

Ion Pair Acidities of 9,9'-Bifluorenyl in THF: pK_2 Is Lower than pK_1 ¹

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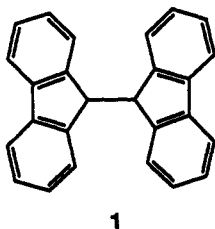
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Summary: The second pK 's in THF for lithium and cesium salts of 9,9'-bifluorenyl are 0.4 and 2.0 pK units, respectively, lower than the first pK 's.

Some years ago we reported² that the difference between the first and second ion pair acidity constants of some indenyl and fluorenyl hydrocarbons in the cesium cyclohexylamide (CsCHA)-cyclohexylamine (CHA) system is less than 1 pK unit. This effect was attributed to simple electrostatic stabilization within the triple ion of the hydrocarbon dianion. Dianions have a valuable role in organic synthesis,³ and the structure of dianions in solution and solid state has attracted the interest of many chemists. For example, semiempirical calculations⁴ have provided confirmation of the proposed type of triple ion stabilization. Such calculations together with NMR spectral interpretations have demonstrated the existence of such carbanion triple ion structures in ether solutions for isomeric 2,2'- and 1,2'-biindenides.⁵

We report here results of our study of ion pair acidities of 9,9'-bifluorenyl 1, in THF, the most synthetically useful solvent in reactions involving organoalkali reagents, using cesium⁶ and lithium⁷ as counterions to form the monosalts $1-M^+$ and disalts $1^{2-}2M^+$.



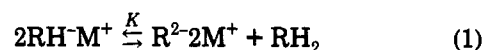
The double indicator technique was used as described in previous publications^{6,7} to derive equilibrium constants relative to an indicator. The results are summarized in Table I. Note that pK_2 is lower than pK_1 by 0.4 pK units for Li and by 2.0 pK units for Cs.

With lithium as the gegenion the transmetalations to give $1-Li^+$ were relatively fast (5-10 min), and it could be observed quantitatively before its partial transformation

Table I. Absorbances (nm) and pK Values

M	λ_{max} ($10^{-3} \epsilon$)		pK_1	pK_2
	$1-M^+$	$1^{2-}2M^+$		
Cs	370(12.5)	409(14.8)	21-21.5	19-19.5
Li	378(13.4)	401(16)	21.16 ± 0.02	20.76 ± 0.02

to the disalt $1^{2-}2Li^+$; pK_1 was found to be 21.16 ± 0.02 . On standing for several days a solution of the monolithium salt of 1 partially disproportionated to $1^{2-}2Li^+$ and neutral hydrocarbon and reached an equilibrium. The equilibrium



constant of eq 1 for $M = Li$ is $K = 2.5 \pm 0.1$, leading to $pK_2 = 20.76$, which is lower than pK_1 by 0.4 pK units.

The same trend but a rather different equilibrium constant for eq 1 was found for Cs as the gegenion. Addition of 1 equiv of (diphenylmethyl)cesium to 1 equiv of 9,9'-bifluorenyl generated mostly the dicesium salt $1^{2-}2Cs^+$ ($\lambda_{max} = 409$ nm) and only a small amount of monocesium salt according to the UV-visible spectrum. Thus, for cesium also pK_2 is lower than pK_1 . Only by adding a large excess of neutral hydrocarbon to push eq 1 to the left did the absorption peak of the monocesium salt at 370 nm become substantial. An absorption peak at 370 nm is common for cesium contact ion pairs of fluorenyl derivatives.⁶

Subtracting the spectrum of dicesium bifluorenyl from the equilibrium mixture gave the spectrum of $1-Cs^+$ ($\epsilon = 12\,500$). This deconvolution of spectra leads to $K = 91 \pm 12$ in eq 1 ($M = Cs$). Thus, pK_2 is lower than pK_1 by 1.96 ± 0.05 pK units. For comparison we prepared 9-methyl-9,9'-bifluorenyl whose cesium salt absorbs at 371 nm ($\epsilon = 13\,200$). This compound cannot form a dianion.

For the cesium scale pK_1 could not be determined directly but is estimated by comparison with the lithium scale⁶ to be about 21.0-21.5; accordingly, pK_2 is 19.0-19.5.

The remarkable difference in ΔpK ($pK_1 - pK_2$) of 0.4 pK units for the lithium scale compared to almost 2.0 pK units for the cesium scale is most probably due to a difference in the nature of the ion pairs involved. Monolithium bifluorenyl is a solvent separated ion pair (SSIP) with $\lambda_{max} = 378$ nm, as are the lithium salts generally of 9-substituted fluorenes.^{8,9} Monocesium bifluorenyl is a contact ion pair (CIP) absorbing as expected at shorter wavelength, 370 nm. On the other hand, the dilithium salt ($\lambda_{max} = 401$ nm) absorbs at shorter wavelength than the dicesium analogue ($\lambda_{max} = 409$ nm) indicative that at least one, and more probably both, lithiums in $1^{2-}2Li^+$ are CIP; that is, the stronger negative charge in the dianion competes more successfully with solvent for lithium cations(s).

(1) Carbon Acidity. 85.

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Note that in an earlier publication² pK_2 was reported to be higher than pK_1 by 0.1 pK units in the cesium cyclohexylamide (CsCHA)–cyclohexylamine (CHA) system. However, careful reexamination reveals that in CHA also pK_2 is lower than pK_1 by approximately 2 pK units. The present results are more accurate and derive from better instrumentation, but the explanation for the relatively low pK_2 values, based on electrostatic interactions within a triple ion, remains unchanged.

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Supplementary Material Available: Two figures with spectra of $1-M^+$, 1^2-2M^+ and equilibrium mixtures (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.