Dimers of Lithium Fluoride and Sodium Hydride

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Abstract: *Ab initio* molecular orbital calculations have been carried out on linear and cyclic dimers of LiF and NaH; in both cases, the cyclic geometry is lowest in energy. The agreement between the experimental and calculated ΔE(dimerization) (58.9 *vs.* 62.8 kcal/mol) for LiF is very good and gives important empirical support to the adequacy of accurate SCF calculation in predicting dimerization energies. We predict a smaller dimerization energy for NaH than LiH and expect that the NaH dimer will be more difficult to observe experimentally than $(LiH)_2$.

In the gas phase and inert matters, alkali halides form stable, cyclic (D_{2h} symmetry) dimers.[2] In a recent paper, the existence of D_{2h} cyclic dimers of LiH has been predicted.[3] In this study we address ourselves to the following questions. (1) What are the structural parameters of the LiF dimer? (2) How does the energy of dimerization of NaH (and by extrapolation Ks, Rb, Cs hydrides) compare with that of LiH? (3) How well can an accurate SCF calculation (which does not include any of the dispersion terms in the intermolecular potential) predict the experimental dimerization energy of LiF, where the experimental ΔE(dimerization) is well established?

Method of Calculation

All calculations were of the *ab initio*, LCAO–MO–SCF type described by Roothaan.[4] The basis set on lithium consisted of the 9s and 3p Gaussians contracted[4a] to (4s, 2p) from ref 3; on hydrogen, (5s, 2p) → (2s, 1p) from ref 3; the fluorine basis was the (9s, 5p, 2d) → (4s, 2p, 1d) used by Bender, *et al.*;[5] and the sodium basis 11s and 7p Gaussians contracted to (6s, 4p).[6] First a search of the potential surface for the monomers LiF and NaH was carried out, to find the minimum energy geometry. Then a complete search of the D_{2h} surface for $(LiF)_2$ and $(NaH)_2$ and a more limited search (keeping the monomer distances fixed) of the linear surface for the two dimers was done. Finally, the potential surface for the C_{2v} form of the LiH dimer proposed by Tyndall and Companion[7] was studied.

Results and Discussion

Table I summarizes the calculations on the LiH, NaH, and LiF monomers. As is typical for near-Hartree–Fock calculations, the bond distances for the monomer are predicted in very good agreement with experiment giving us confidence in the dimer potential surfaces. Since there is no experimental evidence for either $(NaH)_2$ or $(LiH)_2$, a comparison of predicted properties for the linear ($C_{\infty v}$) and cyclic (D_{2h}) dimers of each is in order and this is presented in Table II. It appears from the relative dimerization energies that the LiH dimer would be easier to observe experimentally. Structurally, the two cyclic dimers are very similar, with the metal–metal distance between 0.55 and 0.70 au shorter than the H–H distance, due to the fact that the highest occupied and most strongly bonding orbital (b_{2u}) has a node between the hydrogens, but none between the metal atoms. Extrapolating from our $(LiH)_2$ and $(NaH)_2$ results, we would expect heavier alkali metal hydride dimers to be successively more weakly bound relative to the monomers; this appears to be the case for alkali fluorides,[8] but not alkali chlorides.[9] There is no *a priori* reason why there should be a monotonic decrease in dimerization energies; as one goes down the periodic table, the ionic bonding in the dimer is weaker because of the increased M–X (or M–H) distance, but the monomer bond strength also decreases. These two opposing effects preclude a monotonic trend in dimerization energies *if* they are of the same magnitude energetically.

After we had published our studies on $(LiH)_2$ dimer, we learned of previous theoretical work on this species using semiempirical and empirical methods. Tyndall and Companion, using the diatomics in molecules (DIM) method,[7] predicted a dimerization energy of the D_{2h} dimer of LiH of 28.4 kcal/mol and found a C_{2v} structure of the Li_2H_2 system (with unperturbed diatomics Li_2 and H_2 (bond along the y axis) approaching each other along the z axis) to be the global energy minimum (41.3 kcal/mol lower than 2 LiH). In the D_{2h} dimer, they found r(Li–Li) > r(H–H) in contrast to our studies.[3] In a subsequent paper,[10] they compared their (DIM) results on the D_{2h} dimer of $(LiH)_2$ with those predicted with the Rittner ionic model (RIM), which had previously been applied to alkali halide dimers with some success.[9] The dimerization energy predicted by the ionic model is comparable with that

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(4a) Note Added in Proof. There is an error in ref 3; the coefficients of the 2 component p orbital on Li should be reversed from those given in Table I of ref 3.

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Table I. Monomer Properties

Molecule	E_t, au	r_e, Å[a]	μ,[b] D	(M)[f]	(X)[g]
NaH	−162.33171	1.92 (1.89)	7.13 (6.96)[c]	10.524	1.476
LiH	−7.98262	1.633 (1.595)	5.48 (5.88)[d]	2.662	1.338
LiF	−106.96694	1.56 (1.51)	6.42 (6.28)[e]	2.213	9.787

[a] Experimental value in parentheses from G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J., 1955. [b] Experimental value in parentheses. [c] P. E. Cade, R. F. W. Bader, W. H. Henneker, and I. Keaveny, *J. Chem. Phys.*, **50,** 5313 (1969), near-Hartree–Fock calculation. [d] L. Wharton, L. P. Gold, and W. Klemperer, *ibid.*, **37**, 2149 (1962). [e] L. Wharton, W. Klemperer, L. P. Gold, R. Strauch, J. J. Gallagher, and V. E. Derr, *ibid.*, **38**, 1203 (1963). [f] Mulliken atomic population on the metal atom. [g] Mulliken atomic population on the hydride or halide atom.

Table II. Dimer Structures and Energies

	Cyclic (D_{2h}) Dimers		
	ΔE,[a] kcal/mol	r(M–M), Å	r(X–X), Å
$(LiH)_2$	47.2	2.36	2.73
$(NaH)_2$	37.8	2.88	3.18
$(LiF)_2$	66.7	2.22	2.65
	Linear ($C_{\infty v}$) Dimers		
	ΔE,[a] kcal/mol		r(X···M), Å
$(LiH)_2$	26.0		1.63
$(NaH)_2$	23.4		1.64
$(LiF)_2$	36.4		1.80

[a] Before zero-point energy corrections.

predicted by the DIM method (24.9 kcal/mol (RIM) compared with 31.2 for DIM), but the two methods predict very different minimum energy geometries (DIM, r(Li–Li) = 2.83 Å, r(H–H) = 2.12 Å; RIM, r(Li–Li) = 2.30 Å, r(H–H) = 3.34 Å). Our calculations on $(LiH)_2$ predict a much greater dimerization energy than either of the above models (47.2 kcal/mol) and a minimum energy geometry more closely resembling the RIM than the DIM (r(Li–Li) = 2.36 Å, r(H–H) = 2.73 Å), but with a considerably different hydrogen–hydrogen separation. Our dimerization calculations on $(LiF)_2$ (*vide infra*) give us some confidence in the accuracy of our dimerization energy for $(LiH)_2$, and the ability of accurate SCF calculations to predict molecular geometries to 2–5% supports our predicted structure for $(LiH)_2$.

After learning of the Tyndall and Companion study,[7,11] we have also now examined the possibility of a C_{2v} dimer of Li_2H_2 by carrying out calculations on this structure with the geometrical parameters previously described,[7] varying the intermolecular separation. The results indicate no stabilization (relative to Li_2 and H_2) for a C_{2v} dimer. The *destabilization* at the minimum energy geometry predicted in ref 7 is considerable (24 kcal/mol), so it is unlikely that a larger basis set (ours is only 2.5 kcal/mol from the Hartree–Fock limit for LiH) or configuration interaction (all empirical and theoretical analyses indicate a relatively small contribution to bond formation in cases where the number of electron pairs is the same in reactants ($Li_2 + H_2$) and product (Li_2H_2)) will predict a stable C_{2v} dimer of Li_2H_2. Thus we conclude that the diatomics in molecules method as applied does not correctly predict the relative energies of the D_{2h} and C_{2v} dimers of LiH. It is probable, however, that this failure of DIM is partially due to lack of precise knowledge of the potential curve of $^3\Sigma$LiH since the results are quite sensitive to this potential curve.

The results for the LiF monomer and linear and cyclic dimers are presented in Tables I and II. The computed dimerization energy of $(LiF)_2$, after correction for zero-point energy differences,[12] was 63.5 kcal/mol at a minimum energy geometry of r(Li–Li) = 2.23 Å and r(F–F) = 2.65 Å. Eisenstadt, *et al.*,[8] have determined a dimerization energy of LiF at 1127°K of 58.9 ± 2.1 kcal/mol; after correcting for vibration and rotation contributions to the energy, the calculated dimerization energy is 62.8 kcal/mol at 1127°K.

The calculated and observed dimerization energies are in good agreement and give us further confidence in the ability of accurate SCF methods to predict dimerization energies of ionic species. As far as we know, the geometrical parameters for $(LiF)_2$, unlike those for many other alkali halide D_{2h} dimers, have not been determined experimentally, so our results are a prediction of its structure.

The only previous molecular orbital study of $(LiF)_2$ was that of Kollman, *et al.*,[13] who used a cruder basis set and did not carry out a complete geometry optimization for the D_{2h} dimer; these authors were mainly concerned with showing that the cyclic (D_{2h}) dimer of LiF was lower in energy than the linear dimer, in contrast to what was found for the linear and cyclic dimers of HF.

We would expect the calculated dimerization energy for LiF to be less accurate than that for LiH, since we are much further from the Hartree–Fock limit for LiF; our calculation for the LiF monomer is ~20 kcal/mol from the Hartree–Fock limit. Previous calculations on H-bond dimers[14] as one approaches the Hartree–Fock limit indicate that a more accurate SCF calculation would find a smaller dimerization energy, but it is not clear that this would decrease the ΔE to the experimental value. Our configuration interaction calculations[5] on the LiH dimer and monomer indicate that the correlation energy of two monomers may be *greater* than that of the dimer. Thus, the inclusion of configuration interaction might be necessary to *decrease* the computed dimerization energy of LiF and bring it closer to agreement with the experimental value. At this point, however, one can only say with confidence that the magnitude of the correlation contribution to the LiF dimerization energy is quite small; one still cannot be certain about its sign.

Previous empirical calculations on the LiF dimer in-

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(11) We thank Professor F. O. Ellison for bringing this work to our attention.

(12) The frequencies for ^{7}LiF monomer and dimer were taken from A. Snelson, *J. Chem. Phys.*, **46**, 3652 (1967).

(13) P. A. Kollman, J. F. Liebman, and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 1143 (1970).

(14) P. A. Kollman and L. C. Allen, *Chem. Rev.*, **72**, 283 (1972).

Table III. Dimer Properties

$(LiF)_2$	LiF	$(NaH)_2$	NaH
Orbital Energies			
−26.1535	−26.1004	−40.4645	−40.4923
−26.1535	−2.4384	−40.4645	−2.7732
−2.3993	−1.3621	−2.7455	−1.5215
−2.3960	−0.4844	−2.7453	−1.5215
−1.4231	−0.4617	−1.4968	−1.5208
−1.4189	−0.4617	−1.4951	−0.2715
−0.5581		−1.4947	
−0.5368		−1.4940	
−0.5286		−1.4936	
−0.5271		−1.4934	
−0.5128		−0.3216	
−0.5100		−0.2742	
Atomic Populations			
Li 2.220		Na 10.355	
F 9.780		H 1.645	
Quadrupole Moments[a] (Buckinghams)			
$\theta_{xx} = 13.39$		$\theta_{xx} = 21.28$	
$\theta_{zz} = 0.76$		$\theta_{zz} = -0.19$	

[a] Molecule in xy plane, metal along x axis.

clude three calculations[9,15,16] of varying degrees of sophistication. The simplest calculation,[9] which includes only ionic and repulsion terms, appears to come closest to our calculations and experiment, with a $\Delta E = -57.6$ kcal/mol, $r(\mathrm{Li}\cdots\mathrm{Li}) = 2.26$ Å, and $r(\mathrm{F}\cdots\mathrm{F}) = 2.50$ Å. When one includes polarizability and dispersion terms,[15,16] the agreement is somewhat less satisfactory, although the "second approximation" of ref 16 gives reasonable values for ΔE (−57.0 kcal/mol), $r(\mathrm{Li}\cdots\mathrm{Li}) = 1.83$ Å, and $r(\mathrm{F}\cdots\mathrm{F}) = 2.74$ Å.

The calculated orbital energies, atomic populations, and quadrupole moment components for the cyclic dimers of LiF and NaH are presented in Table III. The properties of $(NaH)_2$ are similar to those of $(LiH)_2$:[3] all of its orbital energies are raised relative to those of the monomer NaH; the metal loses 0.17 electron on dimerization (0.07 lost by Li in $(LiH)_2$); and it has a very large quadrupole moment ($\theta_{xx} = 21.3$ *vs.* 18.6 for $(LiH)_2$). In $(LiF)_2$, the orbital energies (with the exception of the one at −2.4 au) are lowered relative to the monomer, the atomic populations are almost the same as in the monomer, and the quadrupole moment is somewhat smaller than the hydrides. The LiF monomer is much more ionic than the hydrides to begin with, so one can understand the lack of atomic population change upon dimerization by noting that Li has very little further electron charge to dispense. The smaller quadrupole moment for $(LiF)_2$ is partially due to the fact that it is a more compact structure and also to the fact that the fluoride probably holds its charge more tightly than the hydride.

Conclusions

The calculated and experimental energies for the LiF dimer are in good agreement; thus, the predicted structure of $(LiF)_2$ and the predicted structure and relative energetics of LiH and NaH dimerization are "targets" for further experimental work, perhaps employing supersonic nozzle beams.[17]

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X-Ray Photoelectron Spectroscopy of Chlorine Trifluoride, Sulfur Tetrafluoride, and Phosphorus Pentafluoride

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Abstract: The fluorine 1s binding energies for ClF_3, SF_4, and PF_5 have been measured. For equatorial fluorines the values found are 694.76 (4), 695.26 (2), and 695.3 (1) eV, respectively, and for axial fluorines they are 692.22 (3), 692.88 (2), and 694.1 (1) eV, respectively. The inequivalence of the equatorial and axial fluorines is clearly seen and is more pronounced for ClF_3 and SF_4 than for PF_5. The consistently lower binding energies of the axial fluorines are consistent with the idea that these fluorines are bonded to the central atom with partially ionic, three-center bonds. The data are analyzed with a point-charge model to assign charges to the individual fluorine atoms. The results of this analysis are also in accord with the idea of three-center bonding. Comparison is made with results of molecular orbital calculations. The equivalent cores approximation is used to develop a further understanding of the binding-energy shifts, and the relationship between the point-charge analysis and the equivalent cores analysis is discussed.

The central atoms of the molecules PF_5, SF_4, and ClF_3 display higher coordination numbers than do their congeners N, O, and F and each has higher coordination than is required to supply a complete octet of electrons. Structural analyses have shown that each has a trigonal bipyramid structure if the lone pairs of the central atom are included in the structure.[1] The trigonal bipyramid structure is unusual in that the ligand positions are not all equivalent; PF_5, for ex-

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