.86	3.78	8.83	8.83	38	[b]
p-$(CH_3)_2NC_6H_4$	C_6H_5	$C_{17}H_{16}N_2S$	160–162	72.82	72.88	5.75	5.94	9.99	10.17	11.44	11.31	13	8
4-C_6H_5-C_6H_4	C_6H_5	$C_{21}H_{15}NS$	190–191	80.47	80.78	4.82	4.88	4.47	4.57	10.23	10.15	59	[b]
1-$C_{10}H_7$	C_6H_5	$C_{19}H_{13}NS$	93.5–96.5	79.41	79.33	4.56	4.55	4.87	4.90	11.16	11.15	54	[c]
C_6H_5	2-$C_{10}H_7$	$C_{19}H_{13}NS$	145–146.5	79.41	79.44	4.56	4.62	4.87	4.95	11.16	11.32	28	[d]
Styryl	C_6H_5	$C_{17}H_{13}NS$	137–138	77.53	77.55	4.98	4.93	5.32	5.37	12.18	12.24	11	[c]
2-Thienyl	C_6H_5	$C_{13}H_9NS_2$	93.5–95.5	64.16	64.26	3.73	3.97	5.76	5.77	26.35	26.35	23	[b]
3-Pyridyl	C_6H_5	$C_{14}H_{10}N_2S$	104–104.5	70.56	70.66	4.23	4.53	11.76	11.99	13.46	13.50	62	[e]
4-Pyridyl	C_6H_5	$C_{14}H_{10}N_2S$	147–148.5	70.56	70.44	4.23	4.34	11.76	11.64	13.46	13.64	21	[e]
2-(5-Phenyl-thiazolyl)	C_6H_5	$C_{18}H_{12}N_2S_2$	240–241	67.47	67.28	3.78	3.64	8.74	8.67	20.01	19.88	9	[b]

[a] All melting points are uncorrected and were taken on a Fischer-Johns melting point block. Microanalyses performed by Micro-Tech Laboratories, Skokie, Ill. Solvents for recrystallization were either hexane or a mixture of hexane and toluene. [b] F. N. Hayes, B. S. Rogers, and D. G. Ott, *J. Am. Chem. Soc.*, **77**, 1850 (1955). [c] J. Lister and R. Robinson, *J. Chem. Soc.*, 1297 (1912). [d] F. N. Hayes, L. C. King, and D. E. Peterson, *J. Am. Chem. Soc.*, **74**, 1106 (1952). [e] D. G. Ott, F. N. Hayes, and V. N. Kerr, *J. Am. Chem. Soc.*, **78**, 1941 (1956).

EXPERIMENTAL

The compounds in Table II were synthesized by the method of Gabriel[9] from previously reported amides. The specific references for the amides are listed in the table.

Details concerning the experimental methods for obtaining the fluorescence spectra,[8] the ultraviolet absorption spectra,[8] and the pulse heights[6] may be found in previous papers. The infrared absorption spectra may be found in the Sadtler Standard Spectra.[10]

Los Alamos, N. M.

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[9] S. Gabriel, *Ber.*, **43**, 137 (1910).

[10] Samuel P. Sadtler and Son, Inc., Philadelphia, Pa.

[Contribution from the Biomedical Research Group of the Los Alamos Scientific Laboratory of the University of California]

Liquid Scintillators. VIII. The Effect of the Dialkylamino Group[1]

V. N. KERR, F. N. HAYES, D. G. OTT, R. LIER, AND E. HANSBURY

Received March 30, 1959

A number of dialkylamino substituted 2,5-diaryloxazoles have been synthesized. The effect of the dialkylamino group upon the capability of these and other compounds to perform as liquid scintillator solutes is discussed.

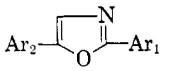
Since 1955, this laboratory has maintained a screening program for potential liquid scintillator solutes.[2] A number of the solutes which contained the dialkylamino group were found to be rather good solutes when compared to the parent compound which would not scintillate at all. Since the time that the screening program was started, there have appeared in the literature a number of instances of the effect of this group upon liquid scintillator solutes.[3–10]

In addition to the beneficial effects of this group, it has also been noted that it can be harmful or ineffective.[5,8,9] The harmful effect of this group appeared with substitution in compounds which already had an appreciable pulse height. Evidently the beneficial effects are here outweighed by the quenching effect.[11]

Until now, observations on the effect of this group have been only incidental to other studies. The dialkylamino substituted oxazoles present an opportunity to study this group with a series of compounds which are notably good scintillator solutes.

TABLE I

Pulse-Height and Spectral Data



Ar_1	Ar_2	I_{max}[a]	c_{max}	λ^{fl}_{max} (mμ)	$\bar{\lambda}$ (mμ)	$\lambda^{abs}_{max_1}$ (mμ)	$\epsilon_1 \times 10^{-4}$
p-$(CH_3)_2NC_6H_4$	C_6H_5	0.95[b]	3.2	403	428	345	4.08
C_6H_5	p-$(CH_3)_2NC_6H_4$	0.87	3.8	426	446	340	3.28
p-$CH_3C_6H_4$	p-$(CH_3)_2NC_6H_4$	0.85	4.2	420	440	339	3.38
p-$CH_3OC_6H_4$	p-$(CH_3)_2NC_6H_4$	0.97	6.4	414	426	337	3.80
p-$(CH_3)_2NC_6H_4$	p-$(CH_3)_2NC_6H_4$	0.69	2.5	422	450	355	4.52
1-$C_{10}H_7$	p-$(CH_3)_2NC_6H_4$	0.66	3.3	470	492	360	2.62
3-Pyridyl	p-$(CH_3)_2NC_6H_4$	0.90	2.7	439	460	352	2.87
N,*N*-Diethyl-4-biphenylamine[c]		0.62	6.1	368	373	301	3.00
Biphenyl[c]		...	...	312	319	...	...

[a] Relative to 2,5-diphenyloxazole at 3 g./l. = 1.00. [b] Ref. (9). [c] Eastman Kodak, recrystallized.

It can be seen from Table I that the presence of

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[1] (a) Work performed under the auspices of the U. S. Atomic Energy Commission. (b) Paper VII: Ref. 10.

[2] F. N. Hayes, V. N. Kerr, D. G. Ott, E. Hansbury, and B. S. Rogers, Los Alamos Scientific Laboratory Report *LA*-**2176**, Office of Technical Services, U. S. Dept. Commerce, Washington 25, D. C. (1958).

[3] J. R. Arnold, *Science*, **122**, 1139 (1955).

[4] H. Gilman, E. A. Weipert, T. Soddy, and F. N. Hayes, *J. Org. Chem.*, **22**, 1169 (1957).

[5] H. Gilman, E. A. Weipert, and F. N. Hayes, *J. Org. Chem.*, **23**, 760 (1958).

[6] H. Gilman, E. A. Weipert, and F. N. Hayes, *J. Org. Chem.*, **23**, 910 (1958).

[7] R. H. Wiley, C. H. Jarboe, Jr., and F. N. Hayes, *J. Org. Chem.*, **23**, 268 (1958).

[8] R. H. Wiley, *et al.*, *J. Org. Chem.*, **23**, 732 (1958).

[9] D. G. Ott, F. N. Hayes, E. Hansbury, and V. N. Kerr, *J. Am. Chem. Soc.*, **79**, 5448 (1957).

[10] V. N. Kerr, F. N. Hayes, D. G. Ott, and E. Hansbury, *J. Org. Chem.* **24**, 1861 (1960).

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