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First and Second Acidity Constants for Some Indenyl and Fluorenyl Hydrocarbons: Coulombic Effects in Ion Triplets[1]

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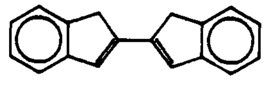
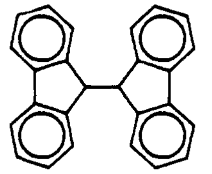
We recently reported that the first and second ion pair p*K*'s in the cesium cyclohexylamide (CsCHA)–cyclohexylamine (CHA) system for 9,10-dihydroanthracene differ by only 3.8 p*K* units.[2] We now report that for 2,2'-biindenyl (**1a**) and 9,9'-bifluorenyl (**2a**) the formation of the dicesium salts of the dicarbanions (**1c** and **2c**) is hardly more difficult than formation of the cesium salts of the monocarbanions (**1b** and **2b**). For comparison, the Δp*K* (pK^2 – pK^1) values are larger for 10,12-dihydroindeno[2,1-*b*]fluorene (**3a**) and 6,12-dihydroindeno[1,2-*b*]fluorene (**4a**). These results are rationalized by simple Coulombic considerations of ion triplet structures.



1



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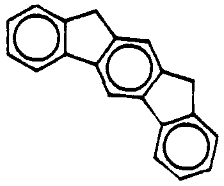

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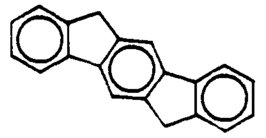

4

a = hydrocarbon
b = mono Cs salt
c = di Cs salt

The p*K* measurement technique[3] is based on a competitive equilibrium between a carbon acid (RH) and an indicator (InH) with their respective cesium salts; these salts exist primarily as contact ion pairs in CHA. The extension of the method to determination of second dissociation constants when the spectra of the mono- and dianion salts differ substantially (**3** and **4**) was summarized earlier.[2] Where the spectra overlap seriously, we use eq 1 and a least-squares technique. The derived first and second pK_{CsCHA} values are summarized in Table I.

$$A_{\lambda T} = \sum a_i A_{\lambda i} \qquad A_{\lambda i} = \epsilon_i C l \qquad (1)$$

The values of the first p*K*'s are unexceptional. The pK^1_{CsCHA} of **1** (19.81) is almost identical with that of indene (pK_{CsCHA} = 19.93). The pK^1_{CsCHA} of **2** (20.51) is substantially lower than that of fluorene (pK_{CsCHA} = 23.04) probably because of relief of steric strain in forming the carbanion; note that pK_{CsCHA} of 9-benzylfluorene is 1.77 p*K* units lower than that of fluorene.[4] The first p*K*'s of the indenofluorenes are slightly lower than for fluorene, as one might expect for phenyl-substituted fluorenes.

Table I. Absorbance (nm) and pK_{CsCHA} Values

	$\lambda_{\max}$ ($10^{-3}\epsilon$)			
RH	R^-Cs^+	$R^{2-}Cs_2^+$	pK^1_{CsCHA}	pK^2_{CsCHA}
1	345 (26.1)	372 (32.0)	19.81[a]	20.27[a]
		391 (29.9)		
2	408 (6.2)	413 (16.0)	20.51[b]	20.65[b]
3	331 (41.0)	343 (28.0)	22.26[a]	25.67[a]
	416 (20.0)	391 (36.0)		
	472 (2.2)	413 (95.0)		
	500 (2.8)	467 (7.5)		
	533 (1.8)	499 (5.0)		
4	370 (12.0)	355 (82.0)	22.24[a]	27.30[a]
	392 (22.0)	428 (16.0)		
	482 (0.8)			
	524 (1.0)			
	562 (0.8)			

[a] ±0.2. [b] ±0.3.

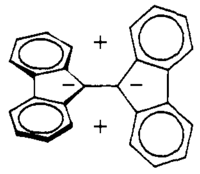

Figure 1. Ion triplet structure of dialkali cation salts of 9,9'-bifluorenyl (**2**).

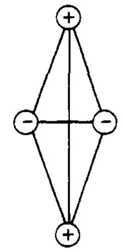

Figure 2. Coulomb interactions for a point charge model of a dication salt of a dicarbanion.

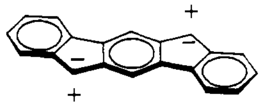

Figure 3. Ion triplet structure assumed for **4c**.

The pK^2_{CsCHA} values, however, are most unusual; Δp*K* is 0.5 for **1** and only 0.14 for **2**. The p*K*'s for **3** and **4** are greater, 3.4 and 5.1, respectively, and differ substantially from each other despite their similarity in structure.

The X-ray crystal structure of a dilithium salt of **2** has been reported;[5] in this structure the two fluorenyl ring planes are twisted with respect to each other, and solvated Li^+ groups are placed above and below the central C–C bond (Figure 1). A similar structure is plausible for the dicesium salt and for the dicesium salt of **1**. In these structures the centers of negative charge in the cyclopentadienyl moieties are close together and give rise to significant electron repulsion. Nevertheless, a simple Coulomb treatment shows that it is this very proximity of charges in an ion triplet that provides added stabilization.

Consider the collection of point charges shown in Figure 2. For such a system the following equation holds for the electrostatic energy, E_{el}:

$$E_{\mathrm{el}} = 1/R_{--} + 1/R_{++} - 4/R_{+-} \qquad (2)$$

where R_{+-} is the distance between positive and negative charges. It is readily shown that E_{el} is negative in the R_{--}/R_{++} range 0.145–6.92; that is, for chemically significant structures the attraction of each negative charge equally to the *two* positive charges

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[1] Carbon Acidity. 64. For paper 63 see: Streitwieser, A., Jr.; Juaristi, E. *J. Org. Chem.* **1982**, *47*, 768.

[2] Streitwieser, A., Jr.; Berke, C. M.; Robbers, K. *J. Am. Chem. Soc.* **1978**, *100*, 8271.

[3] Streitwieser, A., Jr.; Juaristi, E.; Nebenzahl, L. L. "Comprehensive Carbanion Chemistry"; Buncel, E., Durst, T., Eds.; Elsevier: New York, 1980; Chapter 7.

[4] Streitwieser, A., Jr.; Chang, C. J.; Reuben, D. M. E. *J. Am. Chem. Soc.* **1972**, *94*, 5730.

[5] Walczak, M.; Stucky, G. D. *J. Organomet. Chem.* **1975**, *97*, 313.

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compensates for the electron repulsion of even directly bonded carbanion centers. Thus, dicarbanions can be generated with surprising ease *when they are stabilized within an ion triplet of this type.*

In the ion triplets from the indenofluorenes one cesium cation is expected to be close to one 9-fluorenyl-type position, and the other cesium cation is expected to be on the opposite side of the molecular ring plane close to the other 9-fluorenyl-type position (Figure 3). In such a structure, each cation is close to one anion center *but relatively far from the other.* The electrostatic stabilization within the ion triplet is therefore reduced and the second p*K*'s are larger. The difference in pK^2_{CsCHA} between **3b** and **4b** is probably associated with their relationship to the *m*- and *p*-xylene dianions, respectively. In the meta system the carbanion electrons are placed in two nonbonded Hückel MO's; accordingly, *m*-xylene is dimetalated more readily than *p*-xylene.[6]

These principles based on Figure 1 should be applicable generally and undoubtedly rationalize the facile formation of many polylithiated organic compounds; that is, such compounds may be simply envisaged as ion multiplets.[7] Moreover, this view also explains the many examples where a second metalation occurs close to the first.[8]

Acknowledgment. We thank Dr. Bon-Su Lee for preliminary experiments. This research was supported in part by NSF Grants 79-10814 and 82-05696.

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[6] Klein, J.; Medlik, A.; Meyer, A. Y. *Tetrahedron* **1976**, *32*, 51.

[7] See: (a) Kost, D.; Klein, J.; Streitwieser, A., Jr.; Schriver, G. W. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 3922. (b) Schleyer, P. v. R.; Kos, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 448 and papers cited therein.

[8] Some especially pertinent examples are as follows: Shirley, D. A. *J. Org. Chem.* **1960**, *25*, 1189, 2238; **1962**, *27*, 4421. Shatzmiller, S.; Lidor, R., personal communication. See also ref 7b.

Kinetics, Thermodynamics, and Stereochemistry of the Allyl Sulfoxide–Sulfenate and Selenoxide–Selenenate [2,3] Sigmatropic Rearrangements

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The thermodynamic relationships between the II and IV oxidation states (eq 1, Y = S, Se) play a dominant role in determining

$$R_1-\overset{\overset{\displaystyle O}{\|}}{Y}-R_2 \rightleftharpoons R_1-Y-O-R_2 \qquad (1)$$

chemical behavior of sulfoxides, sulfinic, and sulfenic acids and esters, as well as their selenium analogues. It can be argued on the basis of bond strengths that the equilibrium of eq 1 should be more to the right for selenium than for sulfur, and this is supported by some experimental evidence.[2]

We report here the results of a study aimed at quantifying the equilibrium of eq 1, using the system shown in eq 2. Since for Y = Se only the selenenate isomer was detectable at equilibrium it was necessary to employ a kinetic technique (measurement of both k_{12}^{Se} and k_{21}^{Se} to determine the thermodynamic relationship between the isomers.

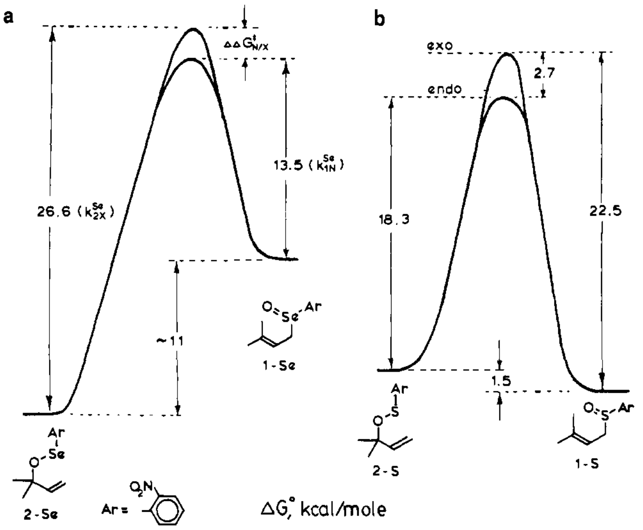
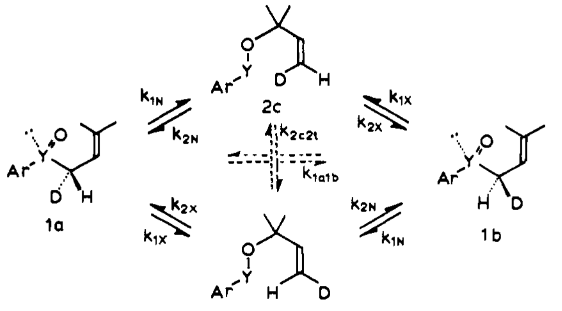
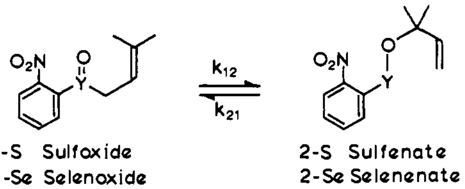


Figure 1. Free energy diagrams for the equilibration of (a) selenoxide **1**-Se and selenenate **2**-Se at −80 °C; (b) sulfoxide **1**-S and sulfenate **2**-S at −30 °C.

Scheme I

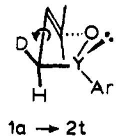


The rate constants k_{12}^{Se} could be directly measured. *o*-Nitrophenyl prenyl selenide was oxidized to the selenoxide **1**-Se (*m*-CPBA, −85 °C), which could be briefly observed at −80 °C by 270-MHz NMR, and the rate was measured ($t_{1/2} \approx$ 6 min, $k_{12}^{\mathrm{Se}} = 0.002\ \mathrm{s}^{-1}$) for its isomerization to **2**-Se.

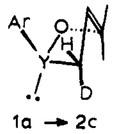


(2)

The rate constant for the reverse process was estimated from the cis–trans isomerization (k_{2c2t}^{Se}) measured between 51 and 80 °C of the deuterium-labeled selenenate **2c**-Se (Scheme I).[3]



1a → 2t
exo (X)



1a → 2c
endo (N)

Unfortunately this is not a direct measure of k_{21}^{Se}. To achieve cis–trans isomerization, **2c**-Se must proceed to **1**-Se by the exo transition state and return endo, or vice versa.[5] Simply proceeding to **1**-Se and returning via the lowest pathway[6] results in no de-

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[1] These results were taken in part from the Ph.D. Thesis of S. Wollowitz, University of Wisconsin–Madison, 1980.

[2] (a) Selenenate–selenoxide: Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 7154. Reich, H. J. *J. Org. Chem.* **1975**, *40*, 2570. Reich, H. J.; Shah, S. K.; Gold, P. M.; Olson, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 3112. Reich, H. J.; Wollowitz, S. *Ibid.* **1982**, *104*, 7051. (b) Sulfenate–sulfoxide: Tang, R.; Mislow, K. *Ibid.* **1970**, *92*, 2100. (c) Selenenic anhydride–selenolseleninate: Reich, H. J.; Hoeger, C. A.; Willis, W. W., Jr. *Ibid.* **1982**, *104*, 2936. Reich, H. J.; Willis, W. W., Jr.; Wollowitz, S. *Tetrahedron Lett.* **1982**, *23*, 3319. Kice, J. L.; McAfee, F.; Slebocka-Tilk, H. *Ibid.* **1982**, *23*, 3323.

[3] Prepared from *cis*-2-methyl-3-buten-2-ol-3,4-d_2 (from 2-methyl-3-butyn-2-ol reduction with $LiAlD_4$ followed by D_2O quench)[4a] and *o*-nitrobenzeneselenenyl chloride.[4b] The 3-deuterio substituent is omitted in Scheme I.

[4] (a) Borden, W. T. *J. Am. Chem. Soc.* **1970**, *92*, 4898. Corey, E. J.; Katzenellenbogen, J. A.; Posner, G. H. *Ibid.* **1967**, *89*, 4245. (b) Behaghel, O.; Seibert, H. *Chem. Ber.* **1933**, *66*, 708.

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