[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE AND THE LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA]

Some Derivatives of Aza-aromatic Heterocycles as Liquid Scintillator Solutes

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A wide variety of polyaryls containing an aza-aromatic heterocycle have been screened as liquid scintillator solutes. In general this heterocycle appears to be less effective than other nitrogen heterocycles, but some striking effects of the dialkylamino derivatives are observed. A number of the compounds are previously unreported, and details of their syntheses are given.

Among the numerous interesting systems suggested, but thus far not investigated, by previous reports[1] of liquid scintillator solutes is the series of polyaryls involving the pyridine nucleus. Most of these compounds are more soluble in aromatic solvents than their benzene analogs, and a wide variety is readily accessible by way of addition of aryllithium reagents to the azomethine linkage and subsequent oxidation of the dihydro intermediate by a method first reported by Ziegler[2] and later refined by many investigators.

This mode of preparation restricts one to α-substituted derivatives, but this series appears to be most promising on the basis of the three 2-pyridyl-5-phenyloxazole isomers previously reported.[1b] In that instance the α-isomer registered a relative pulse height of 0.94, the β-isomer 0.93, and the γ-isomer 0.79, as compared with a value of 1.00 for 2,5-diphenyloxazole, the commonly accepted arbitrary standard.

Included in Table I are a number of dialkylamino derivatives, some of which have rather high values, which seems to confirm the view that this group makes a definite, positive contribution to the scintillation ability of a solute. The first suggestion of the striking influence of this function was noted in the report by Arnold[1d] of high values for 7-diethylamino-4-methylcoumarin and 2-(*p*-dimethylaminophenyl)benzothiazole (0.93 and 0.90, respectively). In the first of these compounds there is a carbonyl function and in the second a sulfur atom in the heterocyclic ring. Both of these are generally believed to give rise to marked decreases n the scintillation ability of a solute.

Of particular interest among the dialkylamino derivatives in Table I is the rather pronounced difference between 2-(*p*-diethylamino and *p*-dimethylaminophenyl)pyridine (0.45 and 0.80, respectively). Although a direct analogy is not available among the quinoline derivatives, corresponding compounds with different nuclear substituents are available. 6-Chloro-2-(*p*-dimethylaminophenyl)quinoline gives a slightly higher value (0.63) than the corresponding diethylamino derivative with the methoxyl group in the 6-position (0.59), and this latter value is higher than the diethylamino derivative of the bare nucleus (0.50). This difference is again favorable to the dimethylamino group in view of previous values,[1b] which show a marked and consistent superiority of methoxy derivatives over the corresponding chloro derivatives of oxazole and oxadiazole. A final observation with respect to dialkylamino compounds is the two instances in which the dimethylaminophenyl moiety is separated from the quinoline nucleus by a vinyl group, 2-(*p*-dimethylaminostyryl)quinoline and 4-(*p*-dimethylaminostyryl)quinoline. There is obviously no ready explanation for the failure of these compounds to scintillate that would also admit the possibility of the corresponding *m*-amino compound having a value of 0.51. It appears necessary to test a greater variety of this type of compound in order to make a more definitive statement with regard to the vinyl group.

The compounds without functional groups seem to indicate that the aza-aromatic heterocycles are clearly inferior to other nitrogen heterocycles. As evidence of this 2-(4-biphenylyl)pyridine, 2,5-diphenylpyrazine,[1b] 3,6-diphenylpyridazine[1b] and 1-(4-biphenylyl)isoquinoline fail to give a significant response, even though all are closely related to *p*-terphenyl. 2,6-Diphenylpyridine, which may be thought of as an analog of 2,5-diphenylpyrrole as well as *m*-terphenyl, fails to give a measurable response. The latter two have been reported as 0.97[1b] and 0.44,[1a] respectively.

The values reported in Table I were measured in the pulse height analyzer previously described,[1b] and all were measured at a concentration of 3 g./l. in toluene except 7, 21, 24, 32, 39, and 41 which, due to limited solubility, were measured as saturated solutions. All values are relative to 2,5-diphenyloxazole which is assigned the arbitrary value of 1.00.

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[1] (a) H. Kallman and M. Furst, *Nucleonics*, **8**, No. 3, 32 (1951); (b) F. N. Hayes, D. G. Ott, V. N. Kerr, and B. S. Rogers, *Nucleonics*, **13**, No. 12, 38 (1955); (c) F. N. Hayes, D. G. Ott, and V. N. Kerr, *Nucleonics*, **14**, No. 1, 44 (1956); (d) J. R. Arnold, *Science* **122**, 1139 (1955).

[2] K. Ziegler and H. Zeiser, *Ann.*, **485**, 174 (1931).

TABLE I

PRIMARY-SOLUTE RELATIVE PULSE HEIGHTS

Compounds	Relative Pulse Height	Ref.
Substituted Pyridine		
1. 2-Phenyl	<0.10	a
2. 2-(4-Biphenylyl)	0.12	a
3. 2,6-Diphenyl	<0.10	b
4. 6-(4-Biphenylyl)-2-phenyl	0.47	c
5. 2-(*p*-Dimethylaminophenyl)	0.80	b
6. 2-(*p*-Diethylaminophenyl)	0.45	d
7. 2,6-Bis(*p*-diethylaminophenyl)	0.15	d
8. 2-(9-Carbazolyl)	0.20	e
9. 2-(10-Phenothiazinyl)	<0.10	f
10. 2-(5-Oxo-10-phenothiazinyl)	<0.10	f
11. 2-(5,5-Dioxo-10-phenothiazinyl)	<0.10	f
12. 4-(*m*-Aminostyryl)	0.49	g
Substituted Quinoline		
13. 2-Phenyl	<0.10	2
14. 4-Methyl-2-phenyl	<0.10	h
15. 4-(1-Hydroxy-1-methylpropyl)-6-methoxy-2-phenyl	0.13	i
16. 4-(α-Hydroxy-α-methylbenzyl)-6-methoxy-2-phenyl	0.13	
17. 4-(α-Hydroxy-α-methyl-*p*-dimethylaminobenzyl)-6-methoxy-2-phenyl	<0.10	i
18. 2-Mesityl	<0.10	j
19. 4,7-Dichloro-2-(*p*-tolyl)	<0.10	k
20. 4,7-Dichloro-2-(*p*-methoxyphenyl)	0.17	k
21. 2-(*p*-Dimethylaminophenyl)-6-chloro	0.63	d
22. 2-(*p*-Diethylaminophenyl)	0.50	d
23. 2-(*p*-Diethylaminophenyl)-6-methoxy	0.59	d
24. 2-(*m*-Diethylaminophenyl)	<0.10	d
25. 2-(*m*-Diethylaminophenyl)-8-methyl	0.57	d
26. 2-[*p*-(Trimethylsilyl)phenyl]	<0.10	c
27. 2-(9-Carbazolyl)	0.14	e
28. 2-[*m*-(Trifluoromethyl)styryl]	<0.10	g
29. 2-(*m*-Aminostyryl)	0.51	g
30. 2-(*p*-Dimethylaminostyryl)	<0.10	g
31. 4-(*p*-Dimethylaminostyryl)	<0.10	g
32. 2-(*p*-Terphenyl-4-yl)	0.12	c
Substituted Isoquinoline		
33. 1-Phenyl	<0.10	2
34. 1-(2-Biphenylyl)	<0.10	c
35. 1-(4-Biphenylyl)	<0.10	c
Benzoquinolines		
36. Benzo[*h*]quinoline	<0.10	l
37. 2-Phenylbenzo[*g*]quinoline	0.27	m
38. 6-Phenylphenanthridine	<0.10	n
39. 9-(*p*-Dimethylaminophenyl)acridine	0.26	d
Bisaza-aromatics		
40. 2,3-Diphenylquinoxaline	<0.10	n
41. 2,3-Bis(*p*-hydroxyphenyl)quinoxaline	<0.10	n
42. 6-Amino-2,3-bis(*p*-methoxyphenyl)-quinoxaline	<0.10	n
43. 2,3-Bis(*p*-methoxystyryl)quinoxaline	0.18	n
44. 2,3-Bis(3,4-dimethoxystyryl)quinoxaline	0.29	n
45. Phenazine	<0.10	o

[a] J. Evans and C. Allen, *Org. Syntheses*, **18**, 70 (1938). [b] H. Gilman and J. T. Edwards, *Can. J. Chem.*, **31**, 464 (1953). [c] See Experimental. [d] H. Gilman and D. Shirley, *J. Am. Chem. Soc.*, **72**, 2181 (1950). [e] H. Gilman and J. B. Honeycutt, *J. Org. Chem.*, **22**, 226 (1957). [f] H. Gilman and R. O. Ranck, *J. Org. Chem.*, in press. [g] H. Gilman and G. Karmas, *J. Am. Chem. Soc.*, **67**, 342 (1945). [h] D. Tarbell, J. Burnett, R. Carlin, and V. Wystrach, *J. Am. Chem. Soc.*, **67**, 1584 (1945). [i] R. A. Benkeser, Doctoral dissertation, Iowa State College, Ames, Iowa, 1947. [j] W. Oldham and I. Johns, *J. Am. Chem. Soc.*, **61**, 3291 (1939). [k] H. Gilman and R. A. Benkeser, *J. Am. Chem. Soc.*, **69**, 124 (1947). [l] H. Skraup, *Monatsh.*, **2**, 163 (1881). [m] H. Gilman and R. D. Nelson, *J. Am. Chem. Soc.*, **70**, 3316 (1948). [n] H. Gilman and H. S. Broadbent, *J. Am. Chem. Soc.*, **70**, 2620 (1948). [o] H. Waterman and D. Vivian, *J. Org. Chem.*, **14**, 289 (1949).

EXPERIMENTAL[3]

6-(4-Biphenylyl)-2-phenylpyridine. A. From 4-biphenylyllithium and 2-phenylpyridine. A solution containing 0.073 mole of 4-biphenyllithium[4] in 200 ml. of ether was added in rapid drops (30 min.) to a solution of 11.3 g. (0.073 mole) of 2-phenylpyridine in 100 ml. of toluene. After refluxing 12 hr., Color Test I[5] was negative. The ether was removed, and the remaining toluene solution was refluxed 8 hr., cooled and carefully poured over crushed ice. The layers were separated and the aqueous layer was washed with 50 ml. of benzene. The combined organic layer was filtered from a small amount of quaterphenyl (formed in the preparation of 4-biphenylyllithium) and dried over potassium hydroxide pellets. Removal of solvents and recrystallization of the residue from benzene gave 4.2 g. (18.7%) of white plates, m.p. 147–148.5°. The analytical sample melted at 150–151°.

Anal. Calcd. for $C_{23}H_{17}N$: C, 89.86; H, 5.57; N, 4.57. Found: C, 89.17; H, 5.87; N, 4.66.

B. From phenyllithium and 2-(4-biphenylyl)pyridine. The previous preparation was repeated using phenyllithium and 2-(4-biphenylyl)pyridine. The yield was 27.2%, and the products were shown to be identical by both mixed melting point and superposition of the infrared spectra.

2-[p-(Trimethylsilyl)phenyl]quinoline. To a stirred solution of 13.0 g. (0.10 mole) of quinoline in 100 ml. of ether was added dropwise a solution of 0.082 mole of *p*-(trimethylsilyl)phenyllithium.[6] When addition was complete the orange mixture was refluxed overnight, and then hydrolyzed with saturated ammonium chloride solution. The ether extract was dried over anhydrous sodium sulfate and the ether distilled. The residue was treated with 20 ml. of nitrobenzene for 15 min. at 180°. After removal of the nitrobenzene at reduced pressure, the remaining viscous liquid was distilled at 165–166° (0.005 mm.). The product, which solidified in the receiver, was recrystallized from ethanol and melted 69–70°. Yield 9.4 g. (42%).

Anal. Calcd. for $C_{18}H_{19}NSi$: Si, 10.13. Found: Si, 10.25.

1-(4-Biphenylyl)isoquinoline. To a stirred solution of 13.0 g. (0.10 mole) of isoquinoline in 150 ml. of ether was added dropwise a solution of 0.085 mole of 4-biphenylyllithium[4] over a period of 45 min. At the completion of the addition the mixture was red-brown, and Color Test I[5] was negative. The reaction mixture was worked up as described for 2-[*p*-(trimethylsilyl)phenyl]quinoline. The residue after distillation of the ether was treated with nitrobenzene for 30 min. at 190°. The nitrobenzene was removed by distillation at reduced pressure, and the residue crystallized from ethanol. The yield was 7.0 g. (45%), melting at 169–170°. The infrared spectrum showed no band at 2.9–3.1 μ indicating the absence of N—H bond.

Anal. Calcd. for $C_{21}H_{15}N$: N, 4.98. Found: N, 4.74.

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(3) All melting points are uncorrected. Reactions involving organolithium reagents were carried out under an atmosphere of dry, oxygen-free nitrogen in sodium-dried solvents.

(4) H. Gilman, E. A. Zoellner, and W. Selby, *J. Am. Chem. Soc.*, **54**, 1957 (1932).

(5) H. Gilman and J. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(6) H. Melvin, Doctoral dissertation, Iowa State College, Ames, Iowa, 1954.

1-(2-Biphenylyl)isoquinoline. The compound was prepared in the same manner as described for the *para*-isomer. The yield was 2.0 g. (14%), melting at 220–221°. The infrared spectrum showed no N—H bonding.

Anal. Calcd. for $C_{21}H_{15}N$: N, 4.98. Found: N, 4.98.

2-(p-Terphenyl-4-yl)quinoline. To a stirred solution of 1.3 g. (0.01 mole) of quinoline in 100 ml. of ether was added a solution of *p*-terphenyl-4-yllithium[7] in 100 ml. of ether. Upon completion of the addition the reaction mixture was yellow and Color Test I[5] was negative. The mixture was worked up and the intermediate oxidized as before. The product, after recrystallization from benzene, melted at 274–275°. The yield was 1.2 g. (37%). The infrared spectrum again showed the absence of N—H bonding.

Anal. Calcd. for $C_{27}H_{19}N$: N, 3.90. Found: N, 3.73.

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[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

The Dinitriles of Acetylenedicarboxylic and Polyacetylenedicarboxylic Acids.[1] I.[2] Dicyanoacetylene and Dicyanodiacetylene

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The synthesis of dicyanoacetylene, C_4N_2, and dicyanodiacetylene, C_6N_2, is described. The pure compound C_6N_2 is stable at room temperature in the absence of oxygen. Vapor pressure, infrared spectral data, and other physical properties are presented and discussed.

A phase of high temperature research currently under investigation in our laboratories is the production of ultrahigh temperatures by means of chemical reactions. The attainment of such temperatures depends upon the exothermicity of the reaction and the thermodynamic stability of the products of combustion. A flame temperature of slightly over 5000°K. has been reached by burning cyanogen with oxygen under pressure to CO and N_2.[3]

It was obvious that higher flame temperatures could be attained with compounds possessing a higher endothermic heat of formation than cyanogen and could also be burned to the same thermally stable products, *i.e.*, CO and N_2. A series of such compounds exists in the dinitriles of acetylenedicarboxylic and polyacetylenedicarboxylic acids or dicyanoacetylene and dicyanopolyacetylene, having the general formula

$$N{\equiv}C{-}(C{\equiv}C)_n{-}C{\equiv}N$$
$$\text{where } n = 1, 2, 3 \ldots.$$

The importance of these compounds in the production of high temperatures has led us to conduct a study of the preparative methods and comparative properties of the individual members in this series. This paper will present and discuss the synthesis and properties of dicyanoacetylene and dicyanodiacetylene.

Kirshenbaum and Grosse[4] found that the first member of the series ($n = 1$), carbon subnitride[5] (C_4N_2) burned with oxygen produces a temperature of 5260°K. at 1 atm. and should produce 5750°K. at 40 atm. With the substitution of ozone for molecular oxygen a temperature of 5520°K. at 1 atm. is expected. C_4N_2 was prepared by the slightly modified method of Moureu and Bongrand.[5]

$$H_3COOC{-}C{\equiv}C{-}COOCH_3 \xrightarrow{NH_4OH} H_2NOC{-}C{\equiv}C{-}CONH_2 \xrightarrow{P_2O_5} N{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$$

The dinitrile, dicyanoacetylene, is a clear colorless liquid, b.p. 76.5°, which solidifies into mono-

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(2) Technical Note No. 3, Report Control No. AFOSR-TN-57-33, Contract No. AF 18(600)-1475, Project No. 7-7968, December 19, 1956, Air Force Office of Scientific Research, Air Research and Development Command, U. S. Air Force, Washington 25, D. C.

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