

tered and the solid washed with cold methanol. The combined filtrates were evaporated to dryness and the residue taken up in water. Bis( $\Delta^2$ -2-oxazoliny), melting at 210–213°, was obtained by adding sufficient alcohol to make the solution 25% and then ether to give a permanent cloudiness. An 87% yield of white needles resulted.

Ultraviolet absorption spectra were obtained with a Beckmann DK 2 Spectrophotometer. Acknowledg-

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2-Mercaptoethylamine hydrochloride from Evans Chemetics, Inc., 2-aminobenzenethiol from American Cyanamide Co., *o*-nitroaniline from National Aniline Division, Allied Chemical and Dye Corp.

BUFFALO, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE AND THE BIOMEDICAL RESEARCH GROUP, LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA]

## Substituted 4,7-Phenanthrolines and Benzo[*f*]quinolines as Scintillation Solutes

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A new synthesis for 4,7-phenanthroline based on *N,N'*-diacetyl-*p*-phenylenediamine has been developed. In reactions with aryllithium reagents it has been shown that 4,7-phenanthroline undergoes mono- and disubstitution reactions at positions 3 and 8. In this manner the 3,8-diphenyl, 3-phenyl, 3-(*p*-tolyl), and 3-*p*-dimethylaminophenyl derivatives of 4,7-phenanthroline have been prepared. In each case the intermediate dihydro compound was isolated. These compounds and the analogous benzo[*f*]quinolines have been evaluated as scintillation solutes. Their behavior as solutes in liquid scintillation systems is shown by calculation and actual light output to involve considerable self-quenching. The 650  $\text{cm}^{-1}$  to 900  $\text{cm}^{-1}$  region of the infrared spectrum has been analyzed for each of the benzo[*f*]quinolines and 4,7-phenanthrolines and is shown to be composed of vibrational frequencies due to the individual aromatic rings involved.

Those substances which have been shown to function most efficiently as solutes in liquid scintillation counting systems are structurally simple materials built up of aromatic rings in continuous conjugation. For example, *p*-terphenyl and 2-phenyl-5-(*p*-biphenyl)oxazole are excellent solutes for liquid scintillation systems. In compounds like 4,7-phenanthroline and benzo[*f*]quinoline which possess phenanthrene-like structures there exists the possibility of building up molecules containing a similar arrangement of rings in continuous conjugation; however, such materials have thus far not been evaluated as scintillator solutes. In this report we wish to describe the preparation and discuss the relative pulse heights of a series of new mono and disubstituted 4,7-phenanthrolines and the corresponding 3-substituted benzo[*f*]quinolines.

Phenanthrolines containing the desired substituents in either or both the 3 and the 8 positions are theoretically available by a number of routes involving either the well-known ring formation reactions<sup>1</sup> of quinoline chemistry or by direct addition to the azomethine bond of the phenanthroline. In view of its generality of application to aromatic bromine compounds the addition of aryllithium reagents to 4,7-phenanthroline was considered to be the best synthetic approach to obtaining such structures. This necessitated a source of 4,7-phenanthroline which is reported to

be available from *p*-phenylenediamine,<sup>2</sup> 6-nitroquinoline,<sup>3,4</sup> or 6-aminoquinoline<sup>5</sup> by the Skraup reaction. In our hands none of these methods were reproducible so the development of a synthesis was undertaken. Conditions have been devised for the use of *N,N'*-diacetyl-*p*-phenylenediamine in the Skraup reaction which give reproducible 60–75% yields of 4,7-phenanthroline. The most efficient oxidizing mixture was found to be nitrobenzene and 96% sulfuric acid with ferrous sulfate as a moderator. In the absence of ferrous sulfate, extensive decomposition of the product takes place. The crude 4,7-phenanthroline was isolated as a black, intractable solid from which the pure material could not be isolated by steam distillation or recrystallization. Purification was, however, readily effected by extracting the crude product with ligroin in a Soxhlet extractor. The procedure described in the experimental section has repeatedly given yields of 60% or over.

The addition of aryllithium reagents to 4,7-phenanthroline was found to proceed smoothly and in good yields as indicated in Table I to yield substituted phenanthrolines according to diagram 1. As in other addition reactions of aryllithium reagents<sup>6</sup> it was found necessary to exclude rigidly all

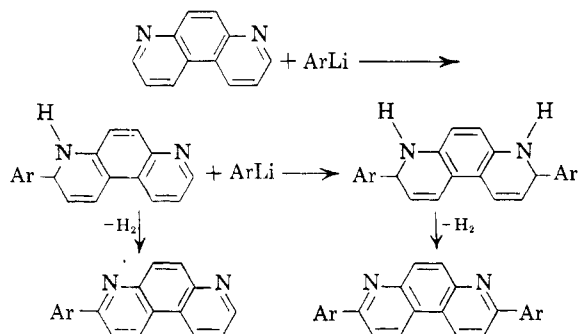
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traces of water from the reaction mixture. It is especially important to dry the phenanthroline which is known to be hygroscopic.<sup>2</sup> The addition proceeds in discreet stages and yields either 3-substituted or 3,8-disubstituted 4,7-phenanthrolines. The initial reaction product in all cases was the dihydrophenanthroline. These materials are spontaneously dehydrogenated in dilute hydrochloric acid solution but show fair stability in basic solution. Both the phenanthrolines and the dihydrophenanthrolines have unusual fluorescent qualities. The fluorescence of the dihydrophenanthrolines is yellow and that of the phenanthrolines blue-white.

TABLE I  
ARYL SUBSTITUTED 4,7-PHENANTHROLINES

Substituent	M.P., °C.	Yield <sup>a</sup>	Nitrogen Analysis	
			Calcd.	Found
3,8-Diphenyl	278	22T	8.43 <sup>b</sup>	8.52
3-Phenyl	188	95A	10.93	11.15
3-( <i>p</i> -Tolyl)	181	80A	10.36	10.49
3-( <i>p</i> -Dimethyl-aminophenyl)	282	62T	14.04	14.05

<sup>a</sup> Recrystallized from T, toluene; A, anisole. Yield in per cent. <sup>b</sup> Calcd. for C<sub>23</sub>H<sub>16</sub>N<sub>2</sub>: C, 86.72; H, 4.85. Found: C, 86.71; H, 4.88.

With the exception of 3-(*p*-tolyl)benzo[f]quinoline which was prepared by *p*-tolyllithium addition, the derivatives of benzo[f]quinoline evaluated here have been previously reported.<sup>7-9</sup> As with the dihydrophenanthrolines the intermediate dihydroquinolines show appreciable stability in basic solutions and are dehydrogenated in dilute hydrochloric acid solutions. The blue-white fluorescence of these compounds is even more pronounced than that of the analogues phenanthrolines.

The infrared spectra of benzo[f]quinoline and 4,7-phenanthroline as well as their homologs are well defined in the C—H region ranging from 650 cm.<sup>-1</sup> to 900 cm.<sup>-1</sup> The data characterizing this

portion of the spectrum is found in Table II. These compounds are structurally analogous to phenanthrene and their spectra should possess at least a qualitative resemblance to that of phenanthrene, which in the 700 cm.<sup>-1</sup> to 825 cm.<sup>-1</sup> region is simple and lends itself to the interpretation that each of the benzene rings is a separate vibrating unit. Thus, one finds in the spectrum of phenanthrene at 732 cm.<sup>-1</sup> a strong band which is characteristic of ortho-disubstituted benzene, a strong band at 815 cm.<sup>-1</sup> and a weaker band at 710 cm.<sup>-1</sup> which are both characteristic of a tetrasubstituted benzene ring with two adjacent C—H bonds. The band at 710 cm.<sup>-1</sup> has been noted<sup>10</sup> as not always occurring; however, in phenanthrene, the benzo[f]quinolines and the 4,7-phenanthrolines it is always present.

In extending the correlations developed for phenanthrene to the benzo[f]quinolines and 4,7-phenanthrolines, the C—H frequencies due to benzene rings are readily assigned. As shown in Table II these bands are shifted towards higher frequencies. Thus the band due to ortho-disubstituted benzene is shifted from 732 cm.<sup>-1</sup> to the range of 745 cm.<sup>-1</sup> to 752 cm.<sup>-1</sup> in the benzo[f]quinoline series. The bands due to a tetrasubstituted benzene ring with two adjacent C—H bands are shifted from 815 cm.<sup>-1</sup> and 710 cm.<sup>-1</sup> to 865–869 cm.<sup>-1</sup> and 781–720 cm.<sup>-1</sup> in the benzo[f]quinolines and to 845–855 cm.<sup>-1</sup> and 705–727 cm.<sup>-1</sup> in the 4,7-phenanthrolines. These assignments are based on the stability of the stronger band to substitution effects, a characteristic most clearly noted in the benzo[f]quinoline derivatives. These data are also presented in Table II.

The assignment of frequencies due to the pyridine rings is more difficult because of the lack of information available on the infrared spectra of substituted pyridine compounds. However, it is known that 2,3-lutidine absorbs at 787 cm.<sup>-1</sup> and 840 cm.<sup>-1</sup> and that other 2,3-disubstituted pyridines absorb in this general region.<sup>11</sup> The spectrum of benzo[f]quinoline has a strong band at 840 cm.<sup>-1</sup> and shoulder at 760 cm.<sup>-1</sup> on the 745 cm.<sup>-1</sup> disubstituted phenyl band. The 3-aryl derivatives of benzo[f]quinoline show alterations of this pattern and also contain a third strong band very close to the 840 cm.<sup>-1</sup> band. Thus the spectrum of 3-phenylbenzo[f]quinoline shows in addition to the appropriate benzene frequencies strong bands at 845 cm.<sup>-1</sup>, 830 cm.<sup>-1</sup>, and 800 cm.<sup>-1</sup>

The spectrum of 4,7-phenanthroline contains a strong band at 835 cm.<sup>-1</sup> and a strong doublet with maxima at 783 cm.<sup>-1</sup> and 790 cm.<sup>-1</sup> showing a relationship to 2,3-lutidine similar to that of benzo[f]quinoline. The 3-aryl and 3,8-diaryl substituted

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


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TABLE II  
 C—H OUT OF PLANE DEFORMATION FREQUENCIES<sup>b</sup>

Ring System	3-Substituent			
Phenanthrene	—	815(s), 710(m)	732(s)	—
Benzo[ <i>f</i> ]quinoline	H	865(s), 720(w)	745(s)	760(sh), 840(sh)
	C <sub>6</sub> H <sub>5</sub> <sup>c</sup>	869(m), 720(w)	750(s)	800(s), 830(s), 845(s)
	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> <sup>d</sup>	869(m), 718(w)	748(s)	792(s), 832(s), 840(s)
	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> <sup>e</sup>	869(m), 718(w)	752(sh)	795(s), 820(s), 835(s)
4,7-Phenanthroline	H	852(s), 705(m)	—	783(s), 790(s), 835(s)
	C <sub>6</sub> H <sub>5</sub> <sup>f</sup>	845(s), 720(m)	—	785(s), 815(s), 835(s)
	C <sub>6</sub> H <sub>5</sub> <sup>g,h</sup>	855(sh), 727(m)	—	775(s), 825(s), 840(s)
	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> <sup>h</sup>	855(s), 720(w)	—	787(s), 832(s), 840(s)
	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> <sup>i</sup>	845(s), 715(w)	—	785(s), 830(s), 840(sh)

<sup>a</sup> Also 8-phenyl. <sup>b</sup> All frequencies are expressed in cm.<sup>-1</sup> <sup>c</sup> Mono substituted phenyl absorption at 690(s) and 765(s). <sup>d</sup> *p*-Disubstituted phenyl absorption at 815(s). <sup>e</sup> *p*-Disubstituted phenyl absorption at 820(s). <sup>f</sup> Mono substituted phenyl absorption at 685(s) and 765(s). <sup>g</sup> Mono substituted phenyl absorption at 680(s) and 767(s). <sup>h</sup> *p*-Disubstituted phenyl absorption at 809(s). <sup>i</sup> *p*-Disubstituted phenyl absorption at 803(s).

4,7-phenanthrolines do not show the doublet, but rather one strong band at about 785 cm.<sup>-1</sup>, a strong band at 830 cm.<sup>-1</sup> to 840 cm.<sup>-1</sup>, and, as with the substituted benzo[*f*]quinolines, a third strong band at 815 cm.<sup>-1</sup> to 832 cm.<sup>-1</sup>

In the light of these data it is apparent that the presence of a disubstituted pyridine ring in this sort of condensed ring system gives rise to two bands in the C—H out of plane deformation region of the infrared. These bands fall at about 840 cm.<sup>-1</sup> and from 760 cm.<sup>-1</sup> to 790 cm.<sup>-1</sup> The introduction of a third substituent adjacent to the C=N bond causes the appearance of a third band which occurs between 815 cm.<sup>-1</sup> and 832 cm.<sup>-1</sup>

TABLE III

Ring system	Solute	Scintillation Data		Fluorescence Spectral Data <sup>a</sup>	
		I <sub>max</sub> <sup>b</sup>	c <sub>max</sub> , g./l.	λ <sub>max</sub> , mμ	λ̄, mμ
Benzo[ <i>f</i> ]quinoline	H	0.07	—	366	386
	C <sub>6</sub> H <sub>5</sub>	0.28	2.1	385	400
	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> <sup>f</sup>	0.33	2.3	388	404
	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	0.72	2.0 <sup>c</sup>	432	444
4,7-Phenanthroline	H	0.07	—	<sup>d</sup>	<sup>d</sup>
	C <sub>6</sub> H <sub>5</sub>	0.11	1.2	<sup>e</sup>	<sup>e</sup>
	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	0.13	1.3	378	416
	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	0.48	0.1 <sup>c</sup>	433	448

<sup>a</sup> 314 mμ Hg-arc line excitation. <sup>b</sup> Measured relative to 3 g./l. 2,5-diphenyloxazole, as pulse heights<sup>1</sup> with a Ba<sup>137</sup> electron source, an evaporated aluminum reflector and a photomultiplier having average S-11 spectral characteristics. <sup>c</sup> Concentration of saturated solution. <sup>d</sup> Response too weak for measurement. <sup>e</sup> Insufficient sample for measurement. <sup>f</sup> M.p. 156°, yield 90%, recrystallized from benzene. *Anal.* Calcd. for C<sub>20</sub>H<sub>15</sub>N<sub>2</sub>: C, 89.18; H, 5.61. Found: C, 89.24; H, 5.55.

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Toluene solutions of the benzo[*f*]quinolines and 4,7-phenanthrolines were subjected to conventional scintillation<sup>12</sup> and spectral<sup>13</sup> tests. The results are presented in Table III.

The parameters, I<sub>max</sub> and c<sub>max</sub>, are the maximum relative light output and the concentration at which this was obtained, respectively. The spectral quantities, λ<sub>max</sub> and λ̄, (obtained from corrected fluorescence spectra) are the most probable wave length and the mean wave length, respectively. The concentration curves for four of these compounds, all of which showed considerable self-quenching, were fitted to the Kallman equation,<sup>14</sup>

$$I = \frac{I_{\infty} R c}{(Q + c)(R + c)}$$

in order to obtain values for I<sub>∞</sub>, the calculated ultimate light output if self-quenching were absent. Values for I<sub>∞</sub> of 0.70 and 0.75 were calculated for 3-phenyl- and 3-*p*-tolylbenzo[*f*]quinoline, respectively, and 0.25 and 0.31 for the correspondingly substituted 4,7-phenanthrolines.

The 3-aryl derivatives of benzo[*f*]quinoline and 4,7-phenanthroline, can be considered as condensed ring analogs of *p*-terphenyl, a very efficient liquid scintillation solute whose value<sup>12</sup> of I<sub>max</sub> is 1.00 (c<sub>max</sub> = 8 g./l.). Inasmuch as carbocyclic analogs such as 2-phenylphenanthrene have not been tested for scintillation properties, it is inappropriate to try to comment at this time on the poor performance of these heterocyclic compounds. The marked improvement of the scintillation properties through substitution of a dialkylamino group on a poor scintillator, as noted in the comparison of 2-phenylbenzothiazole<sup>13</sup> and 2-(*p*-dimethylamino-phenyl)benzothiazole,<sup>15</sup> is clearly evident here but it is unfortunate that limited solubility terminated the rise in the concentration curve of light output for these compounds.

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## EXPERIMENTAL

**4,7-Phenanthroline.** All of the operations in this synthesis were carried out in a well ventilated hood and behind a safety shield. A 12-l. flask equipped with a sealed stirrer and a 400-mm. jacket Allihn condenser is charged with 170 g. *N,N'*-diacetyl-*p*-phenylenediamine, 800 g. 96% sulfuric acid, 200 g. glycerol, 150 g. nitrobenzene, and 84 g. ferrous sulfate heptahydrate. The flask is heated with stirring until the heat of reaction is sufficient to maintain the mixture at steady reflux. After the reaction subsides the mixture is refluxed for 2 hr., diluted with 2 l. of water, and the excess nitrobenzene steam distilled. The strongly acid solution is treated twice with Norite and filtered while hot through an asbestos mat. The liquid is cooled and made basic with ammonium hydroxide. The crude phenanthroline is precipitated as a black, semicrystalline mass which is filtered and dried. The crude product is sewed into a cloth sack and extracted with ligroin (b.p. 66–75°) in a Soxhlet extractor to give 120 g. (75%) of white, crystalline 4,7-phenanthroline, m.p. 173°.

**3-(*p*-Tolyl)-4,7-phenanthroline.** A solution of 50 ml. anhydrous ethyl ether and 4.3 g. (0.025 mole) of freshly distilled *p*-bromotoluene is added very slowly from a dropping funnel to a stirred suspension of 0.4 g. (0.057 g.-atom) of finely chopped lithium ribbon in 100 ml. of anhydrous ether. The reaction is vigorous and the lithium is consumed in 1 hr. The *p*-tolyl lithium reagent thus formed is added dropwise to a stirred solution of 4.7 g. (0.025 M) of 4,7-

phenanthroline in 50 ml. thiophene-free benzene. Initially a red complex is formed which after standing 24 hr. fades to orange. The suspension is shaken in a separatory funnel with 200 ml. water which causes the precipitate to pass into the ether-benzene phase. Evaporation of the solvent leaves the yellow dihydrophenanthroline which vigorously dehydrogenates upon the addition of 6*N* hydrochloric acid to 3-(*p*-tolyl)-4,7-phenanthroline. Two recrystallizations from anisole gave 5.3 g. (80%) of buff needles, m.p. 181°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>: N, 10.36. Found: N, 10.49, 10.48.

The other products listed in the tables were prepared by the same procedure using the appropriate aryllithium reagent. The aryl bromides were distilled just prior to use and the reactions were run under oxygen-free nitrogen. The benzo[*f*]quinoline was prepared as previously described.<sup>16</sup>

**Acknowledgment.** This research was supported in part under Contract No. AT-(40-1)-2162 between the University of Louisville and the Atomic Energy Commission. The authors acknowledge this support with appreciation.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, INDIANA UNIVERSITY]

## Nitration of 3-Phenylquinoline<sup>1,2</sup>

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Mononitration of 3-phenylquinoline gave as the only isolatable product, 3-(*p*-nitrophenyl)quinoline. Further nitration gave two products; the main dinitro compound was proven to be 5-nitro-3-(*p*-nitrophenyl)quinoline. The structure of this substance was proven by synthesis. A modified Skraup reaction using  $\alpha$ -methylacrolein diacetate gave 3-methylquinoline which on nitration resulted in 5- and 8-nitro-3-methylquinoline. The former was oxidized to 5-nitro-3-quinolinecarboxylic acid which was converted to 5-nitro-3-aminoquinoline by way of the azide and urethan. Coupling 5-nitro-3-quinolinediazo hydroxide with dimethylamine gave the corresponding dimethyltriazeno compound which upon decomposition in benzene, produced 5-nitro-3-phenylquinoline. Nitration of the latter gave 5-nitro-3-(*p*-nitrophenyl)quinoline. The synthesis of many other quinoline compounds related to this work is described.

It has been reported by Koenigs and Nef<sup>4</sup> that the nitration of 4-phenylquinoline gave about 60% *p*-nitrophenyl-, 30% *m*-nitrophenyl- and 5% of the *o*-nitrophenyl-quinoline. These were called  $\alpha$ -,  $\beta$ -, and  $\gamma$ -nitro compounds. LeFevre and Mathur<sup>5</sup> found that nitration of 2-phenylquinoline gave about 60% *p*-nitro- and 30% of the *m*-nitro-phenyl quinoline. The latter authors also reported a quan-

titative yield of 2-(*m*-nitrophenyl)quinolinium methosulfate by the nitration of 2-phenylquinolinium methosulfate. Similar ratios of meta and para substitution have been reported by Forsyth and Pyman<sup>6</sup> for the nitration of 2-phenyl- and 4-phenylpyridine. The meta substitution is explained on the basis of ammonium salt formation while the para orientation is explained by attack on the dissociated molecule. The similarity of behavior in the 2-phenyl- and 4-phenyl-quinoline and -pyridine may be attributed to resonance through the vinylogous position in the pyridine ring. A much smaller amount of meta substitution occurred on nitration<sup>7</sup> of 2-benzyl- and 4-benzylpyridine. However, on the basis of vinylogy, it was quite surprising not to

(1) Abstracted from a thesis submitted by B. B. in February 1956, to the Faculty of the Graduate School in partial fulfillment of the requirements for the degree, Doctor of Philosophy, in the Department of Chemistry, Indiana University.

(2) This work was supported in part by the Office of Ordnance Research, contract number DA-33-008-ORD-187.

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