Tetrahedron Vol. 45, No. 16, pp. 5163 to 5174, 1989
Printed in Great Britain.

0040-4020/89 $3.00+.00

AN *AB INITIO* THEORETICAL STUDY OF THE STRUCTURE AND STABILITY OF 1-FLUOROPROPENIDE AND 1,1-DIFLUOROPROPENIDE AND OF THE CORRESPONDING MONOMERIC LITHIATED SPECIES

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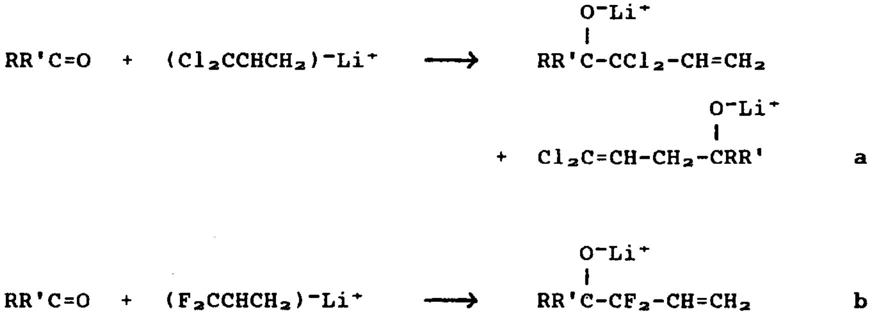
(*Received in UK* 4 *May* 1989)

Abstract. The electron distribution and HOMO polarization induce in the title compounds a different behaviour toward both *hard* and *soft* electrophiles: the results explain the observed α selectivity in difluoroallyllithium, while monofluoroallyllithium is predicted to show a less pronounced preference for the same site of attack.

Introduction. In the last years hetero-substituted allyl anions have been the subject of many experimental works, aimed mainly to the exploitation of new synthetic routes.[1] In particular, *gem*-dihalo allyl anions have been synthesized and studied experimentally by Seyferth, Mauze` and co-workers[2] as to their reactivity and regioselectivity as ambident nucleophiles. For *gem*-dichloro allyl anions (Scheme 1a) they found that carbonyl compounds



$$RR'C{=}O + (Cl_2CCHCH_2)^-Li^+ \longrightarrow RR'\overset{O^-Li^+}{\overset{|}{C}}-CCl_2-CH{=}CH_2 + Cl_2C{=}CH-CH_2-\overset{O^-Li^+}{\overset{|}{C}}RR' \qquad a$$

$$RR'C{=}O + (F_2CCHCH_2)^-Li^+ \longrightarrow RR'\overset{O^-Li^+}{\overset{|}{C}}-CF_2-CH{=}CH_2 \qquad b$$

Scheme 1.

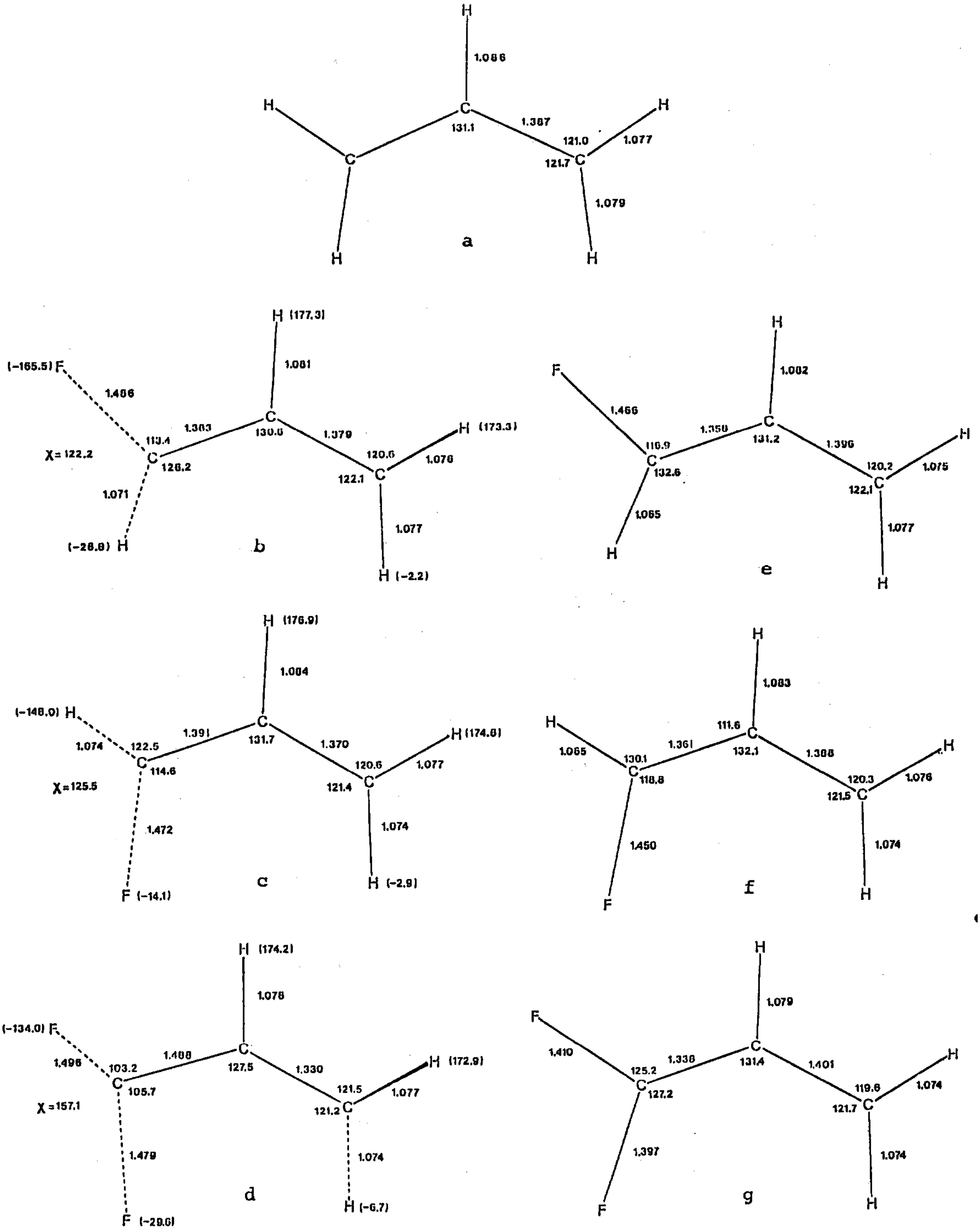
yield different products of attack depending on the substituents on the carbonylic carbon atom, presenting a whole spectrum of product distributions going from a complete α attack to a complete γ attack.[2h] *Gem*-difluoro allyl anions (Scheme 1b) behave quite differently: with every kind of carbonyl compound studied they invariably show complete α selectivity[2a]. Seyferth and co-workers offered an explanation for the selectivity observed in the dichloro anions in terms of preference of the electrophile either for the *hard* terminal carbon atom (γ position, characterized by a greater charge density), or for the *soft* terminal carbon atom (α position, where the substitution by the two chlorine atoms should delocalize the negative charge): *harder* electrophiles would attack the *harder* Cα center, while *softer* electrophiles would attack the *softer* Cγ center. In the dichloro anions charge density differences between the α and the γ position would be smaller than in the similar *gem*-difluoro allyl anions. Seyferth and co-workers, considering that the counter ion should be taken into account in offering an explanation to the complete α selectivity found in these anions, argued that lithium would preferentially engage the γ position, where the charge density would be presumably larger, thus preventing the electrophile from attacking this position.

Theoretical investigations by Schleyer and co-workers[3] on the addition of LiH, $LiCH_3$ and their dimers to formaldehyde have shown that the lithium cation has an important role in the transition structure, *via* its direct interaction with the carbonyl oxygen. This result suggests that in the haloallyl systems the role of the counter-ion might be just the opposite of what was supposed by Seyferth and co-workers, in that it could direct the carbonyl attack just onto the carbon atom to which the counter-ion is more directly bound.

In the present study an extreme situation of deaggregation is modelled by determining the stable structures of two substituted allyl anions, 1-fluoropropenide and 1,1-difluoropropenide, and comparing them with those originating from the association of the anions with a lithium cation. The electron distribution of these molecular systems is discussed in connection with the possibility of attack by a *hard* electrophile. On the other hand, the polarization of the Highest Occupied Molecular Orbital (HOMO) is examined as a factor which could determine the orientation of attack of a *soft* electrophile. The structure, stability and electron distribution of dimeric lithiated species will be the subject of a subsequent study.

Method. The energy minima corresponding to stable structures have been determined by completely optimizing (without any constraint) the geometrical parameters by gradient methods[4] at the RHF level of theory, using the split-valence shell 3-21+G basis set.[5] At the same computational level some related planar structures were optimized (C_S symmetry constraint); these critical points have been characterized by analytical RHF/3-21+G computation and diagonalization of the Hessian matrix (*i.e.* by calculation of the vibrational frequencies). The relative energies have been recomputed introducing correlation effects[6] through perturbative MP2/6-31+G energy calculations, using the RHF/3-21+G geometries. The computations have been performed using the GAUSSIAN82 series of programs[7] on a National AS-9160 computer at CSI-Piemonte (Torino, Italy), and on a VAX Station 3200 at the Istituto di Chimica Organica.

Results and discussion. *Free anions.* Early computations[8] on the parent allyl anion suggested that its geometrical structure slightly departs from planarity, due to a tiny pyramidalization of the terminal CH_2 groups. For sake of comparison the geometry of the allyl anion has been reoptimized at the present level of computation. Two different attempts to determine a non-planar structure were done, starting from structures having either the two terminal CH_2 groups pyramidalized from the same side of the CCC plane, or from opposite sides. Only a completely planar structure was determined in both cases (Fig. 1a; RHF/3-21+G bond lengths in Ångstrom, and angles in degrees). On the contrary, the more stable structures determined for 1-fluoropropenide and 1,1-difluoropropenide were found to be pyramidal at the α carbon.[9] The degree of pyramidalization[10] is smaller in the monofluoro anion and larger in the difluoro anion (Fig.1, χ values). Therefore, the description of the electronic structure of these species differs from that of the allyl anion, especially in that the presence of a fully delocalized π system gradually desappears with increasing substitution of a terminal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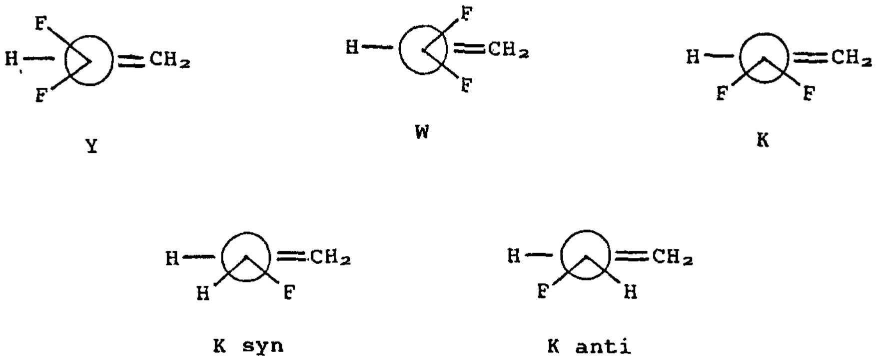
1.086
131.1
1.387
121.0
1.077
121.7
1.079
b
(177.3)
1.081
(−165.5) F
1.486
1.383
113.4
130.6
1.379
(173.3)
X= 122.2
126.2
120.6
1.076
122.1
1.071
1.077
(−28.8) H
(−2.2)
e
1.082
1.466
1.358
116.9
131.2
1.396
120.2
1.075
132.6
122.1
1.065
1.077
c
(176.9)
1.084
(−148.0) H
1.391
1.074
122.5
131.7
1.370
(174.6)
114.6
120.6
1.077
X=125.5
121.4
1.472
1.074
F (−14.1)
H (−2.9)
f
1.083
111.6
1.065
1.361
130.1
132.1
1.388
118.8
120.3
1.076
121.5
1.450
1.074
d
(174.2)
1.078
(−134.0) F
1.408
1.496
103.2
127.5
1.330
(172.9)
105.7
121.5
1.077
X =157.1
121.2
1.479
1.074
F (−29.6)
H (−6.7)
g
1.079
1.410
1.338
125.2
131.4
1.401
127.2
119.6
1.074
121.7
1.397
1.074

Figure 1.

carbon atom. The two anions have been found to exist in three stable conformational isomeric structures related by inversion/rotation of the CHF or CF_2 groups.[9] Here they are labeled for convenience as Y, W, and K structure, as shown in Scheme 2 for 1,1-difluoropropenide. In the case of 1-fluoropropenide two non-equivalent K structures are possible, with the CF bond approximately syn and anti with respect to the $C\beta$-$C\gamma$ bond (Scheme 2).



Scheme 2.

The K structures correspond to the more stable energy minima on the roto-inversion surface (Table 1). The optimized geometries of the K isomers are shown in Fig. 1b,c for 1-fluoropropenide and in Fig. 1d for 1,1-difluoropropenide (RHF/3-21+G bond lengths in Ångstrom, and angles in degrees). In the case of the 1,1-difluoropropenide, two equivalent K conformational isomers, related by a reflection through the CCC plane, are connected by a planar transition structure, whose geometry bears some resemblance to the unsubstituted allyl anion (Fig. 1g). The same situation is found for the *syn* isomer of 1-fluoropropenide, 1f, but in the case of the *anti* isomer the planar structure 1e was characterized as a further minimum on the surface. In the difluoro anion the pyramidal structure is much more stable than the planar (Table 1). This is reflected in the degree of pyramidalization of the CF_2 group (Fig. 1, χ angles).[10,11]

TABLE 1.

Total and relative energies.[a]

Free Anions:			
1-fluoropropenide			
K syn	1c	-215.630534	0.00
syn planar	1f	-215.627830	1.70
K anti	1b	-215.626651	2.44
anti planar	1e	-215.624306	3.91
1,1-difluoropropenide			
K	1d	-314.603893	0.00
planar	1g	-314.576960	16.90
Lithiated Anions:			
Lithium 1-fluoropropenide			
K syn 'external'	2c	-223.117223	0.00
K syn 'internal'	2b	-223.116360	0.54
K anti	2d	-223.115459	1.11
Y γ syn	2e	-223.111822	3.39
Lithium 1,1-difluoropropenide			
K 'external'	2f	-322.085255	0.00
K 'external'	2g	-322.082981	1.43
Y γ	2h	-322.054638	19.21

(a) MP2/6-31+G energies in Hartree, energy differences in kcal mol^{-1}.

Being less pyramidalized at the Cα carbon center, the structure of 1-fluoropropenide departs less from that of the allyl anion. For instance, considering the more stable conformations, the Cα-Cβ bond length is 1.391 Å in the K syn conformation and 1.383 Å in the K anti conformation; the Cβ-Cγ bond lengths are 1.370 Å (K syn) and 1.379 Å (K anti). These values are rather close to the CC bond length value in the allyl anion, 1.387 Å. In the difluoro anion (K conformation) the stronger pyramidalization of the CF_2 group leads to a more localized system, as shown by the Cα-Cβ (1.488 Å) and Cβ-Cγ (1.330 Å) bond lengths, which approximate the tipical values for single and double CC bonds.[12] The structural features just discussed determine both the charge distribution (to which *hard* electrophiles should be sensitive) and the polarization of the molecular orbitals, of which the highest occupied (HOMO) should be of particular importance in the case of attack by a *soft* electrophile. The effect of single and double fluorine terminal substitution on the charge distribution of an allylic system is schematically shown in Table 2.

TABLE 2.

Group Charges[a] and HOMO Polarization.[b]

		Q(CXF)	Q(CH_2)	Q(Li)	P(Cα)	P(Cγ)
Free Anions:						
1-fluoropropenide						
K syn	1c	0.705	0.515	-	0.385	0.304
syn planar	1f	0.615	0.630	-	0.349	0.373
K anti	1b	0.701	0.586	-	0.396	0.330
anti planar	1e	0.651	0.659	-	0.348	0.373
1,1-difluoropropenide						
K	1d	1.171	0.091	-	0.845	0.159
planar	1g	0.748	0.681	-	0.317	0.417
Lithiated Anions:						
Lithium 1-fluoropropenide						
K syn 'external'	2c	0.613	0.148	-.639	0.318	0.198
K syn 'internal'	2b	0.549	0.291	-.632	0.405	0.222
K anti	2d	0.701	0.586	-.582	0.396	0.330
Y syn	2e	0.131	0.233	-.440	0.044	1.085
Lithium 1,1-difluoropropenide						
K 'external'	2f	0.692	-.117	-.567	0.321	0.168
K 'external'	2g	0.971	-.117	-.554	0.543	0.327
Y γ	2h	0.460	0.245	-.464	0.056	1.093

(a) The left *vs.* right charge asymmetry (Q*left* = Q(CXF) + 1/2Q(CH) ; Q*right* = Q(CXF) + 1/2Q(CH)) can be compared to the symmetrical distribution present in the parent allyl anion (Q*left* = Q*right* = 0.5).

(b) The polarization of the HOMO is expressed for Cα and Cγ as the sum of squares of the atomic orbital coefficients.

The charge distribution (6-31+G basis set) is presented as 'group charges', given by the sums of the net atomic charges for the different groups: CHF or CF_2, CH, and CH_2.[13] The "left versus right" charge differences obtainable from Table 2 (see note a) emphasize the polarization of the electron distribution and appears to be consistent with the structural features just discussed. The double fluorine substitution produces a substantial flow of charge toward the CF_2 groups. *The central CH group is depleted of electrons in all anions.*

To better show how the charge distribution could orient the approach of a *hard* electrophile, an energy map has been built for 1,1-difluoropropenide, using the hydrogen ion (a *hard* electrophile) as a probe. The map, obtained moving an hydrogen ion at fixed R distances onto the $F_2C.CH.CH_2$ skeleton (R=3.0, 2.5, and 2.0 Å) shows the following features: (i) the attack by H^+ can proceed both onto the α and γ carbon atoms without any energy barrier;

(ii) two well defined wells are present, approximately centered on the two terminal carbon atoms; (iii) the downhill path leading to the attack on the α carbon is somewhat steeper (and leads to a more stable product[17]); (iv) the zone of the β carbon atom is repulsive. Although such a map cannot of course produce any kinetic evidence, nevertheless it can provide an approximate picture of how a *hard* center could sense the electron distribution.

Also the HOMO is polarized toward the α carbon atom, in both 1-fluoropropenide and 1,1-difluoropropenide. This polarization can be expressed in terms of a parameter, P(X), defined for each atom X in the molecule. Its value, given by the sum of the squares of the HOMO atomic orbital coefficients belonging to that atom, is reported for Cα and Cγ in Table 2.

The results show that, for the extreme case of the free difluoro anion, both a *hard* electrophile, sensitive to the charge distribution, and a *soft* electrophile, sensitive to the 'orbital interaction' and hence mainly to the HOMO polarization, would prefer to direct their attack toward the α terminus of the molecule. The monofluoro anion should be less selective.

Lithiated species. Several minima have been found for both anions, in correspondence to different associations with a lithium counter-ion (Fig. 2; RHF/3-21+G bond lengths in Ångstrom, angles in degrees). For sake of comparison the allyllithium structure, known to be symmetrically bridged,[18] has been reoptimized at the same computational level (Fig. 2a). The optimized geometries for the 1-fluoropropenide-lithium system (1FLi) are shown in Fig. 2b-e while those for the 1,1-difluoropropenide-lithium system (2FLi) are shown in Fig. 2f-h. In all of the structures shown in Fig. 2 lithium is bound both to an allylic carbon atom and to a fluorine atom. In two of them (Fig. 2e and h) the γ carbon is substantially involved in bonding with the counter-ion. Two main differences between 1FLi and 2FLi can be noted. First, it was not possible to determine for 2FLi a critical point in correspondence to a structure similar to 2b for 1FLi: in correspondence to this kind of structure the energy surface presents a very

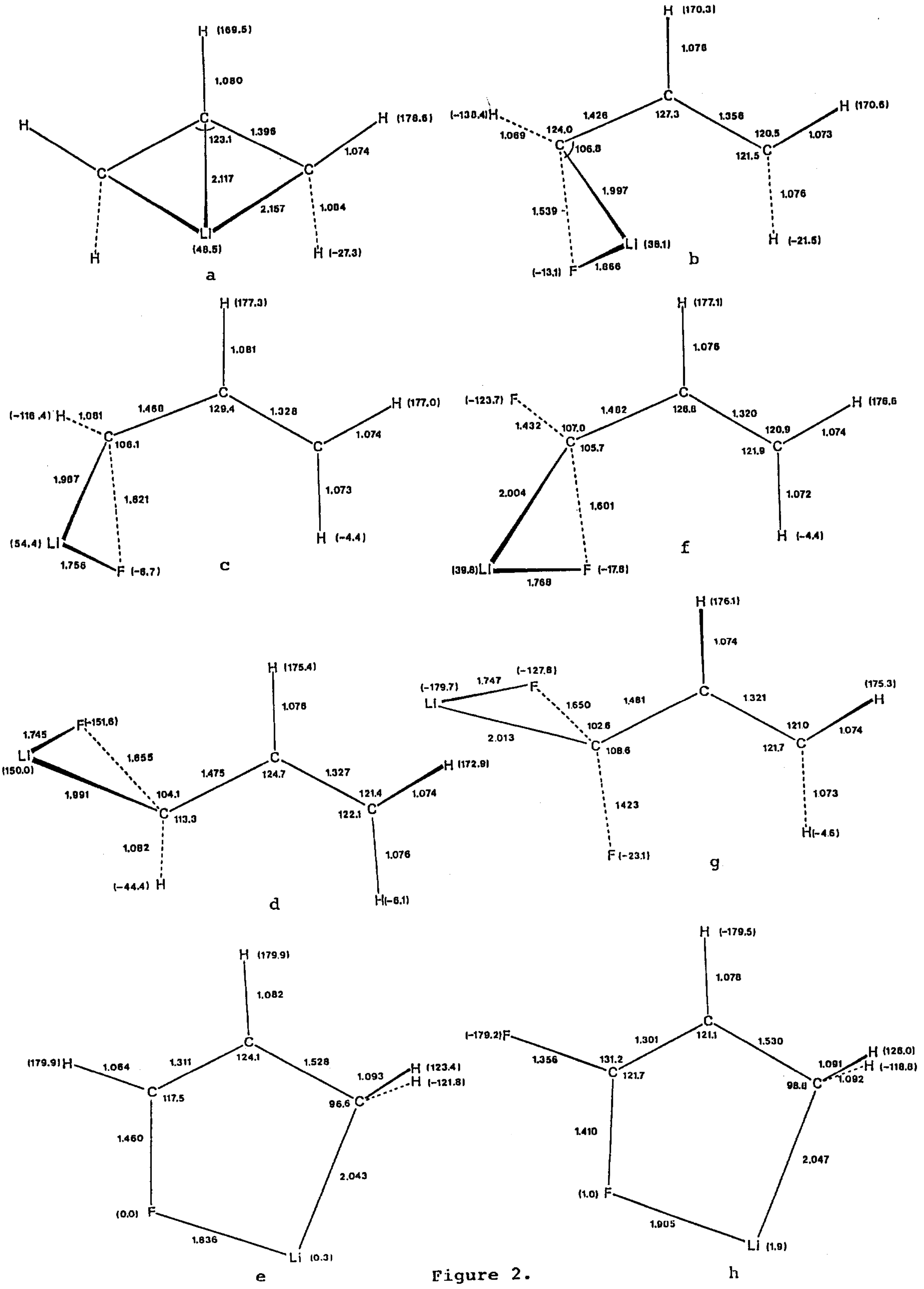

H (169.5)
1.080
H
C
123.1
1.396
H (178.6)
C
1.074
2.117
C
2.157
1.084
Li
(48.5)
H
H (-27.3)
a
H (170.3)
1.076
C
(-138.4)H
1.426
127.3
1.356
H (170.6)
1.069
124.0
C
106.8
120.5
1.073
121.5
C
1.997
1.076
1.539
Li (38.1)
H (-21.5)
b
(-13.1) F
1.866
H (177.3)
1.081
(-116.4) H
1.081
1.460
C
129.4
1.328
H (177.0)
C
106.1
C
1.074
1.987
1.821
1.073
(54.4) Li
H (-4.4)
1.756
F (-6.7)
c
H (177.1)
1.076
(-123.7) F
1.402
C
126.8
1.320
H (176.6)
1.432
107.0
120.9
1.074
C
105.7
121.9
C
2.004
1.601
1.072
H (-4.4)
f
(39.8)Li
F (-17.8)
1.769
H (175.4)
1.076
Li
F(-151.6)
1.745
1.655
(150.0)
1.475
C
124.7
1.327
H (172.9)
1.991
104.1
121.4
1.074
C
113.3
122.1
C
1.082
1.076
(-44.4) H
d
H(-6.1)
H (176.1)
1.074
(-179.7)
Li
1.747
(-127.8)
F
1.650
1.481
C
1.321
(175.3)
H
102.6
1210
1.074
2.013
C
108.6
121.7
C
1423
1.073
F (-23.1)
H(-4.6)
g
H (179.9)
1.082
C
124.1
(179.9) H
1.064
1.311
1.528
1.093
H (123.4)
H (-121.8)
C
117.5
96.6
C
1.460
2.043
(0.0) F
1.836
Li (0.3)
e
H (-179.5)
1.078
C
121.1
(-179.2)F
1.301
1.530
1.356
131.2
H (126.0)
1.091
H (-118.8)
C
121.7
98.8
C
1.092
1.410
2.047
(1.0) F
1.905
Li (1.9)
h

Figure 2.

flat region; the system can move out of this zone (without any energy barrier) toward a minimum corresponding to the structure shown in Fig. 2f. Second, in the case of 1FLi the four minima found are not separated by large energy differences, while in the case of 2FLi structures 2f and 2g are substantially more stable than 2h (Table 1).

A general feature of the lithiated species is that, although the overall system has no net charge, still a polarization of the electron distribution is observable, directed as shown by the group charges (Table 2).[13] The polarization shown, and the possibility that lithium is substantially involved in the transition structures for the carbonyl addition reaction,[3] indicate that the attack could be favoured on the carbon atom closer to the counter-ion. The relative stability and hence the probability of the different structures found for the lithiated anions, suggests that the α carbon can be favoured in the case of 2FLi. The situation could be different in the case of 1FLi, because of the similar stability of the structures where lithium is more directly bound to one of the two terminal carbon atoms, Cα (Fig. 2b-d) or Cγ (Fig. 2e). In the case of attack by a *soft* electrophile on an anionic system (where the allylic HOMO is rather high in energy) the more important orbital interaction is expected to be that between the electrophile's LUMO and the nucleophile's HOMO. The association with the counter-ion changes this situation, in that it lowers significantly the HOMO's energy, thus diminishing the role of the HOMO interaction with the electrophile's LUMO. On the other hand the lithiated species have a rather low energy LUMO, centered on the counter-ion, whose interaction with the HOMO of the carbonyl group could be significant. Thus two orbital interactions have to be considered when dealing with the lithiated species, as indicated schematically in Figure 3, where the HOMO and LUMO[19] of the free anion 1d (left), of formaldehyde (center), and of the lithiated anion 2f (right) are shown (orbital energies from the 6-31+G computations).

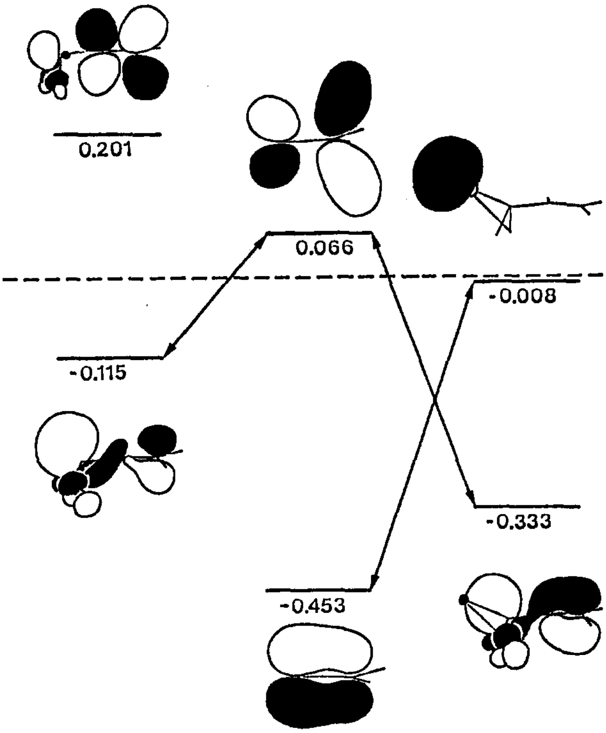


Figure 3.

Because the HOMO of the carbonyl group is polarized toward the oxygen atom, this interaction is maximized if the lithium and oxygen atoms approach in the transition state. It can be noted that because lithium significantly polarizes the HOMO of both 1FLi and 2FLi in the direction of the carbon atom bound to it, and the LUMO of the carbonyl group is polarized toward the carbon atom, the frontier orbitals would as a consequence interact in a more favourable way, if the electrophile approached the allylic system *via* a four-center transition structure (as the one found by Kaufmann and Schleyer for the addition of formaldehyde to methyllithium).[3b]

Aknowledgements. This work has been partially supported by a grant from the Ministero della Pubblica Istruzione and by a computational grant from CSI-Piemonte, Torino. The purchase of the VAX Station 3200 has been made possible by a grant from the Italian C.N.R..

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9. Other possible minima, related by a rotoinversion of the CH$_2$ terminal group, present the localization of a double bond between the Cα and Cβ atoms: the corresponding structures (Kγ, Yγ and Wγ) are significantly less stable than those mentioned above and will not be discussed in this paper. One of them (Yγ) is related to the stable structures of the lithiated species shown in Fig. 4e and h.
10. The pyramidalization angle χ is computed between the CαCβ bond and the normal to the CHF or CF$_2$ plane (a planar structure has χ=90.0°, while a tetrahedral arrangement gives χ =144.7°).
11. The reported values can be compared to the χ values found at the same computational level for the H$_2$CF and HCF$_2$ anions: χ=160.0° and 167.1° respectively.
12. At the same computational level the CC bond length values for ethane and ethene are 1.542 and 1.320 Å respectively.
13. Defining net atomic charges in a Mulliken scheme[14] presents some problems,[15] which can become serious in systems like those studied in the present paper, especially when lithium is present (a clear discussion of this problem can be found in ref.16). For these reasons only a more 'blurred' image of the charge distribution is presented here, in terms of group charges (reducing the problem of overlap partitioning).
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17. The energy of the products of the H$^+$ attack onto the terminal carbon atoms are -313.137090 H (C α) and -313.123886 H (C γ), corresponding to an energy difference of 8.3 kcal mol^{-1} (RHF/3-21+G geometries).
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19. The M.O. drawings of Figure 3 are derived from the graphical output of the program PSI, written by H.B.Schlegel, Wayne State University, U.S.A.