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ORGANIC SALTS AS POWERFUL LANTHANIDE SHIFT DONORS

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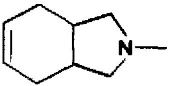
Abstract: The interaction of $Eu(fod)_3$ with organic salts is studied.

Several years ago, one of us expressed the opinion that the chemical shifts observed during the lanthanide shift reagent (LSR) experiment with 1a and 1b might be due to the lanthanide binding to the counter ion.[1] Seeman expanded on this with his report that larger induced shifts were found with quaternary ammonium salts than with free amine.[2] Here we report that the lanthanide induced shifts (LIS) of proton resonances for the sulfide 1c are *smaller* than those for the sulfonium salt 1d.[3] The magnitude of the LIS follow the order 1<2<3<4<6<5 for the sulfide and 1<2<3<4<5<6<7 for the sulfonium salt, indicating a binding site at or around sulfur in both cases. Calculating the induced shifts with PDIGM[4] resulted in a well defined position for the europium in 1c but not for 1d. Both Eu---1c and Eu---1d must be well structured complexes in order to get the straight line plots we observed yet the PDIGM caluclations of 1d do not confirm this.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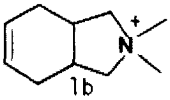

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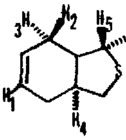
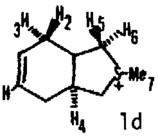


1c



1d

These observations prompt us to report our studies of $Eu(fod)_3$ induced shifts of several ammonium and phosphonium salts. The series we originally intended to study were the tetraethyl ammonium and phosphonium halides in order to quantitatively assess binding constants as a function of anion and cation. Unfortunately, the ammonium iodide is not soluble in solvents suitable for the LIS study, and, whereas the ammonium chloride is soluble as a monohydrate, it is essentially insoluble when anhydrous. Using the second method of Armitage *et. al.*[5] we summarize our results in Table I.

Table I - LIS Results for Organic Salts

	Chloride		Bromide		Iodide	
Ammonium	--------		55.3	56.8	------	K
	--------		41.1 ± 2.5	66.7 ± 3.5	------	ΔB
Phosphonium	>100.0	>100.0	34.8	27.3	No Shift	K
	29.8 ± 0.6	56.5 ± 3.4	41.3 ± 3.9	75.3 ± 2.1	No Shift	ΔB
	$-CH_3$	$-CH_2-$	$-CH_3$	$-CH_2-$		

The magnitude of the induced shifts follow the order Cl>Br>I; i.e., as the sum of the van der Waals radii increase, the r^{-3} distance dependent shift becomes apparent. Since the size of an ammonium center is smaller than a phosphonium center, we anticipate and find a larger induced shift for the ammonium bromide than for the phosphonium bromide.[6]

Several concluding remarks are in order. First, we point out that the counterions of organic salts are extraordinarily good binding sites. In a recent publication, Belaban[9] suggested the LSR was binding to the pi electrons of pyridinium and pyrillium salts. It appears to us that the possibility of an electron deficient pi system acting as a binding site is unlikely.[10] Binding to the counterion was not considered and the conclusions of that paper should be reevaluated.

Finally, Seeman's[2] suggestion of using organic counterions to evaluate ion-ion phenomena in nonpolar media may prove fruitless. If the distance between cation and solvated anion is large, the r^{-3} effect may become critical and the LIS will be small. This would result in statistically meaningless data.

References and Notes:

1. K. B. Lipkowitz, Ph.D. Thesis, Montana State University.
2. J. I. Seeman and R. L. Bassfield, J. Org. Chem., 42, 2337 (1977).
3. Proton assignments for H-5 and H-6 of 1c are based on the larger coupling constants ($J_{4,5}$ = 6.1 cps; $J_{4,6}$ = 5.9 cps) expected for the trans relationship. For 1e, a similar trend is observed ($J_{4,5}$ = 5.5 cps; $J_{4,6}$ = 5.0 cps). The assignments for H-2 and H-3 were based on similar argument ($J_{2,4}$ = 6.0 cps; $J_{3,4}$ = 5.5 cps).
4. M. R. Willcott III, R. E. Lenkinski and R. E. Davis, J. Am. Chem. Soc., 94, 1742 (1972).
5. I. Armitage, G. Dunsmore, L. D. Hall and A. G. Marshall, Can. J. Chem., 50, 2119 (1972). The concentration was varied by a factor of ten. Straight line plots are obtained when a 1:1 ratio of shift reagent:substrate predominate in solution.
6. The observation that the bound chemical shifts, ΔB, for the methylene (quartet) hydrogens are larger than for the methyl (triplet) hydrogens in all cases was unexpected. Two explanations are possible. First, there may be a preferred conformation in which the methyls swing aside allowing the counterion to approach the positively charged nucleus. This would position the methylene hydrogens closer than the methyl hydrogens to shift reagent. Dreiding molecular models are somewhat ambiguous in this regard.

   Alternatively, the fact that "...protons, because of their electron density are particularly susceptible to diamagnetic and paramagnetic effects..."[7] prompts us to suggest that the methylene hydrogens, because they are quite electron deficient, are *more susceptible* to the paramagnetic shift reagent than are the methyl hydrogens. Theoretical expressions used to calculate induced chemical shifts presently have no terms which specifically include the excess charge of the nucleus under consideration.[8] In neutral species, the charge difference between hydrogens are not expected to vary significantly and such a term is unnecessary. However, in organic salts, the alpha hydrogens have significantly higher charge density and should behave quite differently.
7. F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, 1969, p. 58.
8. A. F. Cockerill, G. L. O. Davies, R. C. Harden and D. M. Rackham, Chemical Reviews, 73 (6), 553 (1973).
9. A. T. Balaban, Tetrahedron Lett., 50, 5055 (1978).
10. This conclusion has already been expressed. R. E. Graves and P. I. Rose, J. C. S. Chem. Comm., 631 (1973).

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