To optimize N coordinates about $2N$ such calculations are needed.

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(62) M. J. S. Dewar and M. L. McKee, *J. Am. Chem. Soc.*, in press.

(63) The potential surface contains four valleys intersecting at the origin, two along the x and y axes and two along directions ($x = \pm y$) bisecting them. Along the first two, the origin is a minimum, whereas along the directions

$x = \pm y$ it is a maximum. The ridges separating the valleys lie along lines making angles of $\pm 15°$ with the x and y axes (i.e., $\theta = \pm 15°$, $\pm 75°$, $\pm 105°$, $\pm 165°$). If the optimization is carried out starting with a point in a valley containing the x or y axis, it will lead to the origin.

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A Molecular Orbital Study of Rare Earth Metal Trihalide Molecules

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Self-consistent charge extended Hückel calculations on rare earth metal trihalide molecules give lower total valence electron energies for pyramidal geometries than for planar geometries in agreement with the weight of experimental evidence. A correlation diagram analysis indicates that the dominant factor is enhanced overlap between the metal $5d_{z^2}$ and the halogen p orbitals in the pyramidal geometry. Consistent with this, the charge distribution is most delocalized for the minimum energy structures, providing further indication of the importance of covalency in LnX_3 systems.

Introduction

The view that bonding in rare earth metal compounds, particularly complexes, is substantially electrostatic[1] has been challenged with respect to the lanthanide trihalide molecules on the grounds that a hard-sphere ion model fails to account for the observed bond energies.[2] Although the inclusion of polarization effects brings about agreement,[3] these corrections are sufficiently large that considerable covalency must be inferred (since polarization of the anions means a net movement of electron density into the internuclear region). Furthermore, recent evidence from infrared studies of matrix-isolated trifluoride molecules,[4] from electric deflection of molecular beams of trifluorides,[5] and from electron diffraction studies[6] strongly supports a pyramidal structure for most, if not all, of the lanthanide trihalides; this would be unlikely if the bonding were essentially ionic.

Since the experimental evidence seems to support a significant degree of covalent bonding, it was considered timely to undertake molecular orbital calculations to gain insight into the nature of the bonding and the reasons for the nonplanarity. The large number of electrons in these molecules made an approximate, semiempirical method attractive for these purposes, and it was decided to use the extended Hückel method[7] because of its recent success in applications to transition metal compounds.[8] Also, the method has the ability to illuminate features of electronic structure responsible for geometry. Since the f-electron energies appear to be similar in the free ion, crystalline trihalides,[9] and gaseous molecules,[10] f orbitals were not explicitly included in the calculations; however, the effects of f electrons will be felt in that they influence the empirical parameters used in the calculations. This is the first application of a full, albeit approximate, MO treatment to lanthanide systems.[11]

Method

The calculations were performed using the program ICON8. In this program, a Slater-type nodeless single exponential is used to represent the radial part of the wave function:

$$R(r) = Nr^{n^*-1} \exp[(Z-S)r/a_0 n^*]$$

where n^* is the effective quantum number (in this case the principal quantum number), a_0 is the Bohr radius, r is the distance of the electron from the nucleus, S is a screening constant which was evaluated by the method of Burns,[12] Z is

the atomic number, and N is a normalizing factor.

Coulomb integrals were derived iteratively via a quadratic self-consistent charge procedure using the valence state ionization energy (VSIE) formalism of Ballhausen and Gray.[13] In this procedure, the Coulomb integrals, H_{ii}, are given in terms of three valence configurations for each atomic orbital:

$$-H_{ss} = (2 - e_s - e_p)[e_s(\text{VSIE: } d^2s)] + (e_s - 1)[e_s(\text{VSIE: } d^{n-2}s^2)] + e_p[e_s(\text{VSIE: } d^{n-2}sp)]$$

$$-H_{pp} = (2 - e_s - e_p)[e_p(\text{VSIE: } d^{n-1}p)] + (e_p - 1)[e_p(\text{VSIE: } d^{n-2}p^2)] + e_s[e_p(\text{VSIE: } d^{n-2}sp)]$$

$$-H_{dd} = (1 - e_s - e_p)[e_d(\text{VSIE: } d^n)] + e_s[e_d(\text{VSIE: } d^{n-1}s)] + e_p[e_d(\text{VSIE: } d^{n-1}p)]$$

where e_s, e_p, and e_d are the summed orbital occupations of the s, p, and d orbitals, respectively. The VSIEs are given a quadratic charge dependence:

$$\text{VSIE(of a config}^n) = AQ^2 + BQ + C$$

where Q is the charge and A, B, and C are a unique set of constants for each configuration on each atom. The values of these parameters were determined, using Brewer's energy level data,[14,15] according to the method of Basch, Viste, and Gray.[16] The initial guess for the Coulomb integrals on the lanthanides was taken as $-\text{VSIE}(Q = 0)$ for each configuration. A compilation of orbital exponents $(Z - S)$ and VSIE parameters (A, B, C) for the lanthanides and the halogens is given in Tables 1–3 of the supplementary material.

A Mulliken population analysis is used to determine charge distributions. Calculations were performed for the molecules in both D_{3h} (planar) and C_{3v} (pyramidal) geometries, the latter being done at 5° intervals of out-of-plane angle. The metal–halogen distances were those used earlier.[2,3] Early calculations on LaX_3 (X = F, Cl, Br, I) included halogen d orbitals, but the results differed in no significant manner from calculations using only halogen s and p orbitals. Hence, later calculations did not include halogen d orbitals.

Results from two general procedures are discussed below. The first of these is an extended Hückel calculation with full iteration to charge self-consistency for a particular geometry (FCI), and the second is a calculation varying bond angles (BAV) but using the Coulomb integrals obtained from an FCI calculation for the planar D_{3h} configuration of the molecule.
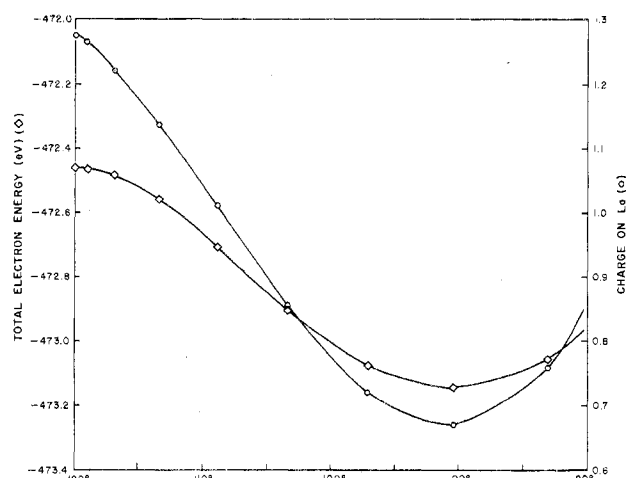
Figure 1. Variation of total valence electron energy and charge with bond angle for LaF_3.

A full charge iteration as a part of the BAV calculation is inappropriate since the iteration is to charge self-consistency and not necessarily to minimum energy. Using fixed Coulomb integrals permits an examination of the effect of varying the bond angle on the valence electron energy. Furthermore, the MO correlation diagrams presented below could not be readily interpreted in terms of variations in atomic orbital overlap during the molecular deformations if the Coulomb integrals were allowed to vary from the values determined at the planar geometries. Combination of FCI–BAV calculations on several molecules did not reveal any departure from the basic conclusions using BAV alone.

Results and Discussion

Probably the most important result of the calculations is the prediction that the molecules are pyramidal. The BAV calculation gives a minimum in the total energy at bond angles less than 120°: 91° for LaF_3, 101° for $LaCl_3$, 99° for $LaBr_3$, and 114° for LaI_3. These may be compared with the experimental values: LaF_3, 117°, determined from infrared spectroscopy on matrix isolated molecules;[4b] $LuCl_3$, 111°, $LaBr_3$, 115.1°; $GdBr_3$, 113.8°; $LuBr_3$, 114.5°, determined by gas-phase electron diffraction.[6] It is not expected that this approximate calculation will give accurate bond angles, particularly since electronic–electronic and nuclear–nuclear repulsions are not taken explicitly into account. Nonetheless, the model reproduces the essential qualitative features of the experimental results and provides insight into the origin of these effects.

The calculated charge on the metal atom is significantly less than 3+, being 1.10+ for LaF_3, 0.66+ for $LaCl_3$, 0.54+ for $LaBr_3$, and 0.38+ for LaI_3 in the planar geometry. These charges are much lower, even in the fluorides, than would be expected for ionic bonding, although the molecular orbital method does tend to exaggerate covalency. The trend in charges shows the expected increases in covalency in the halogen series. The results of the BAV calculation also show a reduction in charge on the metal and, hence, increased covalency upon going from the planar D_{3h} configuration to the pyramidal C_{3v} configuration of the molecule. The charge has a minimum at a bond angle essentially equal to the angle for minimum energy–except for the iodides which give only a local minimum at a bond angle much smaller than the value for minimum energy. (This may well be due to iodine–iodine interactions becoming important at small I–La–I angles.) This concomitant variation of charge with energy supports the importance of covalency in making the pyramidal structure the more stable. The energy and metal atom charge for LaF_3 as a function of bond angle are shown in Figure 1. When

Table I. Minimum-Energy X–Ln–X Bond Angles

	Bond angle, deg			
	LnF_3	$LnCl_3$	$LnBr_3$	LnI_3
La	91	101	99	114
Ce	91	100	99	114
Eu	91	102	101	117
Gd	91	102	101	116
Er	91	103	102	118
Lu	92	105	104	119

Table II. Total Electron Energy and Charge on Metal Atom

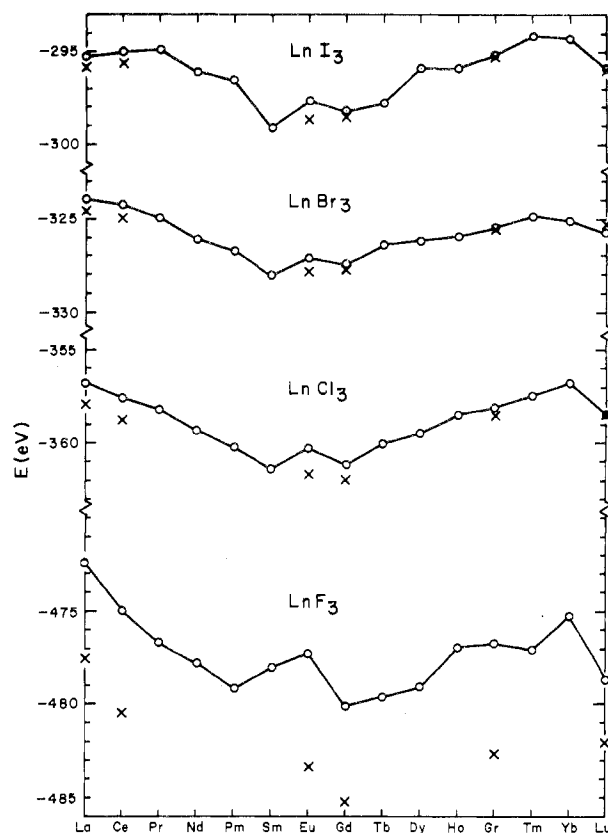|	Energy, eV	Charge on metal
LaF_3	−472.4	1.10+
EuF_3	−477.3	1.06+
GdF_3	−480.0	1.04+
YbF_3	−475.3	1.08+
LuF_3	−478.7	1.05+

Figure 2. Total valence electron energy for planar (O) and minimum energy (X) geometries (full charge iteration) for LnX_3.

an FCI calculation is performed at the angle for minimum energy as determined by the BAV calculation, the total energy is generally lowered even more, but the charge on the metal is increased somewhat (1.06+ for LaF_3, 0.65+ for $LaCl_3$, 0.53+ for $LaBr_3$, 0.37+ for LaI_3), although it is still slightly lower than for the planar geometry. As predicted, this indicates that the pyramidal configuration is indeed more covalent than the planar.

The bond angle for minimum energy increases slightly with increasing atomic number of the lanthanide element, as shown in Table I. The variation of valence-electron energy (FCI) as a function of metal atomic number for the planar configuration is shown in Figure 2 along with the energies of selected molecules (FCI) in their minimum-energy configurations. The variation in charge on the metal atom generally parallels that of the total energy, as shown in Table II. The discontinuities Eu–Gd and Yb–Lu may be related to the half-filled f shell at Gd and the completely filled shell at Lu.
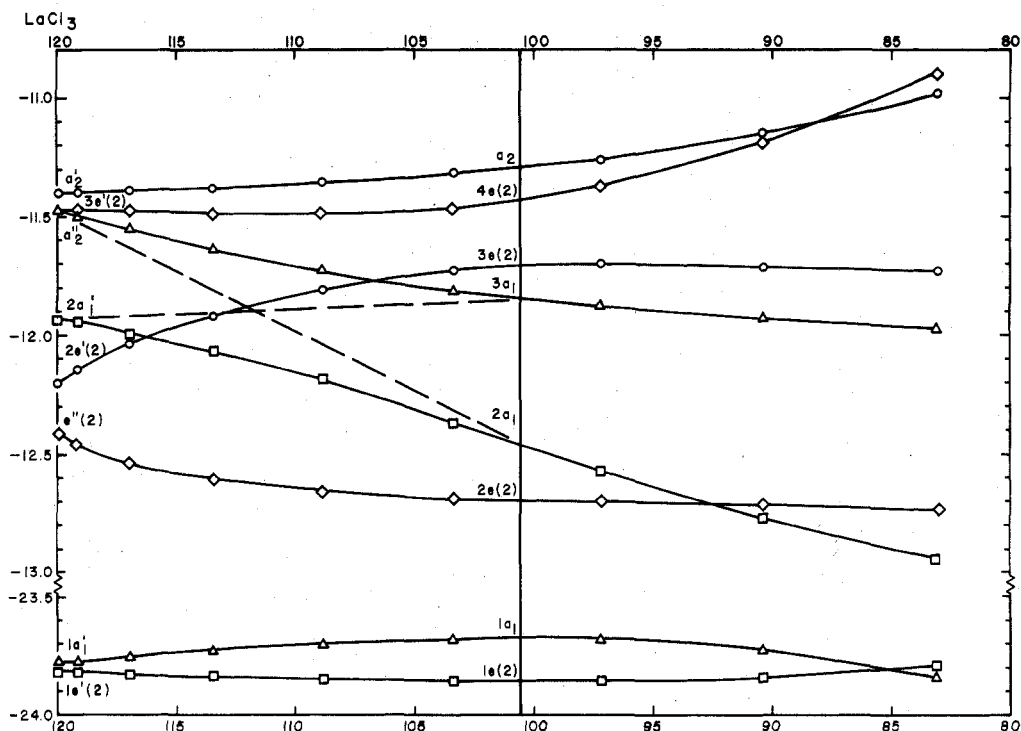
Figure 3. Molecular orbital energies as a function of bond angle in LaCl₃.

It is instructive to examine the occupied molecular orbitals in some detail in order to understand the reasons (in terms of the model) underlying the results discussed above. The energies of the MOs of LaCl₃ as a function of bond angle (from a BAV calculation) are shown in Figure 3. A vertical line is drawn at the angle of minimum total energy. A comparison of orbital energies of the planar D_{3h} configuration and the minimum-energy pyramidal C_{3v} configuration, both from FCI calculations, is shown in Figure 4 which also portrays diagrams of the lanthanum and chlorine orbitals used in forming the molecular orbitals in each configuration. The view in these diagrams is along the threefold axis of the molecule, and the chlorine atoms are displaced below the plane of the paper as the bond angle is reduced. The orbitals most affected by the changes in geometry are a_2'', $2a_1'$, $2e'$, and e''. It appears at first surprising that the a_2'' orbital should be enhanced in stability upon going to $3a_1$ since the orbital diagrams would indicate no significant increase in favorable interactions between lanthanum and chlorine orbitals. However, both a_2'' and $2a_1'$ take on a_1 symmetry as the molecule goes from D_{3h} to C_{3v} and hence become mutually repulsive. The situation can perhaps be viewed as an avoided crossing of orbitals of the same symmetry. An additional factor is that the lowest unoccupied MO is also of a_1' symmetry in the planar geometry. Bending the molecule allows it to mix with the a_1 manifold causing its energy to increase by 0.25 eV concomitant with the decrease in $3a_1$ shown in Figure 3. The enhanced stability of the $2a_1$ orbital in C_{3v} is due to a more favorable interaction between chlorine p orbitals and the lanthanum d_{z^2} orbital:

The increased participation of the lanthanum d_{z^2} orbital in the bonding is documented in the d-orbital occupations given in Table III. While the d_{xz} and d_{yz} contributions decrease upon going from D_{3h} to C_{3v}, the d_{xz}, $d_{x^2-y^2}$, and d_{z^2} all show an increased occupancy with a net increase for the total d-orbital

Table III. Orbital Occupation (Full Charge Iteration)

		LaF₃	LaCl₃	LaBr₃	LaI₃
		Planar D_{3h}			
La	s	0.029	0.092	0.100	0.138
	p (total)	0.001	0.010	0.011	0.069
	$d_{x^2-y^2}$	0.282	0.450	0.471	0.532
	d_{z^2}	0.141	0.248	0.293	0.177
	d_{xy}	0.282	0.450	0.471	0.532
	d_{xz}	0.583	0.543	0.555	0.586
	d_{yz}	0.583	0.543	0.555	0.586
X	s	1.933	1.895	1.925	1.904
	p (total)	5.433	5.326	5.256	5.223
	p_z	1.611	1.637	1.629	1.605
		Pyramidal C_{3v}			
La	s	0.013	0.064	0.069	0.128
	p (total)	0.001	0.010	0.011	0.067
	$d_{x^2-y^2}$	0.410	0.486	0.504	0.537
	d_{z^2}	0.530	0.484	0.517	0.319
	d_{xy}	0.410	0.486	0.504	0.537
	d_{xz}	0.289	0.410	0.431	0.522
	d_{yz}	0.289	0.410	0.431	0.522
X	s	1.938	1.899	1.927	1.905
	p (total)	5.515	5.318	5.250	5.218
	p_z	1.796	1.739	1.714	1.635

occupancy which is the source for increased covalency. The $2e'$ and e'' orbitals both take on e symmetry in C_{3v} and become mutually repulsive, correlating with the 3e and 2e levels, respectively.

Although there are some shifts in the energies of the molecular orbitals, the makeup and bond angle energy dependence of the a_2'', $2a_1'$, $2e'$, and e'' orbitals are generally the same in all the trihalides.

In summary, the results suggest that covalency contributes significantly to the bonding in these molecules, with the degree of covalency increasing in the halogen series. The model predicts pyramidal geometry in agreement with the weight of experimental evidence. The pyramidal configuration affords better interaction between metal d orbitals, particularly the d_{z^2}, and halogen p orbitals, with concomitant enhanced covalency as evidenced by reduced positive charge on the metal atom. Although the level of approximation suggests that the
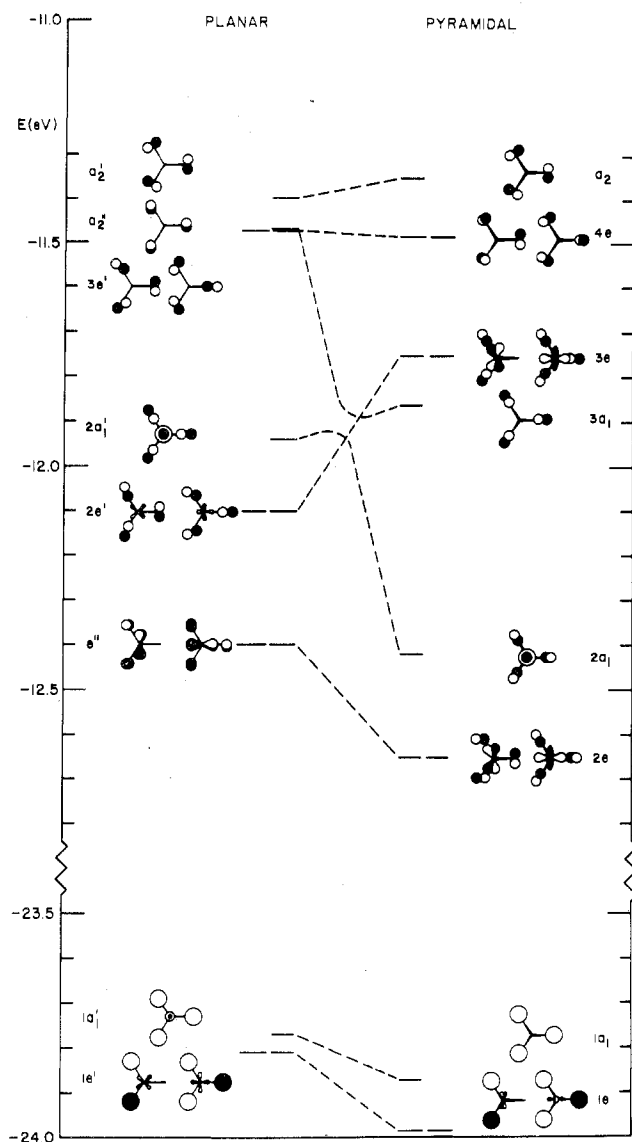
Figure 4. Molecular orbital diagrams for $LaCl_3$ in planar and minimum-energy geometries.

calculations should be used cautiously in terms of quantitative results, the qualitative results provide a basis for a better understanding of the bonding in these molecules and a rationale for their structures.

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