Ion Pair Properties of Lithium and Cesium Salts of Carbazole[1]

Alessandro Abbotto, Andrew Streitwieser,* Manolis Stratakis, and James A. Krom

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720-1460

Received August 13, 1997

Abstract: The lithium salt of carbazole, LiCb, is monomeric in THF in the concentration range $(1-5) \times 10^{-3}$ M. It is a contact ion pair (CIP) with an effective ion pair p*K* of 13.48 on a scale where fluorenyllithium solvent separated ion pairs (SSIP) are 22.90 (per hydrogen). The cesium salt, CsCb, is a mixture of monomer and dimer with $K_2 = 300$ M^{-1}. The monomer forms a 1:1 complex, CsCb·CbH, with $K_c = 62$ M^{-1}. The ion pair p*K* of monomeric CsCb is 19.24.

Introduction

The anion of carbazole has been the subject of various experimental and theoretical investigations over the past two decades. It is well-known that in ethereal solvents the status of carbanions and nitranions can be generally described in terms of an equilibrium between contact ion pairs (CIP) and solvent-separated ion pairs (SSIP), the actual position of the equilibrium depending on many factors such as the anion structure, the counterion, solvent, concentration, and temperature.[2] Optical absorption and emission experiments have shown that the potassium, sodium, and lithium salts of carbazole, indole, and 4,5-iminophenanthrene exist entirely as CIP in tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME), whereas more polar solvents such as hexamethylphosphoric triamide (HMPT) are needed to observe SSIP.[3] By comparison, the lithium salt of the carbon analogue of carbazole, fluorene, was reported in 1965 by Hogen-Esch and Smid to be a mixture of CIP and SSIP in THF solution.[4] In contrast, the large cesium ion always prefers the formation of CIP.[5]

^{1}H, ^{13}C, and ^{7}Li NMR spectroscopy have also been used to gain information concerning the ion pairing and structure of the carbazide salts.[3c,6] In particular, ^{7}Li NMR spectroscopy has proven to be a useful method to determine the σ-like or π-like interaction between the cation and the anionic substrate in the CIP. The results showed that the nitranions of carbazole and indole are associated with the cation through their nitrogen σ lone pairs, whereas fluorenyl anion involves several carbon sites in coordination with lithium, thus forming a π-like complex.

Recently, the Schleyer group found that lithium carbazide crystallizes as a dimer from a THF solution when *n*-BuLi is used as a base,[7] whereas a monomeric species is obtained from *t*-BuOLi/*t*-BuOH in THF.[8] The X-ray structures of cesium and potassium carbazide in the presence of a donating ligand were also obtained; in both cases a dimeric aggregate was found.[9]

Finally, the acidity of carbazole has been reported in several media: DMSO (p*K* = 19.9,[10] 19.6[11]), DME (p*K* = 14.6 (Li), 18.6 (Cs)),[12] and H_2O (p*K* = 21.1,[13] 17.06,[14] 15.16[15]).

The crystal structures do not relate to the state of aggregation of the carbazole salts in solution and, in fact, information relevant to the possible aggregation of carbazide ion pairs in solution is lacking. We recently showed that the cesium salt of diphenylamine has a greater tendency to aggregate than the lithium salt and that the monomer and dimer of the cesium salt have measurably different absorption spectra.[16] In the present study, we compare these properties for carbazole, a closely related but more acidic amine. The aggregation states of the lithium and cesium salts of carbazole (LiCb and CsCb, respectively) have been studied in THF and the equilibrium constants have been determined. We also report the corresponding ion pair acidities of carbazole (CbH) for comparison with previous results. These data further expand the lithium[16,17] and cesium[5,16,17b,18] ion pair acidity scales.

Results

UV−Visible Absorption Spectra of the Anions. The lithium and cesium salts of carbazole were obtained in THF

---

[1] Carbon Acidity. 98. For part 97 see: Streitwieser, A.; Schriver, G. W. *Heteroatom Chem.* **1997**, *8*, 533−7.

[2] For a review, see: *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley: New York, 1972.

[3] (a) Vos, H. W.; Blom, H. H.; Velthorst, N. H.; MacLean, C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 635. (b) Vos, H. W.; MacLean, C.; Velthorst, N. H. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 63. (c) Velthorst, N. H. *Pure Appl. Chem.* **1979**, *51*, 85.

[4] (a) Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1965**, *87*, 669. (b) Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1966**, *88*, 307. (c) Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1966**, *88*, 318.

[5] Bors, D. A.; Kaufman, M. J.; Streitwieser, A. *J. Am. Chem. Soc.* **1985**, *107*, 6975.

[6] Cox, R. H. *Can. J. Chem.* **1971**, *49*, 1377.

[7] Hacker, R.; Kaufmann, E.; Schleyer, P. v. R.; Mahdi, W.; Dietrich, H. *Chem. Ber.* **1987**, *120*, 1533.

[8] Lambert, C.; Hampel, F.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1209.

[9] Gregory, K.; Bremer, M.; Schleyer, P. v. R.; Klusener, P. A. A.; Brandsma, L. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1224.

[10] (a) Bordwell, F. G.; Drucker, G. E.; Fried, H. E. *J. Org. Chem.* **1981**, *46*, 632. (b) Bordwell, F. F. *Acc. Chem. Res.* **1988**, *21*, 456.

[11] Terekhova, M. I.; Petrov, E. S.; Rokhlina, E. M.; Kravtsov, D. N.; Shatenshtein, A. I. *Khim. Geterotsikl. Soedin.* **1979**, 1104.

[12] Petrov, E. S.; Terekhova, M. I.; Basmanova, V. M.; Shatenshtein, A. I. *Zh. Org. Khim.* **1980**, *16*, 2457. The reported acidities are normalized to the DMSO value of fluorene (22.9).

[13] Schulman, S. G.; Capomacchia, A. C. *Anal. Chim. Acta* **1972**, *59*, 471.

[14] Gaboriaud, R.; Halle, J.-C.; Letellier, P. *Bull. Soc. Chim. Fr.* **1976**, 1093.

[15] Balón, M.; Carmona, M. C.; Muñoz, M. A.; Hidalgo, J. *Tetrahedron* **1989**, *45*, 7501.

[16] Krom, J.; Petty, J. T.; Streitwieser, A. *J. Am. Chem. Soc.* **1993**, *115*, 8024.

[17] (a) Gronert, S.; Streitwieser, A. *J. Am. Chem. Soc.* **1986**, *108*, 7016. (b) Kaufman, M. J.; Gronert, S.; Streitwieser, A. *J. Am. Chem. Soc.* **1988**, *110*, 2829.

[18] (a) Streitwieser, A.; Bors, D. A.; Kaufman, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1394. (b) Streitwieser, A.; Ciula, J. C.; Krom, J. A.; Thiele, G. *J. Org. Chem.* **1991**, *56*, 1074.

S0002-7863(97)02839-4 CCC: $15.00

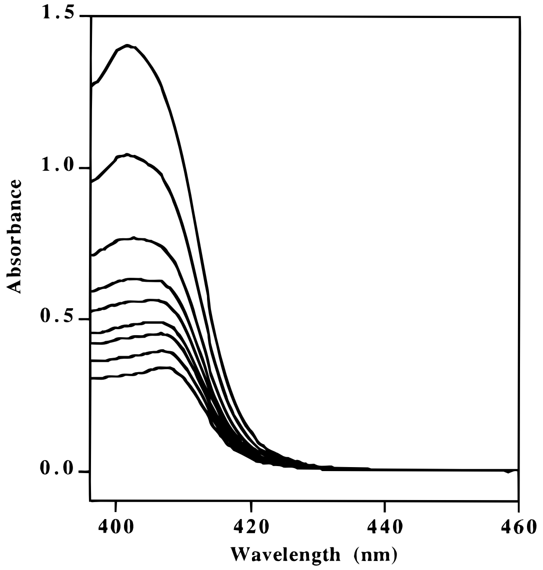

Figure 1. Concentration dependence of the UV−vis spectrum of CsCb in THF at 25 °C showing the equilibrium monomer/dimer. Concentrations range from 6.365×10^{-3} (top spectrum) ($\lambda_{max} = 401.5$ nm) to 1.565×10^{-3} M (bottom spectrum) ($\lambda_{max} = 407.0$ nm) in a 1-mm cell.

solution by using fluorenyllithium and diphenylmethylcesium as the base, respectively. All of the UV−visible experiments were carried out in THF solution at 25.0 ± 0.1 °C. The window of study of the anions was limited at low wavelengths to 390 nm, since neutral carbazole starts absorbing significantly below this value.

The absorption spectrum of LiCb does not depend on the concentration of the anion in the range of concentrations used $((1 \times 10^{-3}) \div (5 \times 10^{-3})$ M). The λ_{max} was found to be 392.0 nm ($\epsilon = 2860 \pm 20$ M^{-1} cm^{-1}). By contrast, the spectrum of CsCb was found to be dependent on the concentration of the anion CsCb as well as the presence of neutral CbH. Because of the latter dependence the absorption of CsCb was studied first in the absence of neutral CbH. The λ_{max} gradually shifted from 401.5 to 407 nm as the concentration of CsCb was changed from 6.365×10^{-3} to 1.565×10^{-3} M. At 404.5 nm the value of the extinction coefficient was found to be independent of the formal concentration of CsCb, $\epsilon = 2110 \pm 4$ M^{-1} cm^{-1}. These spectra are shown in Figure 1.

The dependence of the shape of the absorption spectrum on the concentration of CsCb is indicative that more than one species (aggregates), each with a different absorption spectrum, exist in THF solution. To investigate the number and nature of the aggregates we submitted the data for the absorption of CsCb at nine different concentrations to "singular-value decomposition" (SVD) analysis in the same way as applied previously to the cesium salt of diphenylamine.[16] The experimental data (values of absorbance for each determination at 0.5 nm intervals over the range 500.0−390.0 nm) were decomposed leading to nine spectral bases, each associated with a "singular value", S. The singular values constitute the "weighting factors" by which each basis describes the experimental set of data. Two main singular values were found, $S_1 = 12.15$ and $S_2 = 0.43$. The remaining seven values were found to be between 0.01 and 0.004 and only describe noise. That is, the linear combination of two basis spectra are able to reproduce the nine original experimental spectra, demonstrating that only two distinguishable species are present in solution whose relative concentrations differ in each determination.

The two basis spectra have only a linear-algebraic meaning and are not the actual UV−visible spectra of the two species present in solution. These spectra are obtained from a linear transformation of the basis spectra as described previously.[16] The resulting spectra and extinction coefficients of the two species in solution provide their concentrations at each determination. The assumption that the two species are the monomer $(CsCb)_1$ and dimer $(CsCb)_2$ is consistent with the results of independent ion pair acidity studies described below.

Table 1. Aggregation Equilibria of Cesium Carbazide CsCb

$$2(\mathrm{CsCb})1 \overset{K_2}{\rightleftharpoons} (\mathrm{CsCb})_2$$

$[(\mathrm{CsCb})_1]$ (10^{-4} M)	$[(\mathrm{CsCb})_2]$ (10^{-4} M)	K_2[a] (10^2 M^{-1})
25.2	19.1	3.0
21.1	13.3	3.0
17.5	9.14	3.0
15.4	7.13	3.0
14.2	6.08	3.0
12.9	4.99	3.0
12.2	4.45	3.0
11.0	3.61	3.0
9.8	2.85	3.0

[a] $K_2 = [(\mathrm{CsCb})_2]/[(\mathrm{CsCb})_1]^2$.

The λ_{max} of the monomer $(CsCb)_1$ and of the dimer $(CsCb)_2$ were found to be 408.5 and 401.5 nm, respectively. At 404.5 nm the extinction coefficient for the monomeric species is $\epsilon = \epsilon_{ob} = 2110$ M^{-1} cm^{-1}, while the dimeric species has $\epsilon = 2\epsilon_{ob} = 4220$ M^{-1} cm^{-1}. By using the actual spectra of the monomer and the dimer, the nine experimental spectra were deconvoluted and the concentrations of each species were determined at each step. The data are summarized in Table 1. From these data the equilibrium constant K_2 for reaction 1 was determined to be 3.0×10^2 M^{-1}.

$$2(\mathrm{CsCb})_1 \rightleftharpoons (\mathrm{CsCb})_2 \tag{1}$$

Interaction of CsCb with the Neutral CbH: Formation of the Adduct CsCb·CbH. The UV−vis spectrum of CsCb was found to be dependent on the presence of the neutral as well. This result shows that an interaction between the nitranion Cb^- and neutral CbH occurs in THF solution with the formation of a complex, **C**. Our goal was to investigate and determine the stoichiometry of the adduct between the anion and the neutral and the corresponding complexation constant.

To analyze the experimental spectra of the CsCb in the presence of the neutral CbH we start by assuming that the complex is an adduct between one molecule of the salt CsCb and one molecule of the neutral CbH. This model is obviously the simplest and most likely case. The model was tested for consistency with results from spectroscopic and ion pair acidity studies. By addition of increasing amounts of neutral carbazole to a solution of CsCb in THF the absorption spectrum was found to shift toward the blue. A 5×10^{-3} M solution of CsCb in THF treated with a large excess of the neutral (final concentration was 0.7−1 M) gave rise to a spectrum that was almost insensitive to further additions of CbH. At this point the spectrum is mostly that of the complex. A set of different experiments in which the starting concentration of CsCb was varied from 1.51×10^{-3} to 8.59×10^{-3} M and then treated with excess neutral carbazole to the order of the concentrations above showed that each of the final spectra cannot be considered due only to the absorption of the complex, but that an unknown amount of free CsCb is still present; that is, the conversion to the complex is not complete. Unfortunately, further addition of CbH is limited by its solubility in THF. A procedure of successive interations was therefore used to obtain the spectrum of the complex and the equilibrium constant, K_c, for reaction 2.

$$(\mathrm{CsCb})_1 + \mathrm{CbH} \rightleftarrows \mathbf{C} \tag{2}$$

When both the salt CsCb and the neutral CbH are present in solution, from eqs 1 and 2 the concentrations of all the species are as follows:

$$[(\mathrm{CsCb})_1] = \{\mathrm{CsCb}\}_o - [\mathbf{C}] - 2[(\mathrm{CsCb})_2] \tag{3a}$$

$$[(\mathrm{CsCb})_2] = K_2[(\mathrm{CsCb})_1]^2 \tag{3b}$$

$$[\mathrm{CbH}] = [\mathrm{CbH}]_o - [\mathbf{C}] \tag{3c}$$

where $[\mathbf{C}]$ = concentration of the complex, [CbH] = concentration of the uncomplexed neutral carbazole, $\{\mathrm{CsCb}\}_o$ = initial total formal concentration of cesium carbazide, $[\mathrm{CbH}]_o$ = initial concentration of carbazole.

If we know the concentrations $\{\mathrm{CsCb}\}_o$ and $[\mathrm{CbH}]_o$ and the values of K_2 and K_c, we are therefore able to determine $[(\mathrm{CsCb})_1]$ and $[(\mathrm{CsCb})_2]$ and, by using the actual spectra of the monomer and of the dimer, to obtain the spectrum of the complex by subtraction of these components. We call experiment A that in which the complexation equilibrium is studied and where the concentrations $\{\mathrm{CsCb}\}_o$ and $[\mathrm{CbH}]_o$ are known quantities. The difficulty is that K_c is an unknown quantity and cannot be determined unless the spectrum of the complex is available. The spectrum obtained by treating a THF solution of CsCb with a large excess of CbH was taken as a first approximation to the spectrum of the complex. This spectrum plus the separate spectra of the cesium carbazide ion pairs and of the indicator ion pair were used to fit a total of 20 acidity equilibria from two independent experiments (experiments B and C) (see the Ion Pair Acidity section). The fitting of the 20 acidity equilibria allows the determination of the concentrations of all of the species in solution. In particular, we now know the first approximations to the concentrations of $[(\mathrm{CsCb})_1]$, [CbH], and $[\mathbf{C}]$ in 20 different equilibria. By plotting the values of $[\mathbf{C}]$ vs the values of $[(\mathrm{CsCb})_1]\cdot[\mathrm{CbH}]$ a linear correlation was found (slope = 76.6, intercept = 5.6×10^{-6}, $r^2 = 0.996$). The linearity of the correlation is evidence that the hypothesis of the stoichiometry of the complex is correct. The slope of the line provides us with a first approximation to K_c and, by applying eqs 3a–3c, a first set of values for $[\mathbf{C}]$, $[(\mathrm{CsCb})_1]$, and $[(\mathrm{CsCb})_2]$ is now available for the complexation equilibrium (experiment A). In particular, the concentrations of the monomer and the dimer allow determination of their contributions to the total spectra of their equilibria with the complex. These contributions are relatively small and by subtraction provide the next approximation to the spectrum of the complex itself. This next approximation to the spectrum of **C** was used again to fit the acidity equilibria and a new set of values for K_c, $[\mathbf{C}]$, $[(\mathrm{CsCb})_1]$, and $[(\mathrm{CsCb})_2]$ was obtained. The procedure was repeated until self-consistency was reached—that is, the value of K_c coming from two consecutive sets differed by less than 0.1%. Self-consistency was reached after three iterations. The results are summarized in Table S2 (Supporting Information). The plot of $[\mathbf{C}]$ vs $[(\mathrm{CsCb})_1]\cdot[\mathrm{CbH}]$ is shown in Figure S2 (Supporting Information). The separated spectra of the monomer, dimer, and the complex of cesium carbazide are shown in Figure 3. The extinction coefficient of the complex was found to be 845 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ at 404.5 nm. The complexation constant for reaction 2 is $K_c = 62\ \mathrm{M}^{-1}$.

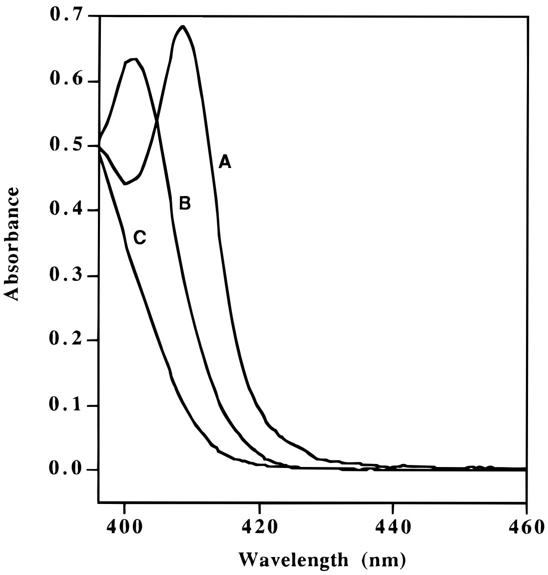

Figure 3. Separated spectra of the monomer $(\mathrm{CsCb})_1$ (spectrum A, $\lambda_{\max}$ 408.5 nm), the dimer $(\mathrm{CsCb})_2$ (spectrum B, $\lambda_{\max}$ 401.5 nm), and the complex $(\mathrm{CsCb})_1\cdot\mathrm{CbH}$ (spectrum C) in THF at 25 °C ($[(\mathrm{CsCb})_1] = [(\mathrm{CsCb})_1\cdot\mathrm{CbH}] = [(\mathrm{CsCb})_2]/2 = 2.522 \times 10^{-3}$ M in a 1-mm cell).

Table 3. pK_a and Extinction Coefficient Measurements of Lithium Salt Carbazole and of CH Acid Indicators in THF[a,b]

compd[c]	$\mathrm{p}K_{\mathrm{Li/THF}}{}^{d}$	$\lambda_{\max}$ (ϵ)
CbH	13.48	392(2860)
Ph–3,4-BF	14.88	394(23900) 418(26000)
9-BpFl	16.98	373(14300) 498(33400) 526(25600)
9-PhFl[e]	17.60	411(25300)

[a] On a per hydrogen basis. [b] For a lithium ion pair acidity scale of other CH acids see ref 17b. [c] Abbreviations: CbH, carbazole; Ph-3,4-BF, 7-phenyl-3,4-benzofluorene; 9-BpFl, 9-biphenylylfluorene; 9-PhFl, 9-phenylfluorene. [d] pK_a values referenced to the SSIP of fluorene at 22.90. [e] Reference 17b.

Ion Pair Acidity. The lithium ion pair acidity of CbH was measured against the indicator 7-phenyl-3,4-benzofluorene (Ph-3,4-BF, pK_{Li} = 14.88;[17] Table 3), equilibrium 4:

$$\mathrm{CbH} + \mathrm{LiPh\text{-}3,4\text{-}BF} \rightleftarrows \mathrm{LiCb} + \mathrm{Ph\text{-}3,4\text{-}BF} \tag{4}$$

The UV–vis spectra of the lithium salt of the indicator, LiPh-3,4-BF, and of the lithium salt of carbazole, LiCb, were used to fit a set of 10 acidity equilibria spectra in the range 650–390 nm. The concentrations of the anions [LiPh-3,4-BF] and [LiCb] were determined directly, and those of the neutrals, [Ph-3,4-BF] and [CbH], by difference from the initial concentrations. The data are collected in Table S4 (Supporting Information). A small deviation of the observed constant K_{obs} for reaction 4 from constancy was attributed to the slight but significant dissociation of the lithium solvent-separated ion pair of the indicator to free ions in THF:

$$\mathrm{LiPh\text{-}3,4\text{-}BF} \rightleftarrows \mathrm{Li}^+ + \mathrm{Ph\text{-}3,4BF}^- \tag{5}$$

The dissociation constant K_d for equilibrium 5 has not been determined in THF but can be reasonably assumed to be comparable to that of similar carbon acids 9-phenylfluorene and 3,4-benzofluorene in THF ($K_d = 1.0 \times 10^{-5}$ M at 25 °C). The spectra of LiPh-3,4-BF SSIP and the free carbanion are sufficiently similar that a straightforward correction using K_d

then provides the value of [LiPh-3,4-BF] to be used in eq 4. The resulting values of K_{obs} are now constant. The dissociation of LiCb to free ions is negligible by analogy to that of lithium diphenylamide ($K_{diss} = 10^{-12}-10^{-11}$ M),[16] and as shown by its relatively low pK (vide infra). The N−Li association in the CIP is substantially stronger than the ion pair association in the indicator SSIP. Moreover, the constancy of the corrected K_{obs} confirms that LiCb is present as one species in THF solutions—that is, aggregation is negligible at these concentrations. Thus, K_{obs} is taken as K_o for equilibrium 4; the resulting mean value of ΔpK (-1.40 ± 0.01) gives the lithium ion-pair pK of carbazole in THF as 13.48 on a scale in which the reference is that of fluorenyllithium SSIP whose pK is taken as 22.90 (per H).[17]

The cesium ion pair acidity of carbazole was measured against the indicator 3,4-benzofluorene (3,4BF, pK_{Cs} = 19.47),[5,17b,18] equilibrium 6:

$$\mathrm{CbH} + \mathrm{Cs3,4BF} \rightleftarrows \mathrm{CsCb} + \mathrm{3,4BF} \qquad (6)$$

The separated spectra of the cesium salt of the indicator, Cs3,4-BF, and of the monomer $(CsCb)_1$, dimer $(CsCb)_2$, and complex of the cesium salt of carbazole were used to fit a total of 26 acidity equilibria recorded in two independent experiments. The concentrations of the ion pair species were determined directly. The concentration of the neutral indicator [3,4-BF] was obtained by difference of the concentration of the corresponding anion, while the value of the neutral uncomplexed carbazole [CbH] was calculated from eq 7:

$$[\mathrm{CbH}] = [\mathrm{CbH}]_o - \{\mathrm{CsCb}\} - 2[\mathbf{C}] \qquad (7)$$

where

$$\{\mathrm{CsCb}\} = [(\mathrm{CsCb})_1] + 2[(\mathrm{CsCb})_2] \qquad (8)$$

is the total concentration of the uncomplexed ion-pair cesium carbazide. The acidity data are summarized in Table S5 (Supporting Information).

The basis spectra of the monomer $(CsCb)_1$ and of the dimer $(CsCb)_2$ were obtained as linear combinations of the chemically meaningless basis spectra derived directly from the SVD output (U_1 and U_2).[16] The assumption that the two distinct species that describe the behavior of the uncomplexed cesium carbazide in solution are actually the monomer and the dimer implies a stoichiometry. The advantage of using the two derived spectra is that the concentrations of the monomer and the dimer can be calculated and therefore the extinction coefficient of each aggregate and the equilibrium constants of dimerization (K_2) and complexation (K_c) can be determined. Alternatively, the deconvolution of the experimental UV−vis spectra using the "direct" components U_1 and U_2 do not make use of any further assumptions but have the limitation that only the total formal concentration of the cesium carbazide ion pairs {CsCb} can be determined. That is, both the derived spectra assuming the stoichiometry of $(CsCb)_1$ and $(CsCb)_2$ and the direct use of U_1 and U_2 lead to the same values of {CsCb}. Next, we use only the values of {CsCb}, as reported in Table 5, to determine the relative acidity K_a and the dimerization constant K_2.

The observed constant K_{obs} of equilibrium 6 is given by

$$K_{ob} = \frac{\{\mathrm{CsCb}\}[\mathrm{3,4\text{-}BF}]}{[\mathrm{CbH}][\mathrm{Cs3,4\text{-}BF}]} \qquad (9)$$

while the true ion pair acidity equilibrium constant K_a is

$$K_a = \frac{[(\mathrm{CsCb})_1][\mathrm{3,4\text{-}BF}]}{[\mathrm{CbH}][\mathrm{Cs3,4\text{-}BF}]} \qquad (10)$$

Algebraic manipulation relates the observed concentration of {CsCb} to the observed quantity {CsCb}/K_{ob} through the following equation:[16]

$$\{\mathrm{CsCb}\} = K_a(\{\mathrm{CsCb}\}/K_{ob}) + 2K_2K_a^{\,2}(\{\mathrm{CsCb}\}/K_{ob})^2 \qquad (11)$$

The plot of {CsCb} vs {CsCb}/K_{ob} is shown in Figure S4 (Supporting Information). Statistics of the correlations of the data reported in Table S5 are shown in Table S6 (Supporting Information). The dimerization constants from acidity experiments B and C were found to be $K_2 = 2.9 \times 10^2$ and 2.5×10^2 M^{-1}, respectively, in excellent agreement with the results from the spectroscopic data, where a monomer/dimer equilibrium was assumed. The ion pair acidity constant with respect to the indicator 3,4-BF was found to be $K_a = 0.86$, from which the ion pair p$K_{Cs/THF}$ of carbazole was calculated to be, after statistical correction, 19.24.

Discussion and Conclusions

This UV−vis study has shown some important and unexpected differences between the lithium and the cesium salts of carbazole in THF solution at 25 °C. LiCb was found to be entirely monomeric whereas CsCb exists as a mixture of three distinguishable ionic species, each with distinct absorption shape, the monomer $(CsCb)_1$, dimer $(CsCb)_2$, and an adduct (or complex) CsCb·CbH. All of the equilibrium constants among these species were determined. The dimerization constant (eq 1) is $K_2 = 3.0 \times 10^2$ M^{-1} and the complexation constant for reaction 2 is $K_c = 62$ M^{-1}. The comparison of acidity equilibria with SVD analysis of spectra as a function of concentration shows that the two distinctive species identified by SVD are the ion pair monomer and dimer; this result is a further example[16] that demonstrates the power of this combination in determining both the extent of aggregation and the stoichiometry of the aggregates even in highly dilute solution. A comparison with the analogous salts of diphenylamine DPA, LiDPA and CsDPA,[16] is instructive. In both cases the lithium salt is monomeric whereas the cesium salt consists of monomers and dimers in the concentration region $10^{-3}-10^{-4}$ M. DPA is less acidic than CbH but its cesium salt is less prone to dimerize ($K_2 = 1.6 \times 10^2$ compared to 3.0×10^2 for CsCb); usually, the more basic anions tend to form the more aggregated ion pairs. In the present case, the enforced planarity of the carbazole ring system undoubtedly results in lower steric congestion in the dimer and leads to a higher dimerization constant although an alternative explanation is implied below.

One striking difference between the two cesium salts, CsCb and CsDPA, is the ability of the former to form an adduct with the neutral species, which was shown to be formed from one molecule of CsCb and one molecule of CbH. A structural hypothesis can be forwarded to account for this different behavior. Ion pairs of nitranions usually coordinate to the nitrogen lone pair. For CsCb, however, we can postulate that π-coordination between the pyrrole anion moiety and the large cesium cation is competitive; in such an ion pair, the nitrogen lone pairs are now available for hydrogen bonding to a free carbazole molecule. For the smaller lithium cation, the π-coordinated structure presumably cannot compete with σ-coordination particularly since the π-coordinated structure has fewer coordination sites for solvation of lithium cation; in the favored σ-coordination structure such hydrogen bonding is now blocked.

Table 7. Comparison of pK_a of Carbazole (CbH) and Diphenylamine (DPA) in Various Solvents

compd	Li/THF[a]	Cs/THF[a]	Li/DME[a,b]	Cs/DME[a,b]	Li,crypt/THF[a,c]	DMSO	H_2O
CbH	13.48[d]	19.24[d]	14.6	18.6	20.0	19.9,[e] 19.6[f]	15.16,[g] 17.06,[h] 21.1[i]
DPA	19.05[j]	24.20[j]	19.9	23.9		24.95[k]	22.44, 23.39[l]

[a] The reported acidities are referred to the DMSO value of fluorene (22.9). [b] Reference 12. [c] THF with lithium cation as the [2.1.1]cryptate: ref 24. [d] This work. [e] Reference 10. [f] Reference 11. [g] Reference 15. [h] Reference 14. [i] Reference 13. [j] Reference 16. [k] Bordwell, F. G.; Algrim, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 2964. [l] Cox, R. A.; Stewart, R. *J. Am. Chem. Soc.* **1976**, *98*, 488.

This hypothesis is supported by theoretical studies[19] and by some X-ray structures. The central 6-π-electron ring of the carbazide anion is understandably better at π-coordination than the extended π-system of diphenylamide anion. Moreover, the fact that the λ_{max} of LiCb is at a shorter wavelength than that of monomeric $(CsCb)_1$ shows that both LiCb and CsCb are CIP in THF solution.[4b,20]

The X-ray structure of a cesium carbazide crystal has been reported.[9] From a 0.2 M solution of carbazole in ether in the presence of *t*-BuOCs and PMDTA (*N,N,N′,N″,N″*-pentamethyldiethylenetriamine), crystals of the cesium nitranion were obtained having a dimeric C_i structure in which the cation is in an apical position with respect to the π-system of the heterocycle and simultaneously facing the σ-nitrogen lone pair of the second molecule. Thus, a π-like and a σ-like interaction occurs simultaneously between cesium and the carbazide in this structure. The formation of the dimer $(CsCb)_2$ in THF solution can be seen as an alternative to complexation but using similar structural motifs. Furthermore, neutral carbazole itself has been reported to form strongly hydrogen-bonded dimeric structures in which the two molecules assume an antiparallel stack geometry, both theoretically (AM1) and experimentally (fluorescence excitation and emission spectra) ascertained.[21] In fact, one can expect that the deprotonation of one carbazole can lead to an even more stable hydrogen-bonded structure, with the atoms of nitrogen of the two carbazole moieties facing one another in the same plane and sharing an atom of hydrogen. Lithium carbazide crystallizes from THF as a dimer.[7] Although even in this case simultaneous σ and π interactions between the cations and the nitranions occurs, unlike other lithium amides, the lithium cation does not occupy the same apical position as was found for cesium, but instead a planar rhomboid N−Li−N−Li configuration is preferred, where each lithium is at the same position with respect to the two molecules of nitranions. Furthermore, when *t*-BuOLi is used as base, a monomeric crystal was obtained from THF, in which the lithium coordinates the nitrogen σ lone pair.[8] In this case, the additional coordination to *t*-BuOH and *t*-BuO$^-$ competes effectively with another LiCb ion pair. These results support the hypothesis that at low concentrations in THF the lithium is bonded to the σ-nitrogen lone pair, and blocks the formation of a hydrogen bond complex with a molecule of CbH.

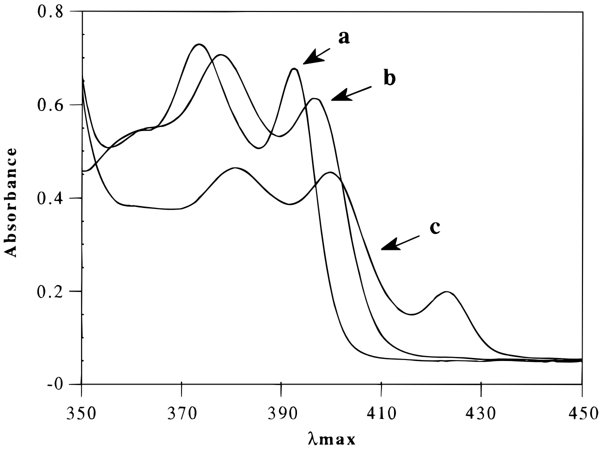

Figure 5. Effect of HMPA on the spectrum of LiCb in THF: (a) in pure THF; (b) in 2 mol % HMPA; (c) in 17 mol % HMPA.

The absence of aggregation recorded for LiCb and LiDPA, at least at the typical concentrations used in our studies, points up a dramatic difference from the situation occurring in many enolate lithium salts of comparable steric bulk for which much higher aggregation numbers are found.[22,23] The additional coordination site provided by the three lone pairs of an oxide ion are clearly decisive in promoting such higher coordination. Nevertheless, the lithium coordination within these aggregates is that of a tight CIP. In LiCb, the lithium is tightly coordinated to the nitrogen and the second nitrogen lone pair is conjugated within the carbazole π-system and less available for aggregation. The strong N−Li interaction in the LiCb CIP is also indicated by its lower basicity relative to CsCb and to the ionic acidity in DMSO (see Table 7). When the lithium cation is cryptated, the ion pair is now effectively an SSIP and the corresponding acidity is lower by more than 6 pK units[24] (see Table 7).

These results may be compared with a limited study of the effect of hexamethylphosphoramide (HMPA) on the LiCb in THF as shown in Figure 5. Addition of 2 mol % HMPA results in a modest change in spectrum; the λ_{max} increases to 397 nm and may reflect peripheral solvation of lithium in the CIP by HMPA. Addition of more HMPA to a mole fraction of 0.17 causes appearance of a new peak at λ_{max} 424 nm that could now be the solvent separated ion pair. At this point 3,4-benzfluorene (Li pK 19.3)[17] is completely deprotonated; thus, LiCb with HMPA is effectively much more basic than in THF alone. A more precise comparison is inappropriate since the solvent has been changed significantly from that of pure THF.

The pK value for CsCb compares well with the free ion value in DMSO, confirming a trend already observed for CsDPA[16] and for cesium salts generally of carbon acids.[5,16,17b,18] The difference in acidity between diphenylamine and carbazole in DMSO (5 pK units) is also found for the cesium and lithium ion pair acidities in THF and DME, showing that the relative stabilization of carbazide anion is about the same in all of these

---

(19) Neuhaus, A.; Streitwieser, A. Paper in preparation.

(20) (a) Carter, H. V.; McClelland, B. J.; Warhurst, E. *Trans. Faraday Soc.* **1960**, *56*, 455. (b) Hoijtink, G. J. *Ind. Chim. Belge* **1963**, *12*, 1371. (c) Buschow, K. H. J.; Hoijtink, G. J. *J. Chem. Phys.* **1964**, *40*, 2501. (d) Buschow, K. H. J.; Dieleman, J.; Hoijtink, G. J. *J. Chem. Phys.* **1965**, *42*, 1993. (e) Velthorst, N. H.; Hoijtink, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 4529.

(21) Taylor, A. G.; Jones, A. C.; Phillips, D. *Chem. Phys.*, **1989**, *138*, 413.

(22) (a) Jackman, L. M.; Lange, B. C. *Tetrahedron* **1977**, *33*, 2737−69. (b) Bauer, W.; Seebach, D. *Helv. Chim. Acta* **1984**, *67*, 1972−88. (c) Arnett, E. M.; Moe, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 7288−93. (d) Abbotto, A.; Streitwieser, A. *J. Am. Chem. Soc.* **1995**, *117*, 6358−9. (e) Abu-Hasanayn, F.; Stratakis, M.; Streitwieser, A. *J. Org. Chem.* **1995**, *60*, 4688−9.

(23) For reviews see: Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624. Jackman, L M.; Bortiatynski, J. *Adv. Carbanion Chem.* **1992**, *1*, 45−87.

(24) Gareyev, R. F.; Antipin, I. S.; Konovalov, A. I. Results to be submitted for publication.

cases. The slightly higher difference in acidity observed in the case of LiCb, with respect to LiDPA, can be interpreted in terms of a somewhat stronger interaction of the lithium cation with the nitrogen atom of the anionic substrate in the former case, perhaps for steric reasons.

Experimental Section

General. Ion pair acidity and spectral studies were carried out in a Vacuum Atmospheres glovebox under an argon atmosphere. The UV−vis spectra were recorded at 25.0 ± 0.1 °C on a computer-driven Shimadzu UV-2101PC spectrometer unit. Details of the apparatus have been previously described.[16] Parameters for UV−vis measurements were as follows: scan speed 200 nm min^{-1}, slit width 2.0 nm, sampling interval 0.5 nm, and cell path length 0.1 cm.

Materials. Anhydrous THF[16] and (diphenylmethyl)cesium (CsDPM)[16] were prepared as described previously. Anhydrous hexane was obtained by distillation over CaH_2. The hydrocarbon indicator acids used in this work either were available from our previous studies or were synthesized by published procedures. All of the indicators were carefully purified prior to use by repeated recrystallization followed by vacuum sublimation.

Carbazole (CbH). Commercial material (99%, Aldrich) was recrystallized twice from absolute EtOH and sublimed three times under vacuum (2×10^{-2} Torr) at 70 °C, mp 245−247 °C (lit.[25] mp 240−243 °C). Further evidence of purity was provided by satisfactory elemental analysis.

Lithium Diisopropylamide (LDA). A 2.16 M solution of *n*-BuLi in hexane (2.3 mL, 5.0 mmol) was added to a solution of freshly distilled diisopropylamine (0.570 g, 5.6 mmol) in anhydrous hexane (5 mL) at 5 °C under nitrogen. After the mixture was stirred for 1 h at room temperature, the solvent and the excess diisopropylamine were carefully removed under vacuum to leave a yellow residue, which was then taken into the glovebox and transferred to a sublimation apparatus. After two sublimations (90−95 °C at 2×10^{-2} mmHg for 48 h, and 75−80 °C at 10^{-3}−10^{-4} mmHg for 24 h) a white crystalline solid (0.10 g) was obtained.

Fluorenyllithium. Commercial fluorene (Aldrich) was recrystallized twice from absolute EtOH, sublimed twice under vacuum, and taken into the glovebox. In the glovebox, freshly sublimed LDA (25 mg, 0.23 mmol) was added to a solution of fluorene (55 mg, 0.33 mmol) in THF (2 mL). The resulting orange mixture was allowed to stand overnight. The solvent and the formed diisopropylamine were removed under vacuum, and the residue was taken into the glovebox. THF (2 mL) was finally added to the yellow solid, giving rise to a bright orange solution (ca. 0.1 M solution of fluorenyllithium in THF). The solution, which was kept in the glovebox at 4 °C, was stable for at least 1 week. After this period, it started to turn slightly darker and was discarded.

Absorption Spectra and Extinction Coefficient of Cesium Carbazide (CsCb) and Lithium Carbazide (LiCb). The spectra were obtained over the wavelength range of 390−700 nm. The neutral carbazole (CbH) does not absorb in this region. A solution of CbH (0.909 mg, 5.436×10^{-3} mmol) and of 9-*tert*-butylfluorene (ca. 0.5 mg) (9-*t*-BuFl, $pK_{Cs/THF} = 24.39$) in THF (0.752 g, 0.854 mL) was prepared in a UV cell, and the baseline spectrum was recorded. Aliquots of a stock solution of CsDPM in THF were added via microsyringe until the absorption of Cs9-*t*-BuFl persisted. At this point the initial carbazole had been converted completely to CsCb. Known amounts of THF were added (about 0.3 g each time) and the absorption spectrum was recorded after each addition. CsCb does not absorb in the region 455−700 nm. This region of the spectrum was used to evaluate the component due to the absorption of Cs9-*t*-BuFl in the nine original spectra. After subtraction of the absorbance band of Cs9-*t*-BuFl, nine spectra of CsCb at different concentrations (from 1.565×10^{-3} M to 6.365×10^{-3} M) were obtained and processed by SVD. The same set of spectra was used to calculate the extinction coefficient at 404.5 nm according to Beer's law (at this wavelength the extinction coefficient was found to be concentration-independent). SVD analysis and the extinction coefficient for the lithium salt LiCb were obtained analogously using fluorenyllithium as a base and its spectrum as end-point indicator of complete deprotonation of CbH.

Absorption Spectra and Extinction Coefficient of the Complex $(CsCb)_1$·CbH (C). The spectra were obtained over the wavelength range of 396−600 nm. A solution of CbH (0.957 mg, 5.723×10^{-3} mmol) and of 9-*t*-BuFl (ca. 0.5 mg) in THF (1.115 g, 1.267 mL) was prepared in a UV cell, and the baseline spectrum was taken. A solution of CsDPM in THF was added via microsyringe until the absorption of Cs9-*t*-BuFl persisted (complete conversion of CbH to CsCb). From this spectrum the concentration of Cs9-*t*-BuFl was determined as described above (9.752×10^{-4} M). Then excess CbH (0.159 g, 0.95 mmol) was added in order to shift the equilibrium toward the formation of the complex, and the spectrum recorded (this spectrum is constituted by the absorption bands of the complex $(CsCb)_1$·CbH and of the unreacted CsCb). From the concentration of Cs9-*t*-BuFl, the fraction of the latest added CbH which was converted to its cesium salt by reaction with Cs9-*t*-BuFl was calculated, and the initial concentrations of CbH and CsCb were exactly determined ($\{CsCb\}_o = 5.49 \times 10^{-3}$ M, $[CbH]_o = 0.750$ M). Using the value of K_c as obtained from the analysis of the ion-pair acidity data (see the Results section), the concentrations of the monomer $(CsCb)_1$, of the dimer $(CsCb)_2$, and of the complex were obtained. This treatment allowed to subtract the absorbance band of CsCb to be subtracted from the original spectrum, leaving only the absorbance band of the complex, which was used to determine its extinction coefficient and to deconvolute the spectra of the ion pair acidity studies.

Ion Pair Acidity Studies. The procedures used in the acidity determinations have been previously described in detail.[16] The lithium[17b] and cesium[18b] ion pair indicator p*K*'s used are those of the revised scales.

Acknowledgment. This research was supported in part by grants from the National Science Foundation and the National Institutes of Health. We are also indebted to Dr. Christoph Lambert for preliminary studies and to NATO for travel funds.

Supporting Information Available: Additional figures (S2, plot of **C** as $[(CsCb)_1][CbH]$; S4, determination of K_a and K_2 from cesium ion pair acidity studies) and tables (S2, determination of K_C; S4, lithium ion pair acidity of CbH; S5, cesium ion pair acidity of CbH; S6, equilibrium constants from Cs ion pair acidity experiments) (5 pages). See any current masthead page for ordering and Internet access instructions.

JA972839T

---

[25] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, 1988.