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BORON PHOTOCHEMISTRY

X. ANILINODIARYL BORANES: THEIR SYNTHESIS AND PHOTOCHEMISTRY

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SUMMARY

A series of stable anilinodimesitylboranes was synthesized. Their mass spectra and nuclear magnetic resonance spectra were studied. The photocyclization of these compounds in the presence of iodine is accompanied by a facile 1,2-methyl migration. The structure of the products has been assigned on the basis of spectral evidence and degradation studies.

INTRODUCTION

The unusual chemical stability of trimesitylborane is well documented[1], and more recently we have reported the high photolytic and chemical stability of the less-hindered aryldimesitylboranes[2]. It seemed possible that the stabilizing effect of the mesityl groups on boron could be utilized to facilitate the isolation of what would otherwise be labile compounds. In particular, we were interested in the synthesis of stabilized anilinoboranes and substituted borinates, so that we could examine their photochemistry and spectroscopy in detail. In this paper we will restrict ourselves to the substituted aminodimesitylboranes.

RESULTS AND DISCUSSION

(Diphenylamino)dimesitylborane (I) has been reported previously[3], prepared from the corresponding (diphenylamino)dichloroborane and mesitylmagnesium bromide. We have now prepared this compound and a series of substituted amino-dimesitylboranes (I)–(IX) by reaction of fluorodimesitylborane with the corresponding amines. The use of butyllithium as base gave the desired products in high yield.

$$RR'NH + BuLi \rightarrow RR'NLi + BuH$$

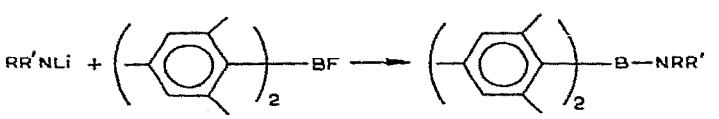


TABLE 1

PHYSICAL DATA FOR THE PREPARATION OF SUBSTITUTED AMINODIMESITYLBORANES

Starting material	*Product No.*	*Product yield (%)*	*Solvent*	*M.p. (°C)*	*Cyclohexane λ_{max} nm (ε)*	*Formula*	*Analysis found (calcd.) (%)*				
							C	*H*	*B*	*N*	*Cl*
Aniline	(II)	86	Ligroin	150–151	267(12,900)	$C_{24}H_{28}BN$	84.4 (84.5)	8.3 (8.3)	3.0 (3.2)	4.4 (4.1)	
N-Methylaniline	(III)	92	Ligroin	136–137	255(11,600)	$C_{25}H_{30}BN$	84.7 (84.6)	8.5 (8.5)	2.9 (3.1)	4.1 (4.0)	
2,6-Dimethylaniline	(IV)	56	Ligroin	198–199	254(17,200)	$C_{26}H_{32}BN$	84.7 (84.6)	9.0 (8.8)	2.9 (2.9)	3.8 (3.8)	
Diphenylamine	(I)	88	Ligroin	219–220	282(5,600)	$C_{30}H_{32}BN$	86.4 (86.2)	7.4 (7.8)	3.6 (3.4)	2.3 (2.7)	
1-Naphthylamine	(V)	97	Ligroin	147–148	304(10,400)	$C_{28}H_{30}BN$	86.2 (85.9)	7.9 (7.7)	2.5 (2.8)	4.0 (3.6)	
N-Methyl-1-naphthylamine	(VI)	71	$C_2H_5OC_2H_4OH$	138–140	294(8,800)	$C_{29}H_{32}BN$	85.9 (85.8)	8.2 (7.9)	2.7 (2.7)	3.3 (3.5)	
2-(Dimethylamino)-aniline	(VII)	51	CH_3OH	132–134		$C_{26}H_{33}BN_2$	81.6 (81.2)	8.9 (8.6)	2.5 (2.9)	6.8 (7.3)	
2,6-Dichloroaniline	(VIII)	52	CH_3CN	182–183		$C_{24}H_{26}BNCl_2$	69.9 (70.1)	6.3 (6.4)	2.4 (2.6)	3.3 (3.4)	17.6 (17.9)
2-Methylaniline	(IX)	45	CH_3CN	160–163		$C_{25}H_{30}BN$	83.9 (84.6)	8.3 (8.5)	2.5 (3.0)	3.8 (3.9)	

The products were purified by extraction with dilute acid and base solutions followed by crystallization, or by passing the crude solution through a column of alumina. Table 1 indicates the scope of the reaction and lists physical data for the products. They are stable to air, water, dilute acid and base, and all gave satisfactory elemental analyses.

I. Mass spectra

The mass spectra of hindered triarylboranes show large parent-*minus*-hydrocarbon fragment ions[2]. The predominant ions obseved for the aminodimesitylboranes are indicated below.

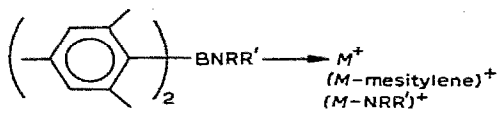


Table 2 lists these fragmentation patterns in order of increasing ease of fragmentation of the B–N bond, as judged by the intensities of the fragment ions relative to the base peak. The bond order of the B–N bond is related to its double bond character, brought about by overlap of the nitrogen 2*p* orbital with the empty 2*p* orbital on boron. In simple aminoboranes, where this overlap is easily achieved, there is evidence of high double bond character in this bond[4].

The mass spectral data for these hindered boranes are qualitatively related to the steric and electronic effects of substituents on the B–N bond. The bulky phenyl and dichlorophenyl substituents in boranes (I) and (VIII) would prevent coplanarity of the *p* orbitals. In the latter compound, the highly electronegative chlorine atoms would decrease the basicity of the nitrogen and reduce the donation to boron, further lowering the B–N bond order. At the other extreme, the stability of the compounds (IV) and (IX) is controlled by the electronic effects of the electron donating methyl

TABLE 2

MASS-SPECTRAL FRAGMENTATION PATTERN[a] (20 eV) OF AMINODIMESITYLBORANES

Product No.	*Dimesitylborane*	*Parent ion* M^+	*Intensity of base* (%)	*Fragment* $(M-NRR')^+$	*Intensity of base* (%)	*Fragment* $(M-mesitylene)^+$	*Intensity of base* (%)
(IV)	2,6-Dimethylanilino-[a]	369	19	249	0	249	100
(IX)	2-Methylanilino-	355	61	249	5	235	100
(V)	1-Naphthylamino-	391	100	249	11	271	69
(III)	*N*-Methylanilino-	355	83	249	18	235	100
(VII)	2-(Dimethylamino)anilino-	384	100	249	20	264	60
(II)	Anilino-	341	44	249	27	221	100
(VI)	*N*-Methyl-1-naphthylamino-	405	100	249	28	285	80
(VIII)	2,6-Dichloroanilino-	(409)	(35)	249	45	(289)	(100)
		(411)	(51)			(291)	(77)
(I)	Diphenylamino-	417	100	249	63	297	95

[a] Results by high-resolution peak matching.

groups. The increased basicity would result in higher donation to boron and higher B–N bond order.

II. NMR spectra

The NMR spectrum of (2,6-dimethylanilino)dimesitylborane (IV) at room temperature in hexachlorobutadiene was complex (Chart 1). The addition of D_2O failed to reveal any exchangeable protons in spite of the presence of an NH group. At 110° (Chart 2), the spectrum was simplified, but even at this temperature, trifluoroacetic acid was required to exchange the NH proton and cause the N–H signal at 5.75 ppm to disappear. The signal broadening which occurs on lowering the temperature of the sample is typical of that observed for restricted rotation of a group about a specific bond in the molecule. Integration data from Chart 2 reveal that the rotating

NUCLEAR MAGNETIC RESONANCE SPECTRA[a] OF (2,6-DIMETHYLANILINO)DIMESITYLBORANE (IV)

CHART 1
Temperature: ambient

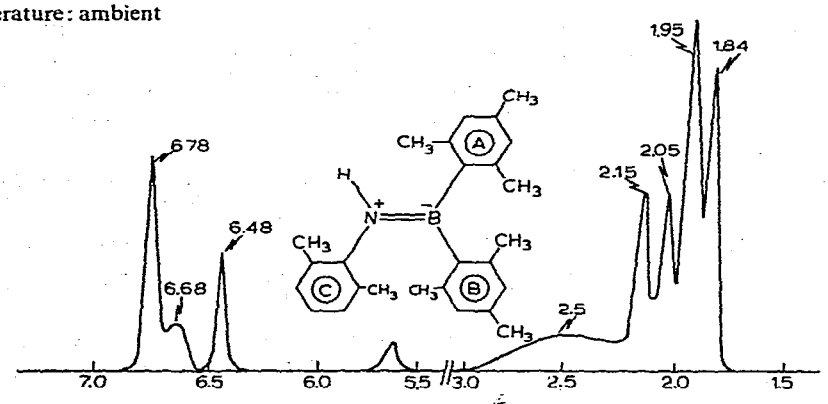
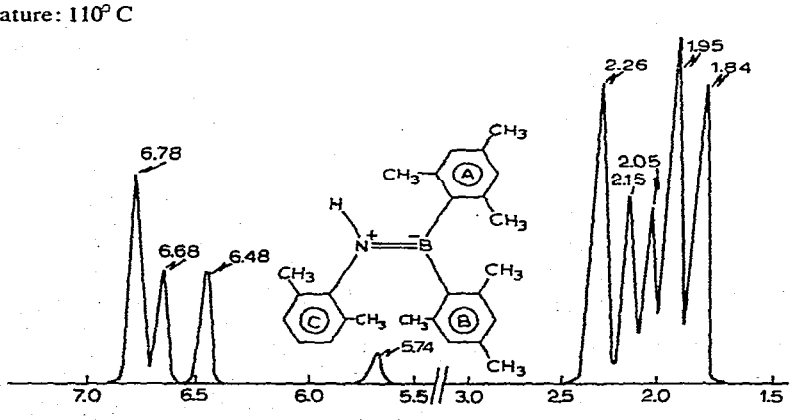


CHART 2
Temperature: 110° C



[a] Solvent, hexachlorobutadiene; R.F. field, 0.03 mG; filter bandwidth, 4 Hz; sweep width, 500 Hz; sweep time, 250 sec.

group must have at least two equivalent methyl groups and two equivalent aromatic protons. The fact that a mesityl group (probably B) is restricted rather than the xylyl group is determined by the integrated aromatic proton signals. The aromatic mesityl group protons must fall in pairs, *i.e.*, δ 6.68 ppm (2 H_B) and δ 6.48 ppm (2 H_A) and the aromatic xylyl protons are, therefore, equivalent at δ 6.78 ppm (3 H_C). The mesityl protons in boranes fall at higher fields than those of other aromatic groups[2,5]. The *ortho*-methyl group protons on the restricted mesityl ring (B) give rise to a signal at 2.26 ppm at higher temperatures.

The mesityl groups are non-equivalent due to the double bond character of the $\rangle\bar{B}{=}\overset{+}{N}\langle$ bond, and to steric effects about the $\rangle\bar{B}{=}\overset{+}{N}\langle$ bond. The signal at δ 6.48 ppm (2 H) is that associated with the rotating mesityl group (A). For the remaining unassigned signals, we would anticipate a 6 H singlet for the xylyl methyls, ring (C), a 6 H singlet for the *ortho*-methyls on ring (A), and singlets for the two *para*-methyl groups on rings (A) and (B). Clearly, these latter signals fall at δ 2.15 and 2.05 ppm, but we cannot unambiguously make assignments. The NMR data for all the compounds are described in Table 3. An examination of the data for the resonances, due to the *ortho*-

TABLE 3

NMR CHEMICAL SHIFTS (δ ppm) OF VARIOUS AMINODIMESITYLBORANES

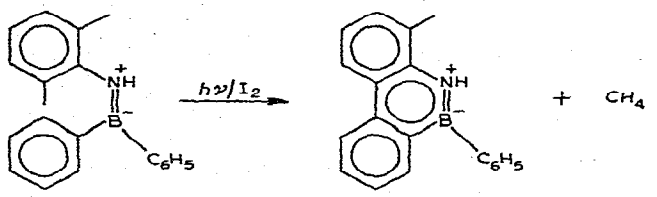
Product No.		*Mesityl group*			*Other signals*		
		o-Methyl hydrogens	*p-Methyl hydrogens*	*Aromatic hydrogens*	*N–H*	*Other nonaromatics*	*Other aromatics*
(II)	Anilino	2.21, 2.35	2.17, 2.35	6.75	5.74[b]	None	6.85
(IV)	2,6-Dimethylanilino	1.95, 2.26[a]	2.05, 2.5	6.48, 6.68[a]	5.74	1.84 (*o*-Xylene methyl hydrogens)	6.78
(III)	*N*-Methylamino	2.2, 2.0	2.1, 2.2	6.6, 6.75	None	3.2 (N–CH_3)	6.9
(I)	Diphenylamino	2.15	2.1	6.6	None	None	6.9
(V)	1-Naphthylamino	2.17, 2.42	2.15, 2.23	6.68, ?	?	None	Many
(VI)	*N*-Methyl-1-Naphthylamino	2.0[a], 2.35[a]	1.88, 2.1	6.25[a], 6.7	None	3.3 (N–CH_3)	Many
(VII)	(2-Dimethylamino)anilino	2.1, 2.28	2.25	6.68	7.55	2.54 (N–CH_3)	6.72, 6.95
(VIII)	2,6-Dichloroanilino	1.98, 2.32[a]	2.15, 2.22	6.52, 6.72[a]	6.04	None	7.08 and others
(IX)	2-Methylanilino	2.04, 2.22	2.18, 2.2	6.6, 6.68	6.1	2.18 (2–CH_3)	6.7

[a] At 110°. [b] Confirmed by adding D_2O to the sample.

methyl groups on the mesityl nucleus, reveals that the high-field signals fall in the very narrow range of δ 1.95–2.17 ppm. The signal at δ 1.84 ppm falls outside this range and has been assigned to the methyls on the xylyl group (C), and that at δ 1.95 ppm to the *ortho*-methyl groups on ring (A). This restricted rotation of a mesityl group at ambient temperatures has been observed for the 2,6-dichloroanilino-, and the (*N*-methyl-1-naphthylamino)dimesitylboranes. The non-equivalence of the mesityl groups has been observed in all cases except for the symmetrical (diphenylamino)dimesitylborane.

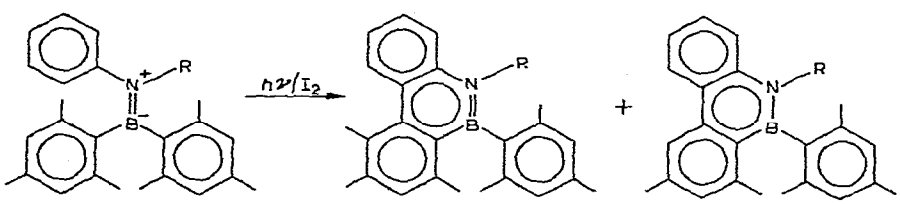
III. Photocyclization

Previously we have reported the oxidative photocyclization of anilinodiphenylboranes substituted in the anilino ring[6,7]. We found that the 2,6-dimethyl derivative (X) photocyclized to yield the monomethylborazarophenanthrene* (XI). The methyl, which would be forced to be at the bridgehead, was eliminated as methane, as indicated by GLC results.



(X) (XI)

By contrast, we now report that under the same conditions anilinodimesitylborane (II) yields only 11% of the demethylated borazarophenanthrene (XII). The major product (89%) is a *B*-mesityltrimethylborazarophenanthrene derivative (XIIIa). In this case, the methyl which would be forced to be at the bridgehead migrates. The structure of the trimethyl derivative is as shown. The reaction of the *N*-phenyl compound (I) is more specific and yields only the derivative (XIIIb) resulting from methyl migration. High-resolution, mass-spectral-peak matching confirmed the elemental analyses and shows the presence of the six methyl groups in the products (XIIIa) and (XIIIb). The NMR spectrum indicated that the migrated methyl group



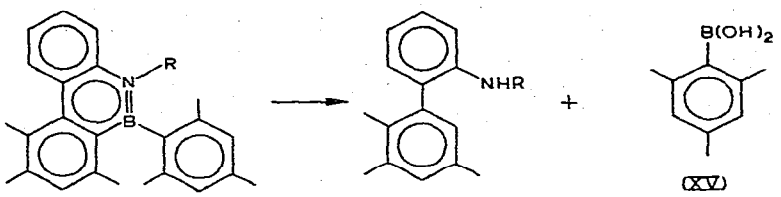
(II), R = H
(I), R = C_6H_5

(XIIIa), R = H
(XIIIb), R = C_6H_5

(XII), R = H

occupied the 4- or 5-position of the borazarophenanthrene system, since only one perihydrogen was apparent at 8.2 ppm. The exact position of the migrated methyl group was determined by characterization of the degradation products. Borazarophenanthrenes have been degraded with cold concentrated sulfuric acid[8]. We were unable to isolate products using this technique, but prolonged boiling of a solution of the borazaro compounds (XIIIa) and (XIIIb) in dilute hydrochloric/acetic acid gave good yields of the desired amines. The fact that this degradation occurs under such mild conditions is surprising, since borazarophenanthrene is reported to be stable under similar conditions. It seems possible that the severe steric strain imposed

* Borazarophenanthrene; Chem. Abstr. name, dibenz[*c*, *e*] [1,2]azaborine.



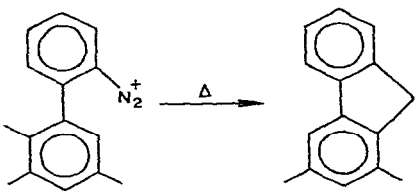
(XIIIa), R = H (XIVa), R = H
(XIIIb), R = C_6H_5 (XIVb), R = C_6H_5

(XV)

on this system by the methyl substitution may restrict coplanarity and delocalization of the π-system, leading to weakening of the B=N bond. In addition, protonation would be facilitated by the electron-donating effects of the methyl groups.

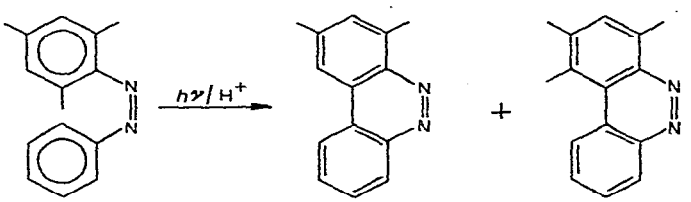
The amino derivative (XIVb) was readily purified and had acceptable elemental analysis. The mass spectrum confirmed the presence of the three methyl groups. The NMR spectrum indicated the presence of three non-equivalent methyl groups. These data proved that the migrated methyl had undergone a 1,2-shift, was retained in the same ring, and the borazarophenanthrene had the structure as indicated in (XIIIb).

Compound (XIVa) was difficult to purify and decomposed rapidly. The NMR spectrum of this compound was, therefore, useless in deciding the location of the methyls. The presence of the 2-methyl group was confirmed by diazotizing the crude amine. The diazonium salt was then converted to the fluorene derivative (XVI) by an intramolecular cyclization[9].



(XVI)

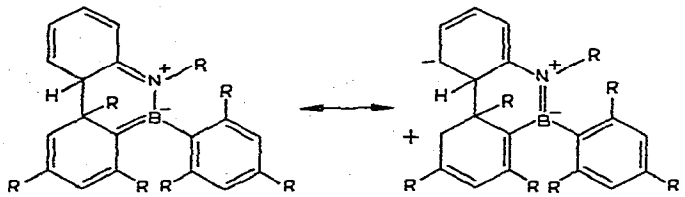
To our knowledge this is the first example of such a facile methyl migration during a photocyclization reaction of a neutral species. Badger, Drewer, and Lewis[10] have reported a very low yield (2%) of a methyl-rearranged product on prolonged irradiation of 2,4,6-trimethylazobenzene (XVII) in 20.5 *N* sulfuric acid to yield two cinnolines [(XVIII) and (XIX)].



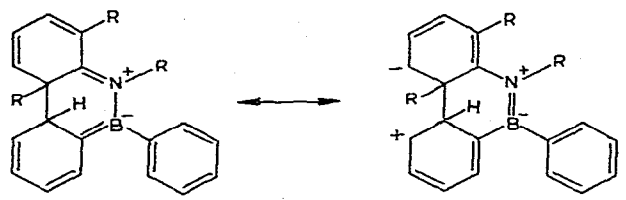
(XVII) (XVIII) (XIX)

In a subsequent paper[11], a mechanism was proposed which involved a carbonium ion rearrangement via a 1,2-methyl shift. This rearrangement occurred after the bond formation between the two aryl rings had taken place. A similar sequence holds for the B–N system, since partially photolized solutions show no evidence of rearranged starting materials.

By analogy with other photocyclization reactions[12], we postulate reduced species (XX) and (XXI) as intermediates.

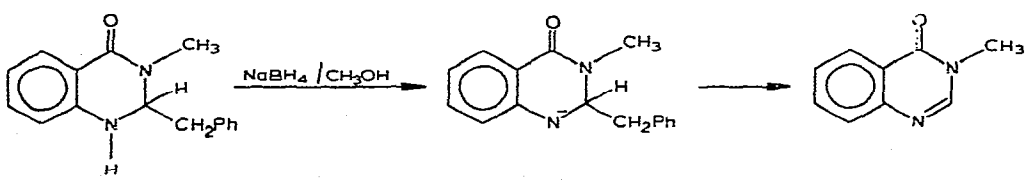


(XX)



(XXI)

The facility with which methyl elimination or migration occurs may be controlled by the charge distributions, particularly in the excited state when charge separated structures are favored. Structure (XX) should facilitate methyl migration (1,2-shift), while structure (XXI) would favor a methyl elimination reaction. Reactions of the latter type have recently been documented[13], *e.g.*,



the driving force being the generation of an aromatic system.

The facile methyl migration could also take place by an electron transfer mechanism via a cation-radical intermediate derived from (XX). However, to account for the specific behavior of the methyl groups, the cationic centre must be localized in the boron-bearing ring.

We are examining the role of iodine in the overall process. The details of our investigation in this area will be the subject of a future publication.

EXPERIMENTAL

All melting points are corrected. The mass spectra were determined with a

CEC 21-110B instrument, equipped with a heated inlet system, as described by Caldecourt[14] but constructed of glass, or on a LKB-9000 gas chromatograph/mass spectrometer. The NMR spectra were determined with a Varian A-60 instrument. Column chromatography was performed using Woelm neutral aluminum oxide with an activity grade of 1 in a 1″ × 24″ column.

Materials

Fluorodimesitylborane was prepared by the method of Brown and Dodson[15]. Eastman grade amines were used without further purification.

Aminoboranes

A solution of the amine (0.2 mol) in ether (150 ml) was dried with potassium carbonate. The dried solution was treated with a hexane solution of n-butyllithium (0.21 mol). A solution of fluorodimesitylborane (0.2 mol) in dry ether (100 ml) was then added, and the mixture stirred for 30 min. The solution was then extracted with water, dried with potassium carbonate, and evaporated to yield the crude product. The crude anilinoboranes were purified by passing a solution in ligroin (b.p. 63–75°) through a column of neutral alumina using ligroin as eluant. The first fluorescent zone was collected, and the solvent evaporated to yield the desired aminoborane. Yields and physical data are listed in Table 1.

1,3,4-*Trimethyl*-10-*mesityl*-10,9-*borazarophenanthrene* (*XIIIa*)

A cyclohexane solution containing anilinodimesitylborane (2 g) and iodine (1.3 g) in cyclohexane (600 ml) was placed in the horizontal, thin-film, photochemical reactor equipped with a quartz insert. (This reactor was described in a previous paper[16].) The reaction vessel was flushed with nitrogen, and the solution was then irradiated for 18 h under a nitrogen atmosphere using a Hanovia 100W 608A-36 lamp. At this time, spectroscopic analysis indicated the desired compound had been formed in 59% yield. The solvent was extracted with three 150 ml portions of the following in sequence: water, sodium sulfite solution, water, 10% sodium hydroxide solution, water. The cyclohexane solution was then dried with magnesium sulfate and evaporated. The residue was purified by ascending column chromatography, using a column (1″ × 12″) containing a 1/1 mixture of silica gel GF-254 and Whatman cellulose CF-11. Ligroin was used as the developing solvent. The sample resolved into three zones. The first zone contained the starting compound (0.5 g). The second contained photocyclized material, and the third contained dimesitylborinic acid and aniline. The second zone was recrystallized three times from ligroin (b.p. 63–75°) to yield a white solid m.p. 227–229°. Despite the sharpness of the melting point, good analytical data were not found on this sample. (Found: C, 83.1; H, 6.9; B, 2.9; N, 4.3. Calcd.: C, 85.0; H, 7.7; B, 3.2; N, 4.1%.) Mass spectral analysis on this sample indicated the presence of some iodinated products. Several minor components were detected by gas-liquid chromatography. The major component (>98%) has a λ_{max} in cyclohexane, 338 nm, ε5,300. This zone was collected, and high-resolution, mass-spectral-peak matching gave the following results: found mass, 339.2167; $C_{24}H_{26}NB$ calcd. mass, 339.2158.

Gas-liquid chromatography on the recrystallization solvents gave a peak with a *m/e* of 325 and a λ_{max} 332, ε4,800, approximately 0.1 g.

1,3-Dimethylfluorene (XVI)

A solution containing the trimethyl derivative (XIIIa) (0.5 g) in acetic acid (50 ml), HCl (5 ml), and water (10 ml) was boiled for 20 min, cooled, diluted with water to 100 ml, made basic with sodium hydroxide, and extracted with ether. The ether solution was concentrated, purified by ascending column chromatography (as described above), and separated into five zones. The fourth zone was the largest and contained the desired *o*-aminobiphenyl derivative. This was recovered by extraction, diazotized with sodium nitrite in dilute acid, and warmed to give the desired fluorene. Chromatography yielded a purified product, yield 0.2 g (70%), m.p. 85–86°. (Found: C, 92.5; H, 7.2. Calcd.: C, 92.8; H, 7.2%.) NMR analyses: $\delta(CH_2)$ 3.74, $\delta(CH_3)$ 2.4 (coupled to 1 aromatic H), $\delta(CH_3)$ 2.44 (coupled to 2 H), H at δ 7.42 and 6.96 ppm.

1,3,4-Trimethyl-9-phenyl-10-mesityl-10,9-borazarophenanthrene (XIIIb)

A solution of (diphenylamino)dimesitylborane (2 g) and iodine (1.3 g) in cyclohexane (600 ml) was placed in the horizontal, thin-film, photochemical reactor and irradiated for 16 h in a nitrogen atmosphere. The product was isolated as before to yield the crude photocyclized product (1.48 g). This was purified by chromatography and crystallized from acetonitrile to give 0.94 g (48%) of the pure photocyclized material, m.p. 228–230°, λ_{max} in cyclohexane 343 nm, ε5,780. The NMR spectrum of the compound also shows only one perihydrogen at 8.2 ppm in addition to the anticipated signals. (Found: C, 86.3; H, 7.6; B, 2.4; N, 3.7. Calcd.: C, 86.5; H, 7.2; B, 2.6; N, 3.4%.)

2',3',5'-Trimethyl-2-aminobiphenyl (XIVb)

A solution of the above (XIIIb) (0.4 g) was placed in a solution of acetic acid (50 ml), concentrated HCl (5 ml) and water (20 ml), and heated under reflux for 16 h. It was cooled, made basic, extracted with ether, and the ether was evaporated to give 0.22 g (80%) of the desired 2',3',5'-trimethyl-2-aminobiphenyl. NMR spectrum shows 3 non-equivalent methyl peaks at δ2.0, 2.22, and 2.26 ppm.

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