A Molecular Orbital Study of CLi_2F_2: Planar 3-Co-ordinate and Pyramidal 4-Co-ordinate Carbon

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CLi_2F_2 is indicated by *ab initio* calculations to have a planar lithium bridged structure having $CLi_2F^+F^-$ ion pair character.

In 1976 Pople, Schleyer, and coworkers[1] reported minimal basis set *ab initio* calculations on CLi_2F_2 which suggested that the most stable configuration of this molecule was the *cis*-planar rather than the tetrahedral structure. This surprising result was attributed in part to the π-acceptor ability of the lithium atom. It is generally agreed, however, that minimal basis set calculations exaggerate the importance of the p orbitals of lithium. In view of this and of the non-classical structures calculated for the related carbenoids $CLiX_nH_{3-n}$ (n = 1—3; X = F, Cl, CN, NH_2, OH)[2—5] we have made an extensive study† of the potential surface of CLi_2F_2 at the 4-31G level.[6]

Geometries were optimized within particular symmetry constraints by analytic evaluation of gradients[7] and Schlegel's

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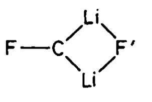
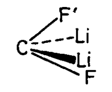
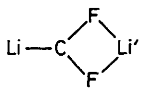
† All the calculations were carried out using the Gaussian 82 series of programs (J. S. Binkley, M. J. Frisch, K. Raghavachari, D. J. DeFrees, H. B. Schlegel, R. A. Whiteside, G. Fluder, R. Seeger, and J. A. Pople, Gaussian 82. Release A, Carnegie-Mellon University) on the University of Sussex VAX computer.



(1) C_{2v}



(2) C_s



(3) C_{2v}

Table 1. Optimum geometrical parameters for the three minima of CLi_2F_2 (1)—(3) and for the C_{2v} *cis*- and D_{2h} *trans*-planar structures. Bond lengths (r) in Å, bond angles (θ) in degrees.

Structure	Geometrical parameter	4-31G optimum value	6-31 + G optimum value
(1)	r(C–F)	1.364	1.383
	r(C–F′)	2.815	2.807
	r(C–Li)	2.118	2.121
	θ(LiCLi)	73.76	75.46
(2)	r(C–Li)	2.254	2.272
	r(C–F)	2.640	2.570
	r(C–F′)	1.804	1.913
	θ(FCF′)	65.00	66.07
	θ(FCLi)	40.16	41.88
(3)	r(C–Li)	1.827	1.830
	r(C–Li′)	2.395	2.424
	r(C–F)	1.617	1.647
	θ(FCF)	91.17	90.79
C_{2v}[a]	r(C–F)	1.539	
	r(C–Li)	1.860	
	θ(FCF)	105.36	
	θ(LiCLi)	127.77	
D_{2h}[b]	r(C–F)	1.850	
	r(C–Li)	1.963	

[a] *cis*-Planar. [b] *trans*-Planar.

algorithm,[8] and the resulting stationary points were characterized by the calculation of harmonic vibrational frequencies:[9] the presence of one or more imaginary frequencies indicates that a structure is not a true minimum (that is, it is only a minimum within the imposed symmetry constraint).

The results of this investigation suggest that none of the C_{2v} *cis*-planar, D_{2h} *trans*-planar, and C_{2v} tetrahedral structures is a minimum on the potential surface. We have nevertheless located three minima. Most stable is the lithium bridged structure (**1**); at an energy some 30 kJ per mol higher is structure (**2**) in which the carbon atom is at the apex of a distorted pyramid; the least stable structure, with an energy over 200 kJ per mol above (**1**), is the fluorine bridged structure (**3**). We have optimized the geometries of each of these three structures, within C_{2v} [structures (**1**) and (**3**)] or C_s [structure (**2**)] symmetry, using the 6-31G basis set[10] augmented by a set of diffuse s and p functions (exponents $\alpha_s = \alpha_p = 0.1076$) on the two fluorine atoms.[11]‡ In Table 1 we give the optimum geometrical parameters of the three minima and of the C_{2v} *cis*- and D_{2h} *trans*-planar structures. The tetrahedral structure is not even a C_{2v} minimum, distorting to C_{2v} pyramidal structure which on relaxation to C_s symmetry distorts slightly to give structure (**2**). The 4-31G (6-31+G) energies of (**1**)—(**3**) and the 4-31G energies of the *cis*- and *trans*-planar structures are, in Hartrees, −251.35363 (−251.60022), −251.34339 (−251.58891), −251.27303 (−251.51653), −251.24038, and −251.17395 respectively.

The results of 4-31G[2] and more extensive[4] calculations on CH_2LiF suggest that the structures we have predicted for CLi_2F_2 will not differ significantly from those that would be obtained with larger basis sets, but that the stability order of (**1**) and (**2**) may be reversed at higher levels of theory. There is as yet no information as to whether inclusion of correlation energy alters the essential structural features of lithiohalogenomethanes.

Structures (**1**) and (**3**) are probably best thought of as ion pairs containing three co-ordinate carbon. In (**1**) we have a carbonium ion, stabilized by σ-donation from lithium and π-donation from fluorine, together with a fluoride ion, while in (**3**) we have a carbanion stabilized by the σ-acceptance of the fluorine and the π-acceptance of the lithium. The much higher energy of structure (**3**) is a manifestation of the strong σ-donor and relatively weak π-acceptor ability of lithium.

The pyramidal structure (**2**) is less easy to understand. All the bonds are long. While the carbon–lithium distance is not much longer than in LiMe (2.02 Å),[12] the carbon–fluorine distances are much longer than normal. The fluorine and lithium Mulliken populations correspond to formal charges of −0.6, −0.7, and +0.65 electrons respectively while the carbon is formally almost exactly neutral. What we appear to have is a structure consisting of an ionic LiF dimer to which a carbon atom is loosely linked, perhaps by quadrupolar induction.

The stability of the ground state of CLi_2F_2 is unlikely to be great. It is stable to all possible singlet carbenes and singlet diatomics by over 300 kJ per mol, and two molecules are stable to C_2F_4 and $2Li_2$ by 480 kJ per mol, but it is unstable to a carbon atom and a LiF dimer by 130 kJ per mol, though it is not easy to estimate the barrier to this dissociation since an intersystem crossing on to the triplet potential surface will be involved. It is unstable to both molecular oxygen and water by over 400 kJ per mol.

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‡ For notational convenience we denote this basis set by 6-31 + G; this notation conventionally denotes the 6-31G basis set augmented with a set of diffuse sp functions on all non-hydrogen atoms (see ref. 11).