Ion-Pair Structures of Divalent Carbanion Salts

Sir:

The existence of contact and solvent-separated ion pairs in solutions of alkali carbanion and radical-ion salts has been well documented by both direct and indirect methods.[1,2] The fluorenyl salts in particular are of importance in this respect, since distinctly separate absorption maxima in the uv and visible spectrum are observed for the two kinds of ion pairs. Very little detailed information is available about the behavior and structure of divalent ion pairs and their interaction with coordinating agents. We wish, therefore, to report some interesting results of studies carried out with barium difluorenyl ($Ba^{2+},F_2{}^{2-}$).

The barium carbanion salt, prepared by stirring fluorene in THF on a barium mirror, shows a typical contact-ion-pair spectrum in THF with an absorption maximum of 347 mμ (Figure 1). Even at −70° in THF, the fraction of contact ion pairs is still 0.8, whereas the sodium salt under these conditions is of the solvent-separated kind. Generally one observes that formation of solvent-separated ion pairs in $Ba^{2+},F_2{}^{2-}$ is considerably more difficult than for F^-,Li^+ or F^-,Na^+. For example, while F^-,Na^+ is essentially a solvent-separated ion pair in 1,2-dimethoxyethane at 25°, the barium salt is a contact ion pair. This behavior is not unreasonable if one assumes a sandwich-type structure for the $Ba^{2+},F_2{}^{2-}$ ion pair, which would hinder solvation of the shielded Ba^{2+} ion. Such a structure is likely in view of nmr data of fluorenyl alkali salts[3] showing the alkali ion to reside above the π cloud of the fluorenyl ring.

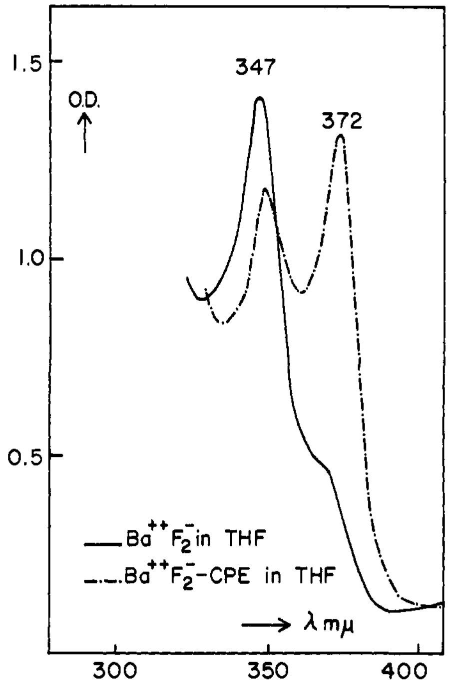

Figure 1. Ultraviolet absorption spectrum for barium difluorenyl in THF at 25° (- - - -) and of its complex with dimethyldibenzo-18-crown-6 (1:1 molar ratio or excess cyclic ether, –·–·–·).

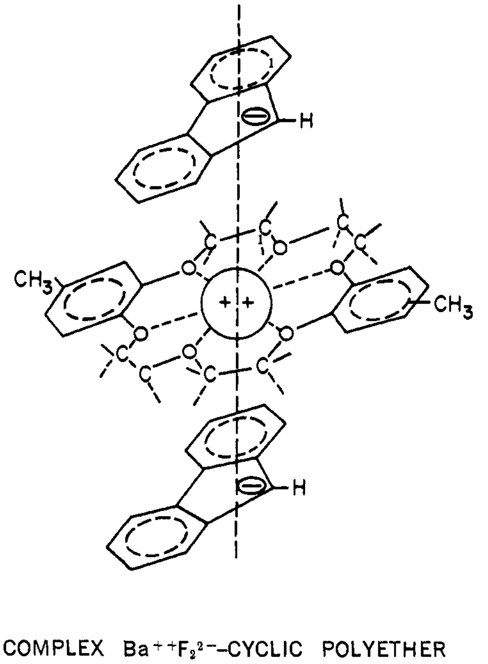

Figure 2. Suggested structure for the 1:1 complex of barium difluorenyl and dimethyldibenzo-18-crown-6 in THF or pyridine.

In agreement with this structure, conductance measurements show that the K_d for the equilibrium $Ba^{2+},F_2{}^{2-} \rightleftarrows [Ba,F]^+ + F^-$ is only $3 \times 10^{-9}\ M^{-1}$ in THF at 25°, as compared to $6 \times 10^{-7}\ M^{-1}$ for F^-,Na^+. Besides a possible difference in the tightness of the two ion pairs, it should be realized that the latter salt yields fully solvated Na^+ ions on dissociation, while the barium salt gives only tight Ba^{2+},F^- ion pairs where solvation can only be on the peripherie of the Ba^{2+} ion.

We recently found that 1:1 complexes of F^-,Na^+ and cyclic polyethers show an absorption spectrum in THF identical with that of a fluorenyl solvent-separated ion pair, *i.e.*, λ_{max} 372 mμ.[4] When equimolar quantities of dimethyldibenzo-18-crown-6 (I) (for the structure see Figure 2) and $Ba^{2+},F_2{}^{2-}$ are mixed in THF, the absorption spectrum reveals approximately equal fractions of contact and separated ion pairs, with respective maxima of 349 and 372 mμ. Even a five times excess of I will not change the spectrum. This interesting observation suggests a structure for the $Ba^{2+},F_2{}^{2-}$–I complex in which the cyclic polyether, with the Ba^{2+} in the hole of the polyether ring, is sandwiched in between the two fluorenyl rings. The spectrum indicates that the solvation is asymmetric, although it is very likely that the Ba^{2+} ion rapidly moves up and down through the hole of the polyether ring, possibly changing the ring conformation when moving. The result is that at any time one fluorenyl ring is close to the Ba^{2+} (a tight ion pair), while the other one is separated from the Ba^{2+} by the cyclic polyether.

When the 60-Mc nmr spectrum of the $Ba^{2+},F_2{}^{-2}$–I complex is taken in pyridine (the solubility is too low in THF) the outer and inner aliphatic polyether ring protons have shifted upfield by 30 and 70 cps, respectively, and the CH_3 protons downfield by 17 cps. For the complex of F^-,Na^+ and I in pyridine the shifts are

---

[1] T. E. Hogen Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307, 318 (1966); L. L. Chan and J. Smid, *ibid.*, **89**, 4547 (1967); **90**, 4654 (1968).

[2] N. Hirota, R. Carraway, and W. Schook, *ibid.*, **90**, 3611 (1968); R. V. Slates and M. Szwarc, *ibid.*, **89**, 6043 (1967).

[3] J. A. Dixon, P. A. Gwinner, and D. C. Lini, *ibid.*, **87**, 1379 (1965).

[4] K. H. Wong, G. Konizer, and J. Smid, submitted for publication.

only 20 and 44 cps upfield for the aliphatic ring protons and 4 cps downfield for the $\mathrm{CH_3}$ protons.[4] In the $\mathrm{Ba^{2+},F_2^{2-}}$ complex, the diamagnetic anisotropy at the aliphatic ring protons is enhanced due to the presence of the second fluorenyl ring (see Figure 2).

The exchange rate of complexed I with noncomplexed I is much slower for $\mathrm{Ba^{2+}F_2^{2-}}$ than for $\mathrm{F^-,Na^+}$. At 60°, which represents the approximate coalescence temperature for the $\mathrm{CH_3}$ peaks of the complexed and noncomplexed cyclic polyether at 0.1 M concentrations in pyridine, the rate constant for the reaction $\mathrm{Ba^{2+},F_2^{2-}{-}I + I^* \rightarrow Ba^{2+}F_2^{2-}{-}I^* + I}$ is in the order of 500 M^{-1} sec^{-1}. For $\mathrm{F^-,Na^+}$ this rate constant in THF[4] is close to 10^5 M^{-1} sec^{-1} and even higher in pyridine. The exchange reaction with the $\mathrm{Ba^{2+}F_2^{2-}}$ complex is probably sterically hindered, but the $\mathrm{Ba^{2+}}$ ion is also more tightly bound to the cyclic polyether. Spectral studies show that in an equimolar mixture of $\mathrm{Ba^{2+}F_2^{2-}}$, $\mathrm{F^-,Na^+}$, and I in THF the cyclic polyether is complexed exclusively to $\mathrm{Ba^{2+},F_2^{2-}}$.

When small quantities of triglyme or pentaglyme are added to a solution of $\mathrm{Ba^{2+},F_2^{2-}}$ in THF, one finds again approximately equal fractions of contact and separated ion pairs, and the same spectrum persists even in the pure glymes. Only when sufficient amounts of coordinating agents like ethylenediamine or hexamethylphosphoramide are added to the THF or dioxane solution of the salt can one observe complete solvent separation, although indications are that the separation occurs in two steps.

Finally, studies of proton abstraction reactions between $\mathrm{Ba^{2+}F_2^{2-}}$ and 3,4-benzofluorene confirm one of our earlier findings,[5] *viz.*, the low reactivity of the free fluorenyl ion as compared to the $\mathrm{F^-,Na^+}$ ion pair. The reaction with $\mathrm{Ba^{2+}F_2^{2-}}$ shows a square-root dependence on $[\mathrm{Ba^{2+}F_2^{2-}}]$, indicating that either $\mathrm{F^-}$ or $\mathrm{Ba^{2+},F^-}$ is the reactive species. The free ion rate constant is approximately 75 M^{-1} sec^{-1}, that for the $\mathrm{Ba^{2+},F_2^{2-}}$ ion pair less than 0.1 M^{-1} sec^{-1}. The high rate constant for $\mathrm{F^-,Na^+}$ ion pair (>3000 M^{-1} sec^{-1}, see ref 5) was interpreted as indicative of the catalyzing role of the $\mathrm{Na^+}$ ion. This, of course, is not possible for the $\mathrm{Ba^{2+},F_2^{2-}}$ ion pair where the $\mathrm{Ba^{2+}}$ is shielded by the two fluorenyl moieties.

Acknowledgment. The support of this research through a grant from the National Institutes of Health (Grant No. GM-15965) and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

(5) T. E. Hogen Esch and J. Smid, *J. Am. Chem. Soc.*, **89**, 2764 (1967).

T. E. Hogen Esch, J. Smid
Chemistry Department, State University of New York
College of Forestry, Syracuse, New York 13210
Received May 14, 1969

Deuterium as an Aromatic Substituent. Fluorine Chemical Shifts in the Monodeuteriofluorobenzenes

Sir:

Secondary deuterium isotope effects have been the subject of numerous studies in recent years.[1] However, relatively little quantitative data are available concerning the replacement of a specific protium, *viz.*, *ortho*, *meta*, or *para*, with deuterium.[2] Although these previous results have indicated that deuterium behaves as an electron donor, a consistent mechanistic explanation, which can account for the magnitudes of the effects, has not been forthcoming.[2a] We have therefore begun an investigation designed to elucidate the responsible interactions.

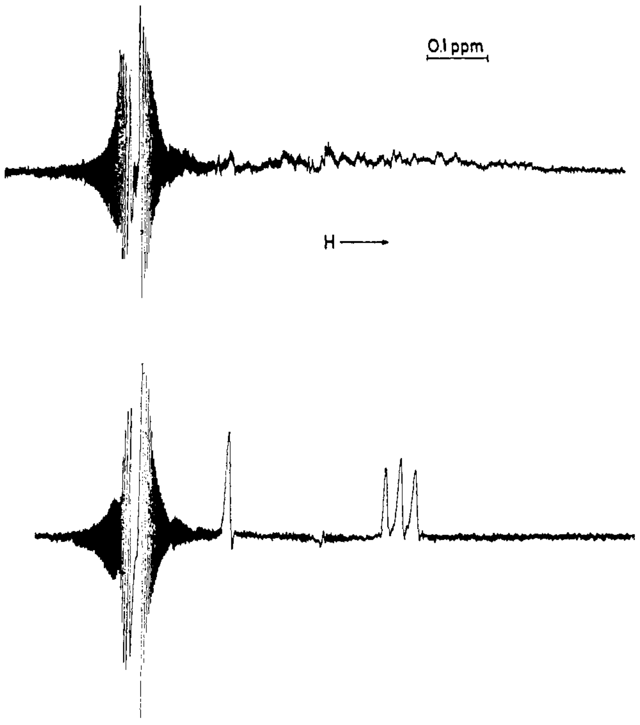

Figure 1. ^{19}F nmr spectrum of fluorobenzene-d_0 and fluorobenzene-2-d in methanol-O-d without, and with, proton decoupling. A higher spectrometer gain was used in the upper (undecoupled) trace.

Taft and coworkers[3] have elegantly shown that the ^{19}F chemical shifts in numerous fluorobenzenes are sensitive measures of substituent interactions. Using the method of Taft we have determined the ^{19}F chemical shifts of the three monodeuteriofluorobenzenes relative to fluorobenzene-d_0.[4] Our results bear on the nature of the deuterium interaction and indicate the potential contribution of direct nonbonded interactions to secondary isotope effects in aromatic systems.

Fluorobenzene-3-d and fluorobenzene-4-d were prepared according to Streitwieser and Mares.[5] Fluorobenzene-2-d was synthesized according to Bak.[6] The nmr samples contained 3–5% (volume) total fluorobenzene (composed of a 3:1 mixture of fluorobenzene-d_1–fluorobenzene-d_0) and 2% 1,1,2,2-tetrachlorotetrafluorocyclobutane (TCTFCB) as an internal lock and reference. The samples were degassed and sealed. The solvents employed were cyclohexane, methanol-

---

(1) For a review, see E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

(2) (a) A. Streitwieser, Jr., and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **89**, 3767 (1967); (b) N. N. Lichtin, *Progr. Phys. Org. Chem.*, **1**, 75 (1963); (c) A. Streitwieser, Jr., and H. S. Klein, *J. Am. Chem. Soc.*, **86**, 5170 (1964).

(3) R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709, 3146 (1963), and references therein.

(4) ^{19}F chemical shifts have been used to probe isotope effects of $\mathrm{CD_3}$ *vs.* $\mathrm{CH_3}$. See D. D. Traficante and G. E. Maciel, *ibid.*, **87**, 4917 (1965).

(5) A. Streitwieser, Jr., and F. Mares, *ibid.*, **90**, 644 (1968).

(6) B. Bak, *J. Org. Chem.*, **21**, 797 (1956).