

height. With hypothetical isotopic labeling, one could characterize this six-center exchange reaction as



where the three product molecules are distinct from the three reactants. The predicted classical barrier height for reaction 3 is 31.1 kcal at the DZ SCF level and 29.5 kcal at the DZ+P SCF level of theory. These barriers are much lower than the 69 kcal predicted for the analogous six-center exchange reaction for three hydrogen molecules.⁴⁴

Concluding Remarks

At four distinct levels of theory, the vibrational frequency shifts in (HF)₂ and (HF)₃ relative to the monomer have been predicted. For three of the four levels of theory, good agreement with the recent dimer experimental results of Pine and Lafferty¹ is found.

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It is hoped that subsequent experiments will confirm the trimer predictions presented here. The theoretical methods used to study the trimer may be readily applied to larger polymeric systems, such as (HF)₄ and (HF)₅. This and related studies on species such as the HCl dimer⁴⁵ show the widening applicability of quantum mechanics to hydrogen bonding.

Acknowledgment. We thank Professor Yuan T. Lee and his collaborators³ for instigating the present research and Professor Herbert L. Strauss for helpful discussions. This research was supported by the Director, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The Berkeley minicomputer for theoretical chemistry is supported and maintained by the National Science Foundation, Grant CHE-8218785.

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Hydrogen Out-of-Plane Bending in Cyclopentadienyllithium

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Abstract: An ab initio SCF MO study is presented of the out-of-plane bending of hydrogens in cyclopentadienyllithium. The effects of basis sets of varying size and possible superposition errors were evaluated. The hydrogens are found to bend away from the lithium cation to a significant degree. Comparable bending is given by an ionic model consisting of a cyclopentadienyl anion and a point positive charge at the lithium location. We attribute the hydrogen bending to a simple Coulombic effect: such bending puts more negative charge on the face of the ring toward the lithium cation. No covalency is implicated in this effect. A reasonable balance between the carbon and lithium bases is obtained by placing a diffuse sp shell on carbon.

There have been many observations of hydrogen bending in cyclopentadienyl (Cp) metal complexes (where the hydrogens bend out of the plane of the Cp ring maintaining the C_{5v} symmetry). Electron diffraction (gas phase) studies have found that the hydrogens bend out of the Cp plane toward the metal 4.6 ± 0.9° in Cp₂Fe,¹ 5° in Cp₂Ni,² 6.5° in Cp₂Mn,³ and 2.9° in Cp₂Cr. X-ray studies show that the hydrogens bend out of the Cp plane away from the metal in CpIn by 4.5 ± 2°⁵ and that the methyl groups of Me₃C₅Sn⁺ bend 4° away from the metal.⁶ Ab initio calculations on CpSi⁺,⁷ CpC⁺,⁷ and CpBeH⁸ show the hydrogens bend in toward the complexed atom by 1.4°, 8.6°, and 0.8°, respectively. Other calculations on CpLi⁹ (DZ basis set) found that the hydrogens bend away from the lithium by 3.6°. Two

major explanations for this bending have been forwarded. Schleyer has supported a "covalency" argument where the p-orbitals of the metal parallel to the Cp ring can interact favorably with the carbon p-orbitals of the Cp ring perpendicular to the Cp plane.⁸⁻¹¹ Bending of the hydrogens causes the carbon p-orbitals to point in the opposite direction. The direction of the bending therefore depends on the relative size of the metal p-orbitals: metals with more diffuse p-orbitals cause the hydrogens to bend away from the metal (see Figure 1).

Alternatively, in systems best described as ion pairs, purely Coulombic forces could lead to bending in the opposite direction.^{8,9} A positively charged metal center will electrostatically favor greater electron density on the face of the Cp ring adjacent to the metal. This is effectively achieved by bending the hydrogens away from the metal, essentially rehybridizing the carbons such that the carbon p-lobe on the side of the metal is increased.

The following study shows that only the latter explanation is consistent with the bending away from the metal in CpLi. Potential calculational problems which can lead to hydrogen bending are also discussed.

Method

Calculations were carried out by using the following programs: a modified version of HONDO¹² and GAMESS on the Lawrence Berkeley

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Table I. Calculated Hydrogen Out-of-Plane Bending Angles for Cp Systems

species ^a	basis set	bending angle, deg	stabilization energy, ^b kcal/mol	force const., kcal/deg ²	total energy, kcal/mol
Cp ⁻	3-21G	0.00	0.00	0.040	-119 920.99
LiCp	STO-3G	6.8			
	DZ ⁹	3.56	0.42		-125 280.74
	3-21G	2.76	0.39	0.051	-124 072.01
	4-31G+	2.52	0.34	0.053	-125 137.71
	4-31G**	1.91	0.18	0.050	-125 194.94
(Li)Cp ⁻	3-21G	2.55	0.25	0.039	-119 931.98
	4-31G**	2.28	0.20	0.038	-120 482.73
	4-31G+	0.23	0.002	0.040	-120 433.19
LiCp(Li)	3-21G	2.35	0.28	0.051	-124 077.51
(+)Cp ⁻	3-21G	1.72	0.15	0.015	-120 101.41
LiCp(+)	3-21G	0.25	0.004	0.060	-124 143.13
(+)Cp ⁻ (Li)	3-21G	1.49	0.11	0.050	-120 109.82

^a(Li) is defined as the lithium ghost orbitals. (+) is a unitary point positive charge. The hydrogens bend away from the element written on the left of the Cp. ^bEnergy of the bent form (of lowest energy) minus the energy of the planar form.

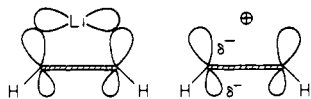


Figure 1.

Laboratory CDC 7600 computer and a modified version of GAUSSIAN-80¹⁶ on the UCB IBM-4341 computer. The bending angle was determined by minimizing the energy at several single point geometries using quadratic interpolation. The symmetry was constrained to be C_{5v} with fixed C-C, C-H, and ring-to-lithium (or lithium model) distances of 1.422, 1.070, and 1.820 Å, respectively. The calculations employed Pople's 3-21G¹³ and 4-31G¹⁴ basis sets.

Results and Discussion

Before determining the origin of the hydrogen out-of-plane bending in CpLi, it is necessary to determine the basis set dependence of such an effect. As can be seen in Table I, there is some dependence of bending on basis set, but even at the relatively large 4-31G** basis set level (d-orbitals on carbon, p-orbitals on hydrogens), the calculations show a bending of the hydrogens away from the lithium by 1.9°. Structures with this basis set are generally rather reliable; thus, such bending is most probably a real phenomenon that should be observable experimentally. Nevertheless, the bending is so slight that one must consider the possibility that even at the 4-31G** level the basis set may not be "large enough". In particular, one must consider a possible basis set superposition error,¹⁵ a calculational pitfall often ignored. In the present case, the lithium basis functions overdescribe the electrons in the vicinity of the lithium nucleus. These basis functions can be used to describe the carbon electrons. Bending of the hydrogens away from lithium puts greater electron density on the lithium face where they can better utilize the diffuse lithium functions. This possible effect was evaluated by using the "counterpoise" method of Boys and Bernardi.^{15d} When lithium "ghost" orbitals (lithium basis functions without a nuclear charge)

are used in place of lithium in CpLi, the hydrogens bend 2.55° and 2.28° away from the lithium with the 3-21G and 4-31G** basis sets, respectively. This shows that even at the 4-31G** level, the carbons are basis set deficient. A better description of the carbon electrons is obtained by using the 4-31G basis set with a diffuse sp shell on the carbons (exponent of 0.08). In this case (Cp⁻ plus lithium basis functions) bending of only 0.23° away from the lithium basis functions is observed, while the hydrogens bend away from lithium 2.52° at the same basis set level for CpLi. The diffuse orbitals accommodate carbon's extra electrons, minimizing the need to use the lithium basis functions to describe the carbon electrons. The Schleyer group has recently shown^{17,18} how the addition of a diffuse sp shell provides an effective description of carbanions even with a relatively small basis set. They also showed that the lithium outer sp shell plays little role in determining the geometry of allyllithium.¹⁹ This result is consistent with such orbitals not being involved in covalent bonds. A recent study of ethynyllithium²⁰ has shown that diffuse orbitals can play an effective role in calculations of organolithium compounds. This study also showed that orbital superposition is an important factor that must be considered generally in computations of organolithium compounds. The present study has also shown the value of diffuse functions in the computation of organolithium compounds. That the orbital superposition error is not the major cause of hydrogen bending even at the 3-21G level is shown by a calculation of the bending angle of CpLi with an additional set of lithium basis functions centered opposite the lithium atom. In this case the hydrogens bend away from the lithium atom by almost the same amount as they do without the ghost orbitals (2.35° vs. 2.76°).

To see if a purely ionic model predicts the proper bending, the hydrogen bending angle was calculated for Cp⁻ with a unitary point charge in the lithium position of CpLi. The hydrogens bend away from the positive charge by 1.7° (3-21G level), a value comparable to that found for a lithium cation. Moreover, a calculation of CpLi with a point positive charge symmetrically disposed from the lithium on the opposite side of the Cp ring shows only 0.3° bending of the hydrogens away from the lithium in a very shallow energy well; the optimal bent form is only 0.004 kcal/mol more stable than the planar form. This result shows that a basis set superposition effect at the 3-21G level is less important than the Coulombic effect of the positive charge. This conclusion is affirmed by calculations of the hydrogen bending angle for Cp⁻ with a point positive charge on one side and a set of lithium ghost orbitals on the other. In this case, the bending is 1.5° away from the positive charge.

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In sum, a positive charge uniformly causes a bending away of ring hydrogens while lithium orbitals cause only a minor perturbation. Only for Cp^- itself without added positive charge do lithium basis functions provide a significant superposition effect.

Conclusion

This study shows that in monomeric CpLi the ring hydrogens are bent away from the lithium to a significant extent and that this bending is essentially a simple Coulombic effect of the cation. The results imply that CpLi can be considered as an ion pair with negligible C-Li covalent interaction. The present results do not preclude the possibility that in some cases ring hydrogens bend away from a metal with diffuse orbitals in order to increase covalent interactions, but they do require some degree of covalency in those cases where the bending is toward the metal. Since the bending in CpIn is away from the metal,⁵ the argument for covalency in this compound must rely on other factors. We note

that the isoelectronic CpTl has been claimed to be ionic based on NMR studies.^{21,22} Finally, this study emphasizes the importance of superposition errors when molecular geometries are calculated and shows that the carbon basis set can be effectively balanced against that of lithium by including a diffuse sp shell on the former.

Acknowledgment. This research was supported in part by Grant No. GM-30369 of the National Institutes of Health, USPH. The VAX 11-750 used in this research was purchased in part with NSF Equipment Grant CHE-82-14313.

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Steric Effects on Rates of Dehalogenation of Anion Radicals Derived from Substituted Nitrobenzyl Halides

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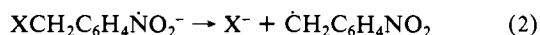
Abstract: One-electron reduction of nitrobenzyl halides produces the anion radicals, which subsequently undergo dehalogenation to form nitrobenzyl radicals. The rate constants for these processes have been studied by pulse radiolysis in aqueous alcoholic solutions. α -Substitution with a methyl group increases the rate of dehalogenation by weakening the C-X bond. On the other hand, substitution with a *tert*-butyl group was found to decrease the rate of dehalogenation considerably. Since the *tert*-butyl is not expected to increase the C-X bond dissociation energy, it is concluded that its effect is a result of steric interaction, which rotates the C-X bond toward the ring plane and thus decreases the overlap between this bond and the ring π system and slows down the transfer of the electron. Other related compounds have also been examined.

Recent results on the $\text{S}_{\text{RN}}1$ reactions¹ of sterically hindered *p*-nitrobenzyl substrates have revealed that not only is the regiochemistry² and stereochemistry³ of this reaction subject to steric effects (namely, branching at the position α to the benzylic carbon), but also reaction rates are greatly reduced in sterically hindered benzylic substrates.² In order to identify the factors that might be causing this rate reduction, the rate of dissociation of anion radicals involved in these and other, as yet unreported, $\text{S}_{\text{RN}}1$ processes were examined.

One-electron reduction of nitrobenzyl halides^{4,5} has been shown to produce initially the anion radicals



which subsequently dehalogenate.



The rate of reaction 2 was found to be controlled to a large extent by the C-X bond dissociation energy. This was deduced from the findings that k_2 increases in the order $\text{X} = \text{F} < \text{Cl} < \text{Br} < \text{I}$ and also increases with additional substitution on the benzylic position.^{4,5} In the present work we examine the effect of substitution with a *tert*-butyl group and the possibility of a steric effect on the rate of reaction 2. We find a substantial decrease in k_2 ,

which is ascribed to a steric effect causing rotation of the C-X bond toward the ring plane.

Method

The pulse radiolysis technique was utilized for monitoring the spectra of the anion radicals produced by reaction 1 and the benzyl radicals formed by the subsequent reaction 2 and for the determination of k_1 and k_2 . The experiments were carried out in deoxygenated (or N_2O saturated) aqueous solutions containing 10–20% *i*-PrOH or *t*-BuOH. Further details on the system and on the experimental conditions are as given previously.^{4,5}

Results and Discussion

α -*tert*-Butyl-*p*-nitrobenzyl Chloride (1). Several solutions containing between 3.8×10^{-5} and 2.3×10^{-4} M of this compound at pH 7 were pulse irradiated, and the rate of reduction by the radical from *i*-PrOH was followed at 310 nm. The second-order rate constant (for $\text{X} = \text{Cl}$, $\text{R} = t\text{-Bu}$) was found to be $k_3 = (1.0 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The transient spectrum monitored after

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