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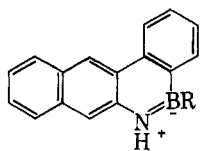
New Heteroaromatic Compounds. XVIII.<sup>1</sup> Boron-Containing Analogs of Benz[a]anthracene<sup>2</sup>

BY MICHAEL J. S. DEWAR AND WERNER H. POESCHE

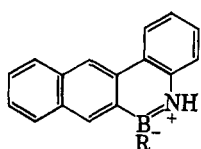
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Previous papers of this series have described a variety of new boron-containing aromatic systems. Here we describe derivatives of 5,6- and 6,5-borazarobenz[a]anthracenes which we have prepared in the hope that they may possess carcinogenic or anticarcinogenic activity.

Dewar, Kubba and Pettit<sup>3</sup> prepared 10-chloro-10,9-borazarophenanthrene by Friedel-Crafts cyclization of the adduct from 2-aminobiphenyl and boron trichloride. We have been extending this synthesis to polycyclic systems related to known carcinogenic hydrocarbons in the hope of obtaining substances with biologically interesting properties. Here we report the synthesis of some derivatives of 5,6- and 6,5-borazarobenz[a]anthracene (I and II).

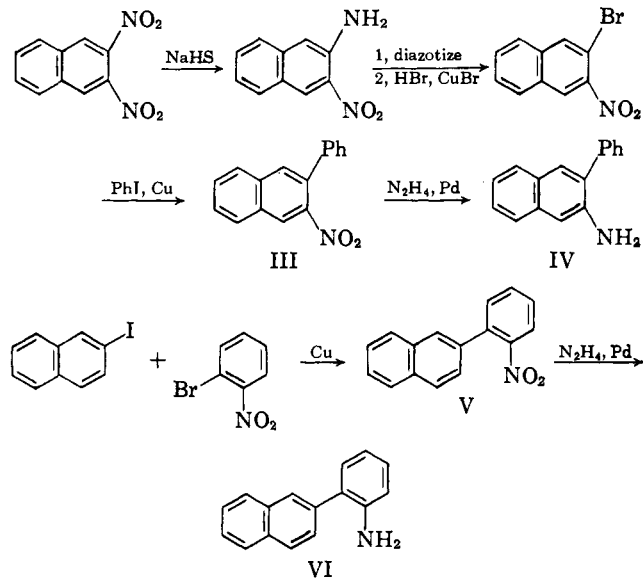


Ia, R = H  
 b, R = Cl  
 c, R = OMe  
 d, R =  $\frac{1}{2}$ O  
 e, R = Me



IIa, R = H  
 b, R = Cl  
 c, R = OMe  
 d, R =  $\frac{1}{2}$ O  
 e, R = Me

The necessary starting materials for these syntheses, 2-amino-3-phenylnaphthalene (IV) and 2-(*o*-aminophenyl)-naphthalene (VI), were prepared by the routes

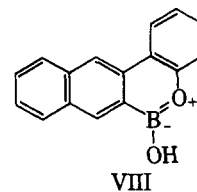
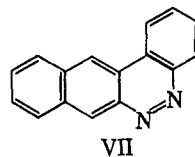


The Ullmann reaction of 2-iodo-3-nitronaphthalene in nitrobenzene gave self-coupling exclusively; however, 2-bromonitronaphthalene gave III in good yield when treated with copper in a large excess of boiling iodobenzene.

Hey and Lawton<sup>4</sup> first prepared V by a Gomberg reaction from *N*-nitroso-2-acetamidonaphthalene and

nitrobenzene and Smith, Clegg and Hall<sup>4</sup> improved the isolation of the products. The synthesis reported here is much more convenient on a large scale.

The amines IV and VI on treatment with boron trichloride and a catalytic amount of aluminum chloride in boiling xylene gave the corresponding chloroborazarobenz[a]anthracenes Ib and IIb. These were converted, without isolation, by hydrolysis and recrystallization from methanol to the methyl ethers Ic and IIc. The structures of these compounds followed from analysis, from analogy,<sup>3</sup> from the presence of a new band at longer wave lengths in the ultraviolet spectrum, and from the conversion<sup>5</sup> of both Ic and IIc to dibenzo[*c,g*]cinnoline (VII) by sodium nitrite in acetic acid. The structure of VII, which has not previously been reported, was in turn indicated by analysis, by its method of preparation, and by the similarity of the ultraviolet spectrum to that of benz[a]anthracene.



The cyclization of VI to derivatives of II rather than to a borazarochrysenes is interesting, given that the  $\alpha$ -positions of naphthalene are the more reactive and that 2-phenylnaphthalene undergoes nitration predominantly in the 1-position.<sup>4</sup> We examined the cyclization product from VI very carefully but could find no evidence for the formation of any ring system other than II. This illustrates very clearly the large steric requirements of the Friedel-Crafts reaction, a reaction which is known to be easily inhibited by *ortho* substituents.

When the diazonium solution from IIc was poured into boiling water instead of being allowed to stand in the cold, nitrogen was eliminated and 6-hydroxy-6,5-borazarobenz[a]anthracene (VIII) was formed. A similar reaction has been reported<sup>6</sup> in the 10,9-borazarophenanthrene series.

Hydrolysis of the ethers Ic and IIc presumably gave the corresponding hydroxy derivatives, which on isolation underwent dehydration to the anhydrides Id and IId. The methyl ethers Ic and IIc reacted normally<sup>7</sup> with methylmagnesium bromide to give the corresponding methylborazarobenzanthracenes Ie and IIe, and with lithium aluminum hydride and aluminum chloride to give the parent compounds Ia and IIa. The anhydrides Id and IId also reacted with methylmagnesium bromide to give Ie and IIe, but the yields were poor and the products tarry.

Dewar and Rogers<sup>8</sup> have studied the charge transfer spectra of complexes formed by various aromatic compounds with tetracyanoethylene (TCNE) and have

(1) Part XVII: M. J. S. Dewar and P. J. Grisdale, *J. Org. Chem.*, **28**, 1759 (1963).

(2) This work was supported by a grant (CY5218) from the Institutes of Health, United States Public Health Service.

(3) M. J. S. Dewar, V. P. Kubba and R. Pettit, *J. Chem. Soc.*, 3073 (1958).

(4) D. H. Hey and S. E. Lawton, *ibid.*, 380 (1940); P. A. S. Smith, F. M. Clegg and J. H. Hall, *J. Org. Chem.*, **23**, 527 (1958).

(5) M. J. S. Dewar and W. H. Poesche, *J. Chem. Soc.*, 2201 (1963).

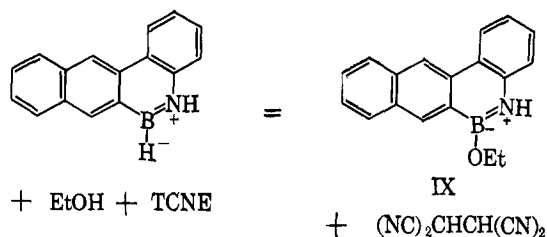
(6) M. J. S. Dewar and P. M. Maitlis, *Chem. Ind. (London)*, 1626 (1960).

(7) M. J. S. Dewar, R. Dietz, V. P. Kubba and A. R. Lepley, *J. Am. Chem. Soc.*, **83**, 1754 (1961).

(8) M. J. S. Dewar and H. Rogers, *ibid.*, **84**, 398 (1962).

shown that the position of the main band can be correlated with the energy of the highest occupied MO of the donor. Using this result, they calculated molecular orbital parameters for boron and nitrogen from the charge transfer bands of various borazarene-tetracyanoethylene complexes. It was, however, emphasized that these values were provisional and would need checking against additional experimental data.

In order to provide such a check we studied the charge transfer spectra of the complexes formed by Ia, IIa and their various derivatives with TCNE in chloroform. No difficulty was encountered with the methyl or methoxy derivatives, Ic, Ie, IIc or IIe, all of which gave stable colorations with TCNE, but the parent compounds (Ia and IIa) reacted rapidly with the acceptor. This reaction was studied in detail in the case of IIa. When chloroform solutions of IIa and TCNE were mixed, the initial green color changed rapidly to violet and then faded, a white precipitate being formed. The ultraviolet spectrum of the final colorless solution was identical with that of IIc and the precipitate was identified as 1,1,2,2-tetracyanoethane (IX). This suggested that alcohol in the chloroform was reacting with IIa in the following way



In confirmation of this we found that Ia and IIa gave stable colors with TCNE in alcohol-free chloroform and that addition of a little alcohol led to the same decoloration and precipitation of IX as observed previously. The hydrides Ia and IIa did not react with alcohol in chloroform in the absence of TCNE. The wave lengths of the various charge transfer bands are shown in Table I.

TABLE I  
CHARGE TRANSFER SPECTRA OF TCNE COMPLEXES

Compound	Wave lengths of charge transfer band, Å.	
Ia	614	
Ic	627	
Ie	620	
IIa	690	477
IIc	701	500
IIe	704	486

We had intended to try to interpret these data using the parameters listed by Dewar and Rogers and their perturbation expression. However, as Dr. Matteson has pointed out to us, there is a numerical error in their paper. The expression for the energy ( $A_i'$ ) of the perturbed orbital  $i$  should read

$$A_i' = A_i + \sum_r a_{ir}^2 (\alpha_r - \alpha_0) + 2 \sum_{r,s} a_{ir} a_{is} (\beta_{rs} - \beta) \quad (1)$$

Using this expression, and the values for the orbital energies estimated by them for 2,1-borazaronaphthalene, 10,9-borazarophenanthrene and 2,7-dibora-1,8-diazaranthracene, we could not obtain satisfactory values for the MO parameters or a satisfactory fit with the new data reported here. It seems that the simple perturbation treatment cannot be used in this case, a very reasonable conclusion since the  $\pi$ -electron distribution in these compounds is probably too uneven for first-order perturbation theory to be applicable.

A more detailed analysis of these results, using more refined MO techniques, will be given elsewhere.

The ultraviolet spectra of Ia and IIa in methylcyclohexane and alcohol-free chloroform, and of their B-methyl and B-methoxy derivatives in chloroform, are shown in Table II. The spectrum of benz[a]anthracene in methylcyclohexane is also listed for comparison.

The ultraviolet absorption spectrum of benz[a]anthracene is typical<sup>9</sup> of an alternant hydrocarbon, showing three strong bands, and one weak band, in the low frequency region. Current theory<sup>10</sup> attributes these to transitions between the highest occupied (2) and next highest occupied (1) orbitals, and the lowest unoccupied (3) and next lowest (4) unoccupied orbitals. The transitions (2  $\rightarrow$  3) and (1  $\rightarrow$  4) correspond, respectively, to the bands designated *para* and  $\beta'$  by Clar<sup>9</sup> and  $L_a$  and  $B_a$  by Platt.<sup>11</sup> The remaining transitions, (1  $\rightarrow$  3) and (2  $\rightarrow$  4), should have the same energy, according to simple MO theory; however, first-order configuration interaction between the two degenerate excited states removes the degeneracy so that the transitions appear as two distinct bands. Calculation<sup>10</sup> shows that one of the resulting transitions (that of lower frequency) should be almost forbidden, the intensity of the other being correspondingly enhanced; this explains the weakness of the  $\alpha(L_b)$  band, and the high intensity of the  $\beta(B_b)$  band, relative to the "normal" *p*- and  $\beta'$ -transitions.

Since Ia and IIa are isoconjugate with benz[a]anthracene, and differ by only two out of the eighteen conjugated atoms, one might expect the ultraviolet spectra of the three compounds to be very similar. The main difference should be an enhancement of the weak  $\alpha$ -band, due to removal of the degeneracy between the (1  $\rightarrow$  3) and (2  $\rightarrow$  4) transitions; this degeneracy is a special feature of alternant hydrocarbons and should not carry over to isoconjugate heteroaromatic systems.

The spectra of Ia and IIa in methylcyclohexane show absorptions around 225  $m\mu$  ( $\log \epsilon \sim 4.4$ ), and around 270  $m\mu$  ( $\log \epsilon \sim 4.7$ ), that can be correlated with the  $\beta'$ - and  $\beta$ -bands of benz[a]anthracene, respectively (222  $m\mu$ ,  $\log \epsilon 4.6$ ; 289  $m\mu$ ,  $\log \epsilon 5.0$ ).

The absorption bands of Ia or IIa in the region 310–370  $m\mu$  at first sight seem attributable to a single electronic transition with much vibrational fine structure; however, a more careful analysis suggests that there are in each case two electronic transitions represented.

In the case of Ia, the distinction seems clear. The gap between the second and third transitions (1810  $\text{cm}^{-1}$  in methylcyclohexane, 1980  $\text{cm}^{-1}$  in chloroform) is too large to be attributed to a skeletal vibration. Moreover, the first two bands, at 351 and 369  $m\mu$  in methylcyclohexane, show a solvent shift of 2  $m\mu$  on passing to chloroform, whereas the bands at 317  $m\mu$  and 330  $m\mu$  remain unchanged. On the basis of intensities and the bathochromic shift on changing to a more polar solvent, the two low frequency bands can be correlated with the  $\alpha$ -band of benz[a]anthracene, and the two high frequency bands with the *p*-band. The separation ( $\sim 1300 \text{ cm}^{-1}$ ) between the  $\alpha$ -bands, and between the three *p*-bands (304, 317, 330  $m\mu$  in methylcyclohexane) lies in the range commonly observed for vibrational fine structure in aromatic compounds.

In the case of IIa, the two bands are superimposed and so more difficult to unravel. However, the spectrum in methylcyclohexane seems to show two pro-

(9) E. Clar, "Aromatische Kohlenwasserstoffe," 2nd Ed., Springer, Berlin, 1952.

(10) M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Phys. Soc.*, (London) **A67**, 795 (1954).

(11) J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).

TABLE II

ULTRAVIOLET SPECTRA OF Ia, IIa AND BENZ[a]ANTHRACENE IN METHYLCYCLOHEXANE AND ALCOHOL-FREE CHLOROFORM, AND OF Ic, IIc, Ie AND IIe IN CHLOROFORM

Absorption maxima in $m\mu$ (log $\epsilon$ )					
Ia		IIa		Benz[a]anthracene	
369 (3.77)	371 (3.66)	365 (3.48)	364 (3.49)	384 (2.95)	387 (2.97)
351 (3.68)	353 (3.64)	360s (3.34)	348s (3.87)	374 (2.74)	377 (2.79)
330 (3.81)	330 (3.83)	347 (3.77)	343 (3.92)	364 (3.45)	367s (3.54)
317 (3.93)	317 (3.89)	341 (3.93)	335 (3.87)	360 (3.71)	361 (3.67)
304 (3.87)	276 (4.66)	333 (3.80)	329 (3.86)	342 (3.86)	345 (3.81)
286 (4.23)	271 (4.66)	326 (3.85)	317s (3.70)	325 (3.81)	330 (3.79)
270 (4.71)	249 (4.46)	313 (3.67)	300 (3.84)	315 (3.72)	319 (3.72)
262 (4.67)		299 (3.84)	289 (4.46)	300 (4.06)	302 (4.07)
247 (4.51)		296 (3.73)	275s (4.74)	289 (4.99)	291 (4.95)
225 (4.41)		288 (4.42)	268 (4.79)	278 (4.88)	280 (4.84)
220 (4.41)		283 (4.43)		269 (4.65)	270 (4.66)
		273 (4.74)		257 (4.56)	260 (4.60)
		266 (4.74)		254s (4.54)	
		237 (4.78)		230 (4.53)	
		228 (4.40)		222 (4.57)	
		222 (4.43)			
Ic	IIc		Ie	IIe	
373 (3.60)	362 (3.40)		373 (3.68)	364s (3.37)	
355 (3.58)	347 (4.04)		354 (3.58)	349 (3.95)	
342 (3.35)	332 (4.01)		328 (4.01)	334 (3.94)	
323 (4.15)	317s (3.74)		314 (4.05)	318s (3.72)	
309 (4.08)	303 (3.65)		301s (4.04)	301 (3.75)	
295 (4.00)	291 (4.09)		287s (4.27)	289 (4.36)	
274 (4.91)	282 (4.32)		274 (4.80)	268 (4.78)	
265 (4.78)	271 (4.83)		265 (4.70)		
257 (4.57)	262 (4.70)		256s (4.56)		
243 (4.52)	252s (3.45)		247 (4.50)		

gressions, each with a spacing of about  $1300\text{ cm}^{-1}$ ; unfortunately, the vibrational structure becomes so indistinct in chloroform that it is impossible to fix the positions of the individual bands with sufficient accuracy to determine if they show solvent shifts. However, analogy with Ia and benz[a]anthracene suggests that the bands at 318, 333, 347 and  $365\text{ m}\mu$  correspond to the  $\alpha$ -band of benz[a]anthracene, and the bands of 313, 326, and  $341\text{ m}\mu$  to the  $p$ -band. Table III compares the estimated positions of the band maxima for the three compounds. According to this analysis the spectra of Ia and IIa are indeed very similar to that of benz[a]anthracene, the main difference being an increase in intensity of the  $\alpha$ -bands in the heteroaromatics, in agreement with theory.

TABLE III

ESTIMATED BAND MAXIMA ( $m\mu$ ) OF  $\pi$ - $\pi^*$  TRANSITIONS IN METHYLCYCLOHEXANE FOR BENZ[a]ANTHRACENE, 5,6-BORAZAROBENZ[a]ANTHRACENE (Ia) AND 6,5-BORAZAROBENZ[a]ANTHRACENE (IIa)

Assignment	Benz[a]anthracene	Ia	IIa
$\alpha$ ( $L_b$ )	384	369	365 <sup>a</sup>
$p$ ( $L_a$ )	342	317	341
$\beta$ ( $B_b$ )	289	271	266
$\beta'$ ( $B_a$ )	222	222	222

<sup>a</sup> Position of band maximum uncertain due to superposition of the  $\alpha$ - and  $p$ -bands.

A comparison of the observed transition energies with those given by various molecular orbital treatments will be given elsewhere.

### Experimental

**2-Nitro-3-bromonaphthalene.**—A solution of 3-nitro-2-naphthylamine<sup>12</sup> (18.8 g.) in boiling acetic acid (670 ml.) was cooled rapidly to  $20^\circ$  and then added to a stirred solution of sodium nitrite in concentrated sulfuric acid (55 ml., 2 M) below  $25^\circ$ .<sup>13</sup>

(12) Prepared by reduction of 2,3-dinitronaphthalene; E. R. Ward and T. M. Coulson, *J. Chem. Soc.*, 4545 (1954).

(13) Cf. H. H. Hodgson and J. Walker, *ibid.*, 1620 (1933).

After 15 minutes the mixture was added to a stirred solution of cuprous bromide (38 g.) in hydrobromic acid (200 ml. of 48%). Next day water was added and the precipitate was extracted with ethanol (250 + 100 ml.). Concentration of the extract to half its volume gave 2-nitro-3-bromonaphthalene (13.5 g., 54%), m.p.  $79$ – $80^\circ$  (lit.<sup>14</sup>  $84^\circ$ ), pure enough for the next step.

**2-Nitro-3-phenyl-naphthalene.**—A mixture of 2-nitro-3-bromonaphthalene (20.8 g.), iodobenzene (55 g.) and copper bronze (31.8 g.) was stirred at  $110^\circ$  for 36 hours. Steam distillation and extraction of the residue with benzene, followed by chromatography from benzene-petroleum ether (1:1) on alumina and recrystallization from methanol, gave 2-nitro-3-phenyl-naphthalene (15.2 g., 74%) as deep yellow prisms, m.p.  $92^\circ$ , raised by recrystallization from methanol to  $96.0$ – $96.8^\circ$ .

*Anal.* Calcd. for  $C_{16}H_{11}NO_2$ : C, 77.09; H, 4.45. Found: C, 77.06; H, 4.51.

**3-Phenyl-2-naphthylamine.**—Hydrazine hydrate (20 ml.) was added gradually to a mixture of 2-nitro-3-phenyl-naphthalene (6.0 g.) and palladized charcoal (0.2 g. 10%) in boiling ethanol (230 ml.). After 1 hour, water was added to the filtered solution, giving an almost quantitative yield of 3-phenyl-2-naphthylamine, which crystallized from 90% methanol as a white powder, m.p.  $82.7$ – $83.5^\circ$ .

*Anal.* Calcd. for  $C_{16}H_{13}N$ : C, 87.64; H, 5.98. Found: C, 87.49; H, 5.80.

**5-Methoxy-5,6-borazarobenz[a]anthracene.**—A solution of 3-phenyl-2-naphthylamine (10 g.) in dry xylene (160 ml.) was added slowly with stirring to a cooled (ice) solution of boron trichloride (7.0 g.) in dry xylene (45 ml.) under nitrogen. Aluminum chloride (0.2 g.) was then added and the temperature raised over 4 hours to  $140^\circ$  and held there overnight. The cold solution was taken up in a mixture of ether (500 ml.) and benzene (250 ml.), washed with water, dried ( $MgSO_4$ ), and evaporated on a steam-bath. The residue (10.6 g.) was dissolved in hot absolute methanol (500 ml.) and the solution concentrated and left in a freezer ( $-15^\circ$ ). The treatment with methanol was repeated, giving 5-methoxy-5,6-borazarobenz[a]anthracene (Ic) (4.2 g., 31%) as a white powder. A sample was recrystallized from methanol for analysis, the crystals being filtered and handled in an efficient drybox; m.p.  $159^\circ$  (evacuated capillary).

*Anal.* Calcd. for  $C_{17}H_{14}BNO$ : C, 78.80; H, 5.45; N, 5.41. Found: C, 78.83; H, 5.59; N, 5.34.

**Bis-(5,6-borazaro-5-benz[a]anthryl) Ether.**—The combined filtrates from the previous experiment were evaporated nearly to dryness and left in a freezer. The precipitate of bis-(5,6-

(14) N. McLeish and N. Campbell, *ibid.*, 1106 (1937).

**borazaro-5-benz[a]anthryl ether (Id)** (0.85 g.) was washed with methanol and crystallized from toluene; m.p. 322°. The total yield of cyclized product was thus 38%. A sample was dried under vacuum at 140° for analysis.

*Anal.* Calcd. for  $C_{22}H_{22}B_2N_2O$ : C, 81.40; H, 4.70; N, 5.93. Found: C, 81.58; H, 5.13; N, 6.04.

The same product was formed from the methyl ether (Ic) on exposure to air.

**5-Methyl-5,6-borazarobenz[a]anthracene.**—An ethereal solution of methylmagnesium bromide (12.5 ml. of 0.6 *M*) was added to a cold (ice-bath) stirred solution of the methyl ether Ic (1.3 g.) in dry ether (40 ml.) with exclusion of moisture, and stirring continued for 24 hours, first at 0°, then at room temperature. Evaporation of the filtered solution and sublimation at 150° (0.005 mm.) gave **5-methyl-5,6-borazarobenz[a]anthracene (Ie)** which crystallized from petroleum ether (b.p. 60–68°) in small white needles, m.p. 160–161.3°.

*Anal.* Calcd. for  $C_{17}H_{14}BN$ : C, 83.99; H, 5.80. Found: C, 84.07; H, 5.61.

**5,6-Borazarobenz[a]anthracene.**—A standardized ethereal solution of lithium aluminum hydride (1.35 mmoles) was added to a solution of the methyl ether Ic (1.00 g., 3.86 mmoles) in dry ether (40 ml.), followed by aluminum chloride (0.045 g., 0.45 mmole). The mixture was boiled under reflux for 2 hours, then filtered and the filtrate evaporated and sublimed. **5,6-Borazarobenz[a]anthracene** was collected at 130° (0.005 mm.) as a white powder, m.p. 139° dec.

*Anal.* Calcd. for  $C_{16}H_{12}BN$ : C, 83.88; H, 5.28. Found: C, 83.50; H, 5.60.

**2-(*o*-Nitrophenyl)-naphthalene.**—A mixture of 2-iodonaphthalene<sup>15</sup> (65.0 g.), 1-bromo-2-nitrobenzene (56.0 g.) and copper bronze (46.5 g.) was stirred 40 hours at 110°. After steam distillation of unchanged reactants, the residue was extracted with chloroform. Evaporation of the extract and recrystallization from methanol gave 2-(*o*-nitrophenyl)-naphthalene (38.5 g., 60%), m.p. 101° (lit.<sup>4</sup> 101°).

**2-(*o*-Aminophenyl)-naphthalene.** (a) **By Catalytic Reduction.**—A solution of 2-(*o*-nitrophenyl)-naphthalene (9.0 g.) in ethanol (450 ml.) was hydrogenated (initial pressure 30 p.s.i.) over palladized charcoal (0.3 g. of 10%) until 97% of the theoretical amount of hydrogen had been absorbed. Concentration of the solution gave 2-(*o*-aminophenyl)-naphthalene (6.0 g., 76%), m.p. 95–97° (lit.<sup>4</sup> 95°). (b) **By Reduction with Hydrazine Hydrate.**—Hydrazine hydrate (45 ml.) was added slowly to a mixture of 2-(*o*-nitrophenyl)-naphthalene (32 g.) and palladized charcoal (1.0 g. of 10%) in boiling ethanol (1.4 l.). After 1 hour the solution was filtered and concentrated, giving the amine (22 g., 78%), m.p. 95–96°. A further crop could be obtained by adding water to the filtrate and concentrating until cloudy.

**Bis-(6,5-borazaro-6-benz[a]anthryl) Ether.**—A solution of 2-(*o*-aminophenyl)-naphthalene (22.0 g.) in dry xylene (350 ml.) was added slowly to an ice-cold stirred solution of boron trichloride (13.0 g.) in dry xylene (100 ml.). Aluminum chloride (0.5 g.) was then added and the mixture heated during 4 hours to 140° and held at 140° with stirring overnight. The product was taken up in ether (450 ml.) and benzene (50 ml.), shaken twice with water, dried ( $MgSO_4$ ) and evaporated on a steam-bath. The residue was dissolved in a hot mixture of benzene (650 ml.) and ether (400 ml.) and petroleum ether (500 ml., b.p. 90–100°) added. The solution was then concentrated until cloudy and cooled slowly, giving **bis-(6,5-borazaro-6-benz[a]anthryl) ether** (10.4 g.), m.p. 261–264°. Further concentration of the filtrate

gave a second crop (4.8 g.), m.p. 264–265°, and evaporation of the filtrate from this gave a residue (8.6 g.), m.p. 225–247°. Recrystallization of the first fractions from toluene (charcoal) raised the m.p. to 275.5°.

*Anal.* Calcd. for  $C_{32}H_{22}B_2N_2O$ : C, 81.40; H, 4.70; N, 5.93. Found: C, 80.94; H, 4.69; N, 5.93.

**6-Methoxy-6,5-borazarobenz[a]anthracene.**—Bis-(6,5-borazaro-6-benz[a]anthryl) ether (12.7 g.) was dissolved in hot absolute methanol (500 ml.), the solution concentrated to 350 ml. and allowed to cool, when **6-methoxy-6,5-borazarobenz[a]anthracene** (10.5 g., 75%) separated in needles, m.p. 174–176°, raised by recrystallization from methanol (charcoal) to 183–184° (evacuated capillary).

*Anal.* Calcd. for  $C_{17}H_{14}BNO$ : C, 78.80; H, 5.45; N, 5.41. Found: C, 78.37; H, 5.16; N, 5.65.

**Evidence for the Absence of a Borazaro-chrysene in the Product from Cyclization of 2-(*o*-Aminophenyl)-naphthalene.**—The filtrate from the methyl ether IIc was evaporated and combined with the residue of crude material (m.p. 225–247°) from IIc. The mixture was recrystallized from absolute methanol, giving IIc (4.80 g.). The filtrate from this was evaporated to dryness under vacuum and the ultraviolet spectrum of the remaining dark brown oil measured. The spectrum was identical with that of IIc, no other bands being present.

**6-Methyl-6,5-borazarobenz[a]anthracene.**—A solution of methylmagnesium bromide (15 ml. of 1 *M*) was added dropwise to a stirred mixture of IIc (2.6 g.) and dry ether (100 ml.) at room temperature. After 2 hours the solution was filtered, diluted with moist ether, then shaken with water and dried ( $CaCl_2$ ). Evaporation gave crude **6-methyl-6,5-borazarobenz[a]anthracene** (2.12 g., 87%), m.p. 136–140°, raised by sublimation at 120° (0.1 mm.) to 141–143°.

*Anal.* Calcd. for  $C_{17}H_{14}BN$ : C, 83.98; H, 5.80; B, 4.45; N, 5.76. Found: C, 83.76; H, 5.77; B, 4.43; N, 5.81.

**6,5-Borazarobenz[a]anthracene.**—A standardized ethereal solution of lithium aluminum hydride (1.00 mmole) was added slowly to a mixture of IIc (1.00 g., 3.86 mmoles) and dry ether (30 ml.) at 0°. Aluminum chloride (0.04 g., 0.30 mmole) was then added and the mixture boiled under reflux for 2 hours, then filtered and evaporated. Sublimation of the residue at 120° (0.005 mm.) gave 6,5-borazarobenz[a]anthracene (0.58 g., 65%) which after resublimation had m.p. 136.5–137° dec.

*Anal.* Calcd. for  $C_{16}H_{12}BN$ : C, 83.89; H, 5.28; N, 6.11. Found: C, 83.43; H, 5.08; N, 6.42.

**6-Hydroxy-6,5-boroxarobenz[a]anthracene.**—Concentrated hydrochloric acid (10 ml.) was added to a solution of IIc (2.0 g.) in hot acetic acid (20 ml.) and the mixture cooled quickly to 5° and diazotized with sodium nitrite (0.60 g.) dissolved in a little water. After 2 hours, the solution was added with stirring to boiling water (300 ml.) and boiling continued for 30 minutes. Next day the precipitate was collected and recrystallized twice from toluene (charcoal) giving **6-hydroxy-6,5-boroxarobenz[a]anthracene** (1.20 g., 64%) as pale yellow shining needles, m.p. 279.5–281°.

*Anal.* Calcd. for  $C_{16}H_{11}BO_2$ : C, 78.09; H, 4.51. Found: C, 78.37; H, 4.72.

**Measurement of Spectra.**—The spectra were measured with a Cary model 14 recording ultraviolet spectrophotometer using reagent grade chloroform as solvent except where otherwise stated. The measurements for the parent compounds Ia and IIa, and for their TCNE complexes, were made in alcohol-free chloroform.

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