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EQUILIBRIUM CH-ACIDITY IN CYCLOHEXYLAMINE: THE AROMATIC 9-MESITYL-9-BORAANTHRACENE ANION*

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Summary

Equilibrium acidities of 9-mesityl-9,10-dihydro-9-boraanthracene and of its 10-phenyl derivative have been determined toward lithium cyclohexylamide in cyclohexylamine. After correction for Lewis adduct formation with the solvent the CH-acidities of both compounds were found to be essentially the same, i.e. 15.8 relative to 9-phenylfluorene, whose pK is taken as 18.49. From the CH-acidities of the 9,10-dihydro-9-boraanthracene systems and the UV spectra it is concluded that the 9-boraanthracene anion shows aromatic stabilization.

Introduction

Compounds of type I have two acidic centres: a base can either abstract a proton from C-10, which is a Brönsted acidic centre, to yield an anion (II-1) the negative charge of which could be delocalized due to the empty 2*p* orbital of boron (II-2), or it can attack directly the boron atom, which is a Lewis acidic centre, to yield an adduct (III). By introducing the bulky mesityl group on boron we aimed to eliminate direct base attack on boron as a possible interfering reaction [1]. Reaction of Ia with tert-butyllithium in benzene [2, 3] or with n-butyllithium in ether or tetrahydrofuran [3] indicated that direct attack on the boron centre is indeed unfavourable, at least kinetically.

While chemical reactions of the 9-mesityl-9-boraanthracene anion [2, 3] (IIa) and of its 10-phenyl derivative [4] (IIb) can generally be explained on the basis of structure II-1, the UV spectra [2, 4] (see below) and preliminary calculations [5] indicate the contribution of the resonance structure II-2. In order to

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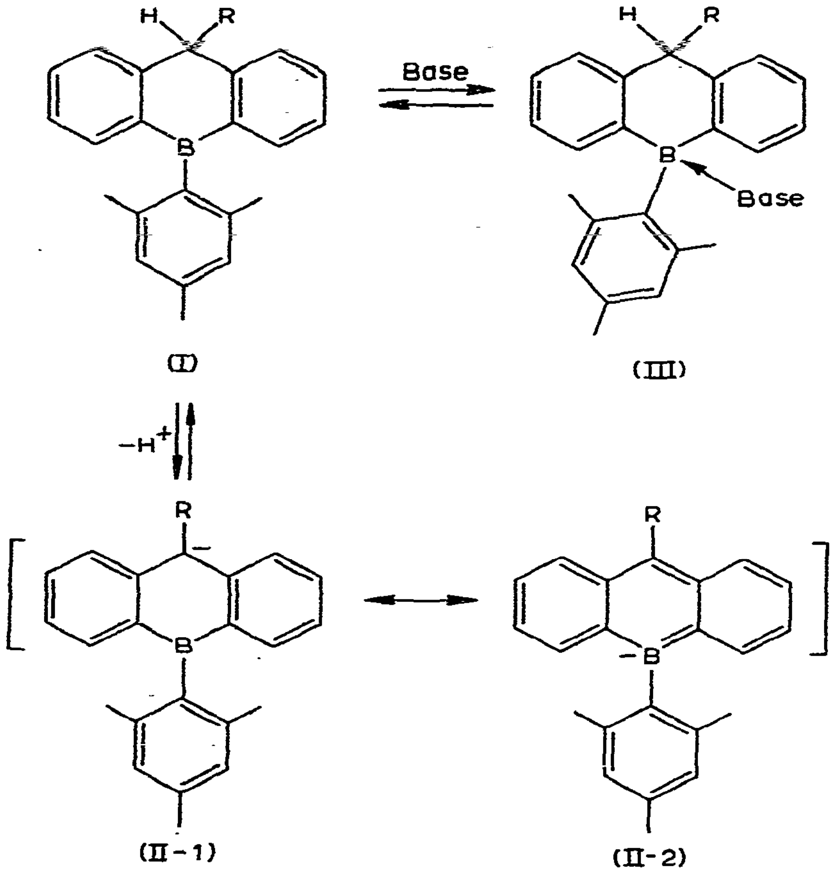


(a, R = H ; b, R = C_6H_5)

obtain more quantitative insight into the degree of any aromatic (Hückel $4n$ + 2 rule) delocalization of the negative charge in II, we decided to study the equilibrium acidity of system I. We chose the Streitwieser method [6], i.e. determination of relative acidities based on competitive equilibria with lithium cyclohexylamide in cyclohexylamine between I and a standard compound of known acidity, because a great number of relative acidities useful for comparison have been reported for this system. This method gives quantitative values for the ion-pair acidities, but for hydrocarbons with highly delocalized conjugate bases, such values compare well with the corresponding ionic acidities [6].

Results

The equilibrium measurements are summarized in Table 1. The pK values indicate relative "apparent" acidities based on competitive equilibria with lithium cyclohexylamide in cyclohexylamine:

$$AH + B^-Li^+ \rightleftarrows A^-Li^+ + BH$$

$$K = \{[BH]_o - [B^-Li^+]\}[A^-Li^+]/\{[AH]_o - [A^-Li^+]\}[B^-Li^+]$$

TABLE 1
SUMMARY OF EQUILIBRIUM CONSTANTS[a, b]

No.[c]	n[d]	AH	BH	K	pK[e]	$K' \times 10^{-1}$	pK'[e]
1	13	Ia	9-PF	79 ± 9[a]	16.60 ± 0.05[a]	55 ± 8[b]	15.75 ± 0.06[b]
2	4	Ib	9-PF	175 ± 16[a]	16.25 ± 0.04[a]	42 ± 7[b]	15.87 ± 0.07[b]
3	4	Ib	Ia	2.4 ± 0.5[a]	16.22 ± 0.11[b, f]	46 ± 13[b, f]	15.85 ± 0.12[b, f]

[a] The uncertainties listed are the results of the multiplication of the standard deviations of the mean by a factor for 95 per cent confidence limits, this factor ranging from 3.5 for 4 experiments to 2.2 for 13 experiments [7]. [b] The accumulated uncertainties were obtained from the uncertainties in the elements by a root-of-squares procedure [7] and have also a 95 per cent confidence level. [c] Series number. [d] Number of experiments. [e] pK of the first listed compound, relative to pK[9-phenylfluorene(9-PF)] = 18.49 [11]. [f] From the series 1 and 3.

The absorbances at selected wavelengths of the anionic spectra at equilibrium were used to calculate $[A^-Li^+]$ and $[B^-Li^+]$. From the known amounts $[AH]_0$ and $[BH]_0$ the "apparent" equilibrium constants K were calculated.

The UV spectra of I in cyclohexylamine revealed that the molar extinction coefficients (ϵ_C) of the bands in the region studied in this solvent (cyclohexylamine absorbs appreciably below 270 nm) were much smaller than those in n-hexane [3] (ϵ_H), although in both solvents above 270 nm the shapes of the spectra were nearly identical. Evaporation in high vacuum of cyclohexylamine solutions of I gave unchanged I according to the ^{1}H NMR spectra. Successive additions of portions of n-hexane to the cyclohexylamine solutions of I led to an almost linear increase in ϵ over the wavelength region studied. In Fig. 1 the variation of ϵ with solvent composition is represented for Ia (for Ib this variation is analogous).

A reasonable explanation of this behaviour is Lewis adduct formation, as the higher wavelength bands of triarylborons, which are associated with the empty boron 2*p* orbital, vanish when the central atom is complexed with a nucleophile [8—10]. On this interpretation, the residual higher wavelength bands in cyclohexylamine solution originate from uncomplexed I. As in the equilibria: I + base ⇌ III, cyclohexylamine is present in very large excess in the dilute solu-

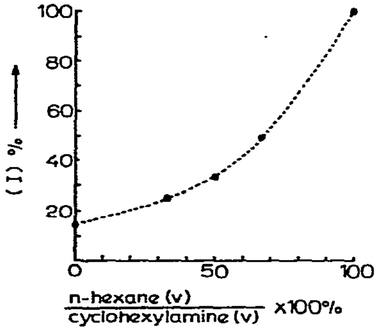


Fig. 1. UV spectra of Ia in cyclohexylamine/n-hexane solutions. Variation of molar extinction coefficients ϵ with solvent composition above 270 nm.

TABLE 2

SOME DATA ON THE EQUILIBRIUM: I + base[a] $\rightleftarrows$ III

	I (%)[b]	K_{eq}[c]
Ia	14.3 ± 1.2[d]	0.69 ± 0.06[e]
Ib	41.5 ± 5.8[d]	0.16 ± 0.03[e]

[a] The base is the solvent cyclohexylamine. [b] Obtained from I = $\epsilon_C \times 100/\epsilon_H$ at different wavelengths (see text). [c] K_{eq} = [III]/[I][base]. [d,e] See notes a and b in Table 1, respectively; the uncertainties listed have a 95% confidence level.

tions used, the percentage of uncomplexed I present is nearly constant; in Table 2 these percentages of uncomplexed I obtained from the relation: I = $\epsilon_C \times 100/\epsilon_H$ at different wavelengths, and the corresponding K_{eq} are collected. For the carbanionic equilibria it is reasonable to suppose that the same Lewis equilibrium holds for the amount of unanionized I and therefore a correction is necessary. To convert the "apparent" equilibrium constants K, in which the Lewis interaction is not taken into account, into "absolute" equilibrium constants K', from which this very specific solvent-solute interaction is eliminated, the relations used are simple, e.g. $K' = K \times \epsilon_H/\epsilon_C$ for the series 1 and 2 in Table 1. The values obtained for K' and pK' are included in Table 1.

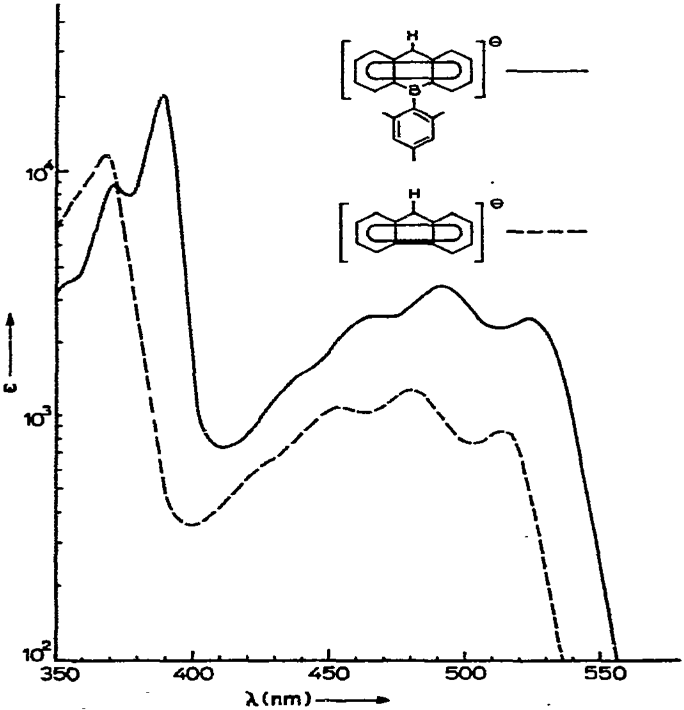


Fig. 2. Visible spectra of IIa and fluorenyl anion. Lithium salts in cyclohexylamine.

The method and apparatus used for the p*K* measurements were essentially those of Streitwieser [11]. The major practical obstacle was to generate the boraanthracene anions (II) unambiguously. The Streitwieser procedure [11] of direct injection of butyllithium into the cyclohexylamine solutions of I led to varying proportions of the desired anions II and of side product(s), which gave rise to additional absorption bands in the visible spectra. We did not investigate these side product(s), but the observation of the same interfering bands (see Experimental) in all these attempts, indicated that the side product(s) may be one (or more) well defined species, being a weaker acid than I; for on direct injection of an insufficient amount of butyllithium into cyclohexylamine solutions of larger amounts of I the spectrum of pure II was observed.

As solutions of lithium cyclohexylamide have appreciable absorption below 375 nm [12], the lower wavelength parts of the visible spectra of II, which are represented in Figs. 2 and 3, were obtained by the latter procedure, using insufficient amounts of n- or tert-butyllithium. By special techniques (see Experimental for details) the formation of the side product could be avoided.

In the presence of excess base, solutions of II in cyclohexylamine were stable for at least several days, whereas the equilibrium mixtures usually decayed slowly by roughly 10% of the total amount of the two anions concerned per day. Equilibrium apparently was established instantaneously. The cyclohexylamine solutions of II obeyed Beer's law, showing that the conversion of I into II by lithium cyclohexylamide goes to completion.

When the ion-pair concentrations calculated from the spectra of equilibrium mixtures were used to calculate the absorbances at other wavelengths of the visible spectra, we could simulate the whole curve within the limits of reproducibility of the absorbance measurements, indicating that the individual spectra are additive.

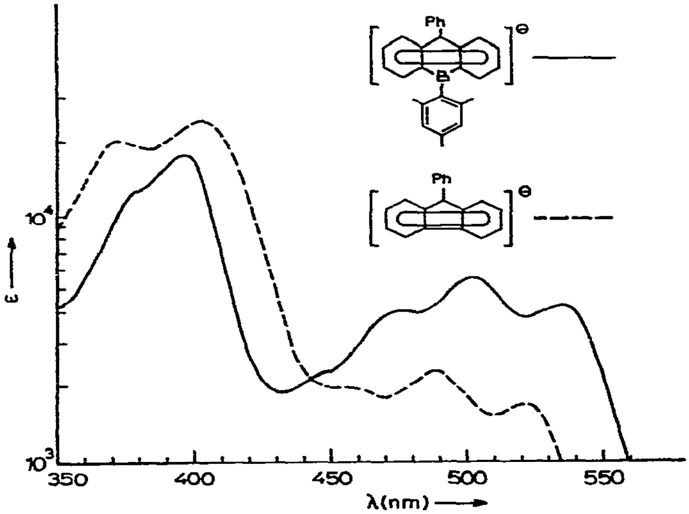


Fig. 3. Visible spectra of IIb and 9-phenylfluorenyl anion. Lithium salts in cyclohexylamine.

Discussion

From Figs. 2 and 3 it is apparent that the correspondence between the visible spectra of II and those of the "iso-π-electronic" (9-phenyl)fluorenyl anions is striking. It is remarkable that the resemblance between the spectra of IIa and IIb is much better than in the case of the corresponding fluorenyl anions. The intensive absorption band at 403 nm in the visible spectrum of the 9-phenylfluorenyl anion points to an extensive conjugative participation of the 9-phenyl group in the fluorenyl anionic chromophoric system [13]. On the other hand, according to the visible spectra (see Figs. 2 and 3), there is essentially no such participation in the boraanthracene anion IIb, indicating a (nearly) perpendicular position of the 10-phenyl group with respect to the boraanthracene plane. This behaviour of IIb is completely analogous to that of the 10,10-dimethyl-9-phenyl-9,10-dihydro-9-anthryl anion [13] and of 9-phenylanthracene [14], 10-phenyl-9-phosphaanthracene [15], and 10-phenyl-9-arsaanthracene [16]. Evidently, the more favourable geometric situation of the central five-membered ring in the fluorene system permits more coplanarity of a phenyl group than a central six-membered ring, for which steric interference with the hydrogens at C-4 and C-5 is severe.

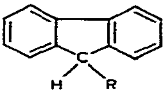
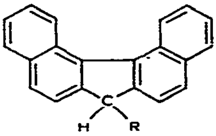
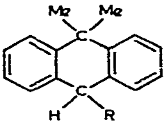
The visible spectra of II (see Figs. 2 and 3) show two band regions. Variation of solvent induces a shift to longer wavelengths with increasing solvent polarity, the shift (in $\bar{\nu}$) being larger for the higher wavelength region by a factor of about 1.5. The constant spacing between the individual bands in both regions in different solvents (toluene, benzene, cyclohexylamine) suggests that these bands belong to the same electronic transitions and represent vibrational fine structure.

From Table 2 it is clear that for Ib the equilibrium: I + base $\rightleftarrows$ III, lies much more on the side of the reactants than for Ia, which is in accordance with expectation. Steric interference by the 10-phenyl group in Ib effects a restricted rotation [3, 4] of the mesityl group around the B—C(mesitylenic) bond, and it is reasonable to assume that the presence of the 10-phenyl moiety similarly diminishes the accessibility of the boron centre.

It is apparent that the construction of a general acidity scale, a considerable task for the CH-acids [17, 18], is even more complex for trivalent boron containing CH-acids, as the "apparent" pK values will strongly depend on factors which influence the Lewis adduct stabilities, apart from the general effects on the pK values of "normal" CH-acids.

In Table 3 the pK values of some selected compounds are tabulated. When the pK' value of I is compared with that of 9,9-dimethyl-9,10-dihydroanthracene, the difference ($\Delta pK = 30.25-15.8 = 14.45$) corresponds roughly (different gegenions, apart from other effects which influence the pK values of CH-acids [17, 18, 20]; in this connection see also the last sentence of the Introduction) to a free energy difference of 19.8 kcal/mol (see Fig. 4); these free energy differences reflect roughly differences in ground state π-energies of the CH-acids and of their conjugate bases [21]. Therefore, the π-stabilization energies of the CH-acids must be taken into account: To obtain the π-energy difference between the conjugate bases the value of 19.8 kcal/mol would increase roughly with the unknown extra π-stabilization energy in I due to the empty $2p$ orbital of boron,

TABLE 3
pK VALUES OF SOME SELECTED CH-ACIDS[a]

	R = H	R = C_6H_5	ΔpK
	22.8[b]	18.5[b]	4.3
	16.8[c]	14.8[c]	2.0
	30.25[d]	28.01[d]	2.24

[a] For more examples see ref. 17 and 18. [b] Lithium cyclohexylamide in cyclohexylamine; ref. 11. [c] Dimethyl sulfoxide/ethanol/0.01 *M* sodium ethoxide; ref. 19. [d] Cesium cyclohexylamide in cyclohexylamine; ref. 6.

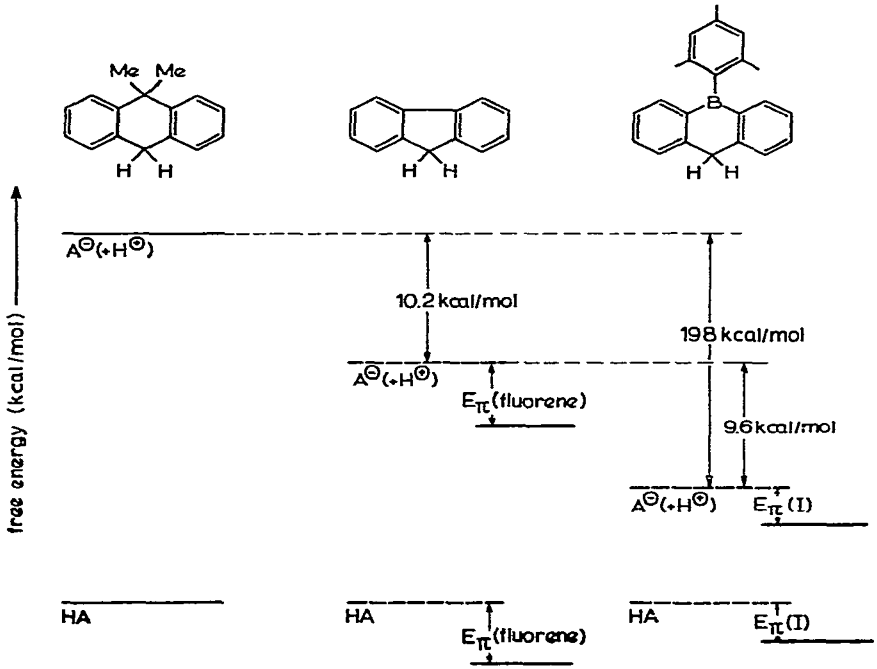


Fig. 4. Idealized schematic representation of π-energy differences. The free energies of the CH-acids (HA) are arbitrary. Dashed lines: no π-interaction assumed between the benzene rings in HA; full lines: π-interaction between the rings in HA is taken into account (see text).

as in the hydrocarbon the boron centre is replaced by a saturated carbon atom which acts as insulator between the two benzene rings (see Fig. 4); the inductive influence of the mesityl group in I on the p*K* value is presumably slight (see below for a discussion of analogous effects of the phenyl group). Depending on the assumptions and the method of computation used, a stabilization energy of 11 [22] - 28 [23] kcal/mol has been attributed to the central ring in anthracene; our value of 19.8 + E_{π}I ≈ 22.8 ± 2 kcal/mol (see below for the estimate of E_{π}I) falls within this range.

The acidity gap between I and fluorene is surprising, as the Δp*K* corresponds roughly to a free energy difference of 9.6 kcal/mol; as the extra π-stabilization energy due to the C(aryl)—C(aryl) bonding in fluorene is 4.4 ± 0.5 kcal/mol [22], II is more stable than the fluorenyl anion by an amount of about 5.2 kcal/mol, which value is to be augmented (see Fig. 4) by the unknown extra π-stabilization energy in I; this extra π-stabilization energy is expected to be about the same as that of triphenylborane, which is reported to be 3 ± 2 kcal/mol [24]. According to the criterion of ground state stabilization II may be expected to be about 8.2 ± 2.5 kcal/mol more stable than the fluorenyl anion and can therefore clearly be designated "aromatic". The acidity of I contrasts strongly with that of 9,9-dimethyl-10-phenyl-9,10-dihydro-9-silaanthracene [25], the acidity of which (p*K* 27.4) does not differ markedly from that of its carbon analogue (p*K* 28.0 [6]). A final comment should be made on the interesting aspect that the acidities of Ia and Ib are essentially the same; Ib is probably an even weaker acid than Ia, but the difference is very slight and not significantly outside the experimental error. This acidity relation can be attributed to several factors.

(a). First, the Δp*K* value of fluorene and 9-phenylfluorene is reduced substantially in the corresponding dibenzo derivatives (see Table 3); it appears that the "need for extra stabilization" is less in the intrinsically more stabilized carbanion.

(b). The second factor becomes apparent when we consider the Δp*K* values of fluorene and 9-phenylfluorene along with those of the corresponding 9,10-dihydroanthracene series: In the 10,10-dimethyl-9-phenyl-9,10-dihydro-9-anthryl anion there is a strong steric interference between the 9-phenyl group and the 1- and 8-hydrogens (resulting in only inductive acid-strengthening by the phenyl group); this interference is reduced substantially due to the more favourable geometry of the central 5-membered ring in the 9-phenylfluorenyl anion [13], resulting in both inductive and conjugative acid-strengthening by the phenyl group. In IIb both effects are acting in the same direction and therefore it is not surprising that the Δp*K* value in the 9,10-dihydroanthracene series vanishes in the 9,10-dihydro-9-boraanthracene series.

(c). The inductive influence of the 10-phenyl group can be overcompensated by rotational entropy effects [6] as a third contributing factor. Molecular models indicate that in the most stable conformation of Ib the 10-phenyl group (in an axial position) can rotate rather freely, this rotational entropy being lost in IIb because of the increased steric interaction with the 4- and 5-hydrogens, as is evidenced by the visible spectra of II (see above).

(d). A fourth factor may be steric inhibition of solvation at the centre of highest charge density by the 10-phenyl group in IIb. (According to reactivity studies [3], C-10 is the centre of highest charge density.)

Experimental

The vessel used was essentially the same as Streitwieser's [11] and consisted of a cylindrical flask carrying two stopcocks, two quartz absorption cells (about 1 cm and 1 mm path length), and a stoppered vertical side arm. One stopcock carried a ground joint for attachment to the vacuum line and the second was fitted with a serum cap. For each run the apparatus was flame-dried, by attaching it to the vacuum line and heating with a blue flame for several minutes in high vacuum. The quality of the quartz cells had not changed appreciably after a year's use. The apparatus was of a size suitable for fitting into the cell compartment of a Perkin—Elmer 137 spectrophotometer. The solid compounds were pipetted (in n-hexane solutions) or rinsed (with dry benzene) into the side-arm; the solvents used were pumped off on the vacuum line. Cyclohexylamine (previously dried by reflux under nitrogen on sodium metal for several days and distillation: stored on lithium cyclohexylamide [12]) was vacuum distilled into the vessel. Using a Hamilton gas-tight syringe, the butyllithium solutions were injected through a serum cap, whenever possible in a nitrogen-filled glove box. All measurements were performed at room temperature. Melting points are uncorrected.

Materials

Fluorene was purified by crystallization, preparative gas chromatography, and sublimation, m.p. 115-116° (lit. [26] m.p. 116-117°), 9-phenylfluorene by crystallization and sublimation, m.p. 145.0-145.5° (lit. [27] m.p. 145°). 9-mesityl-9,10-dihydro-9-boraanthracene [2, 3] (Ia) (m.p. 131-134°) and 9-mesityl-10-phenyl-9,10-dihydro-9-boraanthracene [4] (Ib) (m.p. 181-183°) were described earlier; n-hexane was freshly distilled under nitrogen from lithium aluminum hydride; stock solutions of Ia or Ib in n-hexane were prepared and kept under nitrogen. Benzene was distilled from sodium wire and stored over it.

Extinction measurements

(a). 9-mesityl-9,10-dihydro-9-boraanthracene (Ia). The spectra of IIa were obtained by pipetting a known amount of Ia in n-hexane, pumping off the n-hexane, pipetting 10 ml of benzene, degassing and, after thawing, injecting an excess of 1.4 *N* tert-butyllithium in n-pentane [the benzene was not air-free (see above); in rigorously air-free benzene the side product(s) (see below) was generated along with IIa under otherwise identical conditions]. After 45 minutes the benzene was pumped off and cyclohexylamine vacuum distilled into the vessel. Visible spectrum of IIa: in benzene [2], λ_{max}(nm)(ϵ_{max}): 334 (4860, sh), 351 (9490), 367 (17780), 418 (5980), 434 (6220); in cyclohexylamine: 353 (3220, sh), 371 (8800), 389 (20530), 468 (2610), 492 (3485), 523 (2580). Direct injection of n- or tert-butyllithium into cyclohexylamine solutions of Ia was accompanied by additional bands at 420 (max) and 585 (sh) nm. The best spectra of IIa were obtained following the above procedure via benzene, using insufficient amounts of tert-butyllithium and larger amounts (ca. 30 mg) of Ia; these spectra were used to calculate the lower wavelength ϵ values and in the equilibrium experiments the amounts of the two carbanionic species present.

(b). 9-mesityl-10-phenyl-9,10-dihydro-9-boraanthracene (Ib). The spectra of IIb were obtained by injecting an excess of 2.25 *N* n-butyllithium in n-hexane or 1.4 *N* tert-butyllithium in n-pentane on the walls of the vessel, containing a solution of Ib in cyclohexylamine, and rinsing the base slowly down in high vacuum with the amine solvent. The best spectra were obtained using insufficient amounts of the lithium bases and larger amounts (ca. 30 mg) of Ib; these spectra were used to calculate the lower wavelength ϵ values and in the equilibrium experiments the amounts of the two carbanionic species present. Visible spectrum of IIb: In cyclohexylamine, λ_{max}(nm) (ϵ_{max}): 397 (18000), 471 (4000), 503 (5570), 536 (4290).

(c). Fluorene and 9-phenylfluorene. Streitwieser's procedure [10], using excess of n-butyllithium injected directly into the cyclohexylamine solutions as well as the indirect method via benzene (see part *a*), gave spectra and ϵ values in complete agreement with those reported [12]. [We observed the maxima at slightly different wavelengths (see below) presumably due to a systematic error of our spectrophotometer.] The method of using insufficient amounts of base was utilized to determine the lower wavelength ϵ values. Visible spectra: Fluorenyl anion (cyclohexylamine), λ_{max} (nm) (ϵ_{max}): 368 (11560), 454 (1040), 480 (1280), 514 (840); 9-phenylfluorenyl anion (cyclohexylamine): 372 (19930), 403 (24530), 459 (1920), 490 (2250), 523 (1670); lit. [12], fluorenyl anion: 452 (1080), 477 (1300), 510 (827), and 9-phenylfluorenyl anion: 452 (1950), 487 (2280), 520 (1690).

Equilibrium measurements

(1). Table 1, series 1. Amounts used: 14.0 to 43.1 mg of Ia and 38.9 to 216.7 mg of 9-phenylfluorene in 10 ml of cyclohexylamine. The carbanionic solutions were generated via the benzene method (see extinction measurements, part *a*) using an insufficient amount of base. Spectral scans were taken immediately after thawing and after several hours of standing at room temperature. Equilibrium was apparently instantaneous. Additional tert-butyllithium was added by injecting a drop of the base solution on the glass wall of the vessel and rinsing the base slowly down with the amine solvent in high vacuum; after pressurizing with nitrogen and thawing, a spectral scan was immediately made followed by another scan after several hours of standing at room temperature. This procedure was repeated until the ion-pair concentrations were too large to measure. The calculated equilibrium constants did not change on these additions of base.

(2). Table 1, series 2. Amounts used: 30.7 mg of Ib and 342.9 mg of 9-phenylfluorene in 10 ml of cyclohexylamine. The anions were generated as described above (see extinction measurements, part *b*), using an insufficient amount of the base. Additional drops of base solution were added as described above (see part *1*) with relation to the equilibrium constants, see part *1*. Equilibrium is apparently instantaneous.

(3). Table 1, series 3. Amounts used: 155.5 mg of Ia and 42.8 mg of Ib in 10 ml of cyclohexylamine. See part *1* also.

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