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Equilibrium structures of isolated (halogenated) fluorolithiomethanes☆

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Abstract

Equilibrium structures of isolated fluorolithiomethanes (**1–3**), chlorofluorolithiomethanes (**4–6**), bromofluorolithiomethanes (**7–9**), and bromochlorofluorolithiomethane (**10**) have been calculated at the HF/6-31+G(d,p) and MP2/6-31+G(d,p) levels. Depending on the number of halogens and the computational method employed, five distinct minimum structures could be recognized, viz. normal tetrahedral without coordination of halogen (**T**), trigonal bidentate with coordination of carbon and halogen to lithium (**BCX**), tetrahedral tridentate with coordination of carbon and two halogens to lithium (**TCX2**), quadrilateral bidentate with coordination of two halogens to lithium (**BX2**), and bipyramidal tridentate with coordination of three halogens to lithium (**TX3**). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Fluorocarbanion; Fluorohalocarbanion; Fluorolithiomethane; Fluorohalolithiomethane; Fluoromethyllithium; Fluorohalomethyllithium; Ab initio calculation

1. Introduction

Carbanion chemistry is a powerful tool for organic synthesis. Carbanions bearing both electropositive metal and electronegative halogen atoms at the central atom (so-called *carbenoids*) exert, due to a strong interaction between the metal and halogen atoms, a significant low stability [1–3] which limits their synthetic use. Although bromo- and chlorocarbenoids have intensively been studied [1–3], little attention has been paid to fluorocarbenoids [4]. Organolithium compounds are widely used in synthetic organic chemistry [5] and are suitable for analysis by NMR spectroscopy [6]. However, in contrast to other metals such as zinc or cadmium, highly electropositive lithium brings additional instability into the fluorocarbenoid molecule. The manner of decomposition of both alkane- [7] and alkene-based [8] fluorocarbenoids have been studied. Until now, only one example of the synthetic use of a non-stabilized alkane-based fluorocarbenoid, dibromofluoromethyllithium, at low temperature has been published [9]. Computational feasibility has made simple fluorinated carbanions [10] and fluorinated derivatives of methyllithium [11,12] a promising target for computational chemists. However, in the latter case many calculations either have not been performed at a sufficient computational level [13–15], or are not readily available [16–18]. Moreover, all information about fluorolithioalkanes deals with compounds not containing other halogens, the presence of which should improve their stability [9].

We wish to report, here, the results of our study of potential energy surfaces for isolated fluorolithiomethanes containing all combinations of bromine and chlorine atoms with emphasis on structures and relative energies of individual conformational minima. Structures and relative energies of transition states leading to decomposition, as well as the role of simulated solvents [19] will be addressed in future articles.

2. Computational method

Molecular modeling (MM2) and semi-empirical (AM1) calculations were carried out with the HYPERCHEM [20] program. Ab initio calculations were performed using the PC GAMESS version [21] of the GAMESS (US) QC package [22]. The energy minima were determined by complete optimization of the geometrical parameters by gradient methods [23–25] using the 6-31 + G(d,p) basis set [26–30] with d polarization functions on Li, C, halogens and p polarization function on H [31], and with diffuse functions on Li, C and halogens [32], at the RHF and MP2 [33,34] levels of theory (although a use of more flexible 6-311+ G(d,p) basis set would be desirable, it is not parametrized for

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☆ Part 2 in the series "Fluorinated carbanions".

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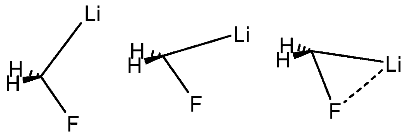
bromine in PC GAMESS). Vibrational frequencies were calculated for all species to characterize them as minima [35]. Calculated charges at carbon atoms were based on Mulliken [36] and Szabo and Ostlund [37] population analyses. Starting structures were chosen to correspond to all possible variants of lithium coordination related to the five structures given below and were generated with the HYPERCHEM [20] program.

3. Results and discussion

3.1. Summarized results

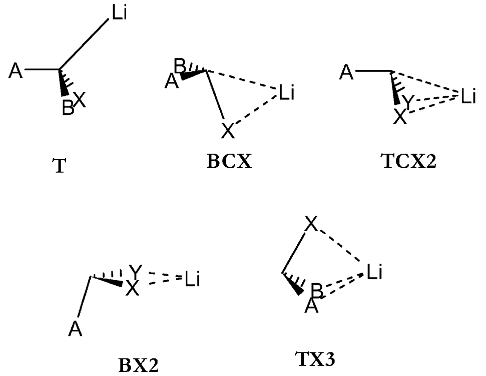
Isolated fluorocarbenoids display characteristic distorted structures which cannot be calculated accurately by molecular modeling and semi-empirical methods. Therefore, ab initio calculations with a sufficiently saturated basis set including polarization and diffuse functions at HF and MP2 levels had to be employed (see Fig. 1).



	1, MM2	**1**, AM1	**1** MP2/6-31+G(d,p)
Li-C-F angle	109.3°	72.7°	60.1°
C-F length	139.2 pm	141.5 pm	158.3 pm

Fig. 1. Role of method in the computation of fluoromethyllithium (**1**).

We have studied potential energy surfaces of 10 fluorolithiomethanes containing all possible combinations of bromine, chlorine and fluorine atoms: three fluorolithiomethanes, viz. fluoromethyllithium (**1**), difluoromethyllithium (**2**), and trifluoromethyllithium (**3**); three chlorofluorolithiomethanes, viz. chlorofluoromethyllithium (**4**), chlorodifluoromethyllithium (**5**), and dichlorofluoromethyllithium (**6**); three bromofluorolithiomethanes, viz. bromofluoromethyllithium (**7**), bromodifluoromethyllithium (**8**), and dibromofluoromethyllithium (**9**); and the mixed halogen compound, bromochlorofluoromethyllithium (**10**). Five distinct structures depending on the computational level, number and type of halogens could be recognized. The first structure, occurring as the minimum only at the HF level, resembles a normal arrangement for tetravalent carbon with sp^3 hybridization; we designate it here with the acronym **T** as tetrahedral. The second structure, which could be found in most compounds, is characterized by strong coordination of one halogen atom to lithium; we designate it here with the acronym **BCX** as bidentate from the point of view of lithium atom with coordination to carbon and halogen. The third structure with tetrahedral arrangement, found mostly in compounds with at least two identical halogens, was assigned as **TCX2** with the name reflecting the tridentate coordination of lithium to carbon and two halogens. Closely related to the **TCX2** structure is the fourth structure, which is characterized by the absence of coordination of lithium to carbon and was designated with the acronym **BX2** as an expression of coordination of lithium to two halogens. The final structure contains lithium coordinated to three atoms, halogens or hydrogen, with the shape of a trigonal bipyramid and was assigned the acronym **TX3** that meant tridentate coordination of lithium to the atoms. All five structures are shown in Fig. 2.



X, Y = halogen; A, B = H, halogen

Fig. 2. Equilibrium structures of (halogenated) fluorolithiomethanes.

Equilibrium structures of fluorolithiomethanes **1**–**10** calculated at the HF and MP2 levels together with their relative energies (in kJ/mol) are listed in Table 1 Difluoromethyllithium (**2**) and trifluoromethyllithium (**3**) are the only compounds, which were computed at the HF level to form normal tetrahedron arrangement along the central carbon atom as a local minimum at the potential energy surface. These minima vanish at the MP2 level. On the other hand, many structures split to halogenocarbene and lithium halide at the HF level, but they exist as local minima when electron correlation (MP2) is included. Surprisingly, in all cases coordination of fluorine to lithium results in less stabilization then coordination to other halogens, chlorine or bromine. Detailed information about energies, geometry of equilibrium structures, and charges on the carbon atom based on Mulliken or Lowdin population analyses, is given in Table 2.

Due to the electron-withdrawing properties of halogen atoms, the carbon atom in most fluorolithiomethanes studied bears either negligible negative charge, or even exerts positive charge. This property is most striking in the **BCX** structures which bear two fluorine atoms not coordinated to lithium. Thus, structures **3 BCF**, **5 BCCl**, and **8 BCBr** are strongly influenced by the electron-withdrawing character of fluorine atoms.

Table 1
Geometries of fluorolithiomethanes **1**–**10** and their relative energies (kJ/mol)

Compound	HF/6-31 + G(d,p)				MP2/6-31 + G(d,p)					
CH_2FLi(**1**)	BCF	TH_2F			BCF	TH_2F				
	0	103			0	97				
CHF_2Li(**2**)	T	BCF	TCF_2	BF_2	BCF	TCF_2				
	26	0	18	25	0	12				
CF_3Li(**3**)	T	BCF[a]	BF_2	TF_3	BCF	BF_2	TF3			
	18	0	15	16	0	9	7			
CHClFLi(**4**)	BCF	BCCl[a]	BClF[a]		BCF	BCCl				
	30	0	43		3	0				
$CClF_2Li$(**5**)	BCF	BClF[a]			BCF	BCCl[a]	TCF_2	BClF[a]	$TClF_2$	
	78	0			36	0	56	27	37	
CCl_2FLi(**6**)	BCF	TCl_2F			BCF	BCCl	$TCCl_2$	BClF	BCl_2	TCl2F
	0	12			9	0	11	34	15	18
CHBrFLi(**7**)	BCBr[a]	BBrF[a]			BCBr					
	0	45			0					
$CBrF_2Li$(**8**)					BCBr[a]	BBrF[a]	$TBrF_2$			
					0	28	43			
CBr_2FLi(**9**)	BCF	BCBr[a]	BBrF[a]	BBr2[a]	BCF	BCBr	TCBr2	BBr_2	TBr_2F	
	71	0	40	8	27	1	0	4	7	
CBrClFLi(**10**)	BCF	BCCl	BClF[a]	BBrCl[a]	BCF	BCBr	BCCl	BBrF	BBrCl	TBrClF
	56	0	37	1	29	0	19	35	19	23

[a] In these cases, the distances between the halogen and lithium atoms exceeded the sums of van der Waals diameters and hence these compounds should be regarded more as complexes of the corresponding carbenes with lithium halides.

Table 2
Energies (hartree), bond lengths (ppm), bond angles (°), and carbon atom charges for minimum structures of fluorolithiomethanes **1**–**10**

Compound	Type	Level	Energy	Bond lengths				Bond angles			Charge on C	
				C–F	C–Li	C–H	C–H	F–C–Li	H–C–Li	H–C–Li	Mull.	Low.
CH_2FLi (**1**)	BCF	HF	−145.885817	158.3	194.1	108.4	108.4	57.9	124.9	124.9	−0.33	−0.17
	TH2F	HF	−145.846506	159.1	215.3	110.3	110.3	50.1	70.8	70.8	−0.28	−0.25
	BCF	MP2	−146.218859	158.3	195.2	109.1	109.1	60.1	125.4	125.4	−0.37	−0.22
	TH2F	MP2	−146.182173	157.8	214.3	111.0	111.0	52.5	70.9	70.9	−0.31	−0.28
				C–F	C–Li	C–H	C–F	F–C–Li	H–C–Li	F–C–Li		
CHF_2Li (**2**)	T	HF	−244.741316	140.8	201.3	108.4	140.8	104.1	134.7	104.1	0.34	0.23
	BCF	HF	−244.750950	156.4	196.1	108.2	135.9	58.0	133.3	118.4	0.21	0.27
	TCF2	HF	−244.744361	147.2	191.2	107.8	147.2	66.9	163.7	66.9	0.05	0.25
	BF2	HF	−244.741598	153.2	232.0	108.5	153.2	48.9	117.4	48.9	0.10	0.21
	BCF	MP2	−245.252663	158.6	197.1	109.2	139.8	59.7	136.6	116.5	0.10	0.22
	TCF2	MP2	−245.248004	150.8	192	108.8	150.8	69.2	165.9	69.2	−0.01	0.21
				C–F	C–Li	C–F	C–F	F–C–Li	F–C–Li	F–C–Li		
CF_3Li (**3**)	T	HF	−343.628911	136.6	203.2	136.6	136.6	115.0	115.0	115.0	0.84	0.50
	BCF[a]	HF	−343.635946	229.1	218.4	127.8	127.8	42.3	120.5	120.5	0.56	0.62
	BF2	HF	−343.630203	151.9	241.2	151.9	131.7	46.4	46.4	106.6	0.64	0.56
	TF3	HF	−343.629784	143.7	217.4	143.7	143.7	58.8	58.7	58.8	0.65	0.55
	BCF	MP2	−344.304523	164.1	200.5	135.7	135.7	57.5	126.1	126.1	0.53	0.53
	BF2	MP2	−344.301388	158.6	245.4	158.6	134.2	46.6	46.6	107.4	0.46	0.52
	TF3	MP2	−344.302049	148.6	222.2	148.7	148.6	58.5	58.5	58.6	0.50	0.52
				C–F	C–Li	C–H	C–Cl	F–C–Li	H–C–Li	Cl–C–Li		
CHClFLi (**4**)	BCF	HF	−604.795218	152.2	194.8	107.7	179.8	59.9	136.1	117.8	−0.16	−0.08
	BCCl[a]	HF	−604.806835	129.5	211.1	108.9	266.4	122.9	123.6	51.8	0.23	0.30
	BClF[a]	HF	−604.790157	136.4	270.6	109.1	293.8	42.7	100.2	43.7	0.18	0.26
	BCF	MP2	−605.252010	157.2	196.6	108.8	178.2	60.5	135.1	118.1	−0.23	−0.13
	BCCl	MP2	−605.253255	140.6	198.7	109.2	196.9	116.4	139.3	69.6	0.05	−0.01
				C–F	C–Li	C–Cl	C–F	F–C–Li	Cl–C–Li	F–C–Li		
$CClF_2Li$ (**5**)	BCF	HF	−703.661550	150.3	197.0	179.3	133.0	60.3	123.8	129.0	0.30	0.26
	BClF	HF	−703.691161	133.6	299.1	375.2	125.9	66.1	33.6	93.3	0.54	0.58
	BCF	MP2	−704.290371	158.7	199.5	177.7	136.7	59.5	127.5	124.7	0.14	0.21
	BCCl[a]	MP2	−704.303908	130.9	216.4	281.1	130.9	123.6	48.0	123.6	0.42	0.53
	TCF2	MP2	−704.282641	150.5	196.8	174.1	150.5	67.3	167.9	67.3	−0.04	0.18
	TClF2	MP2	−704.289816	147.3	229.6	197.5	147.3	56.8	65.1	56.8	0.07	0.30

Table 2 (*Continued*)

Compound	Type	Level	Energy	Bond lengths				Bond angles			Charge on C	
				C–F	C–Li	C–Cl	C–Cl	F–C–Li	Cl–C–Li	Cl–C–Li		
CCl_2FLi (**6**)	BCF	HF	−1063.695204	148.5	196.0	177.5	177.5	61.5	125.2	125.2	−0.15	−0.10
	TCl2F	HF	−1063.690773	139.1	238.8	196.2	196.2	55.2	63.9	63.9	−0.07	0.10
	BCF	MP2	−1064.282142	157.3	198.7	177.0	177.0	60.4	124.8	124.9	−0.25	−0.14
	BCCl	MP2	−1064.285671	136.4	201.4	210.3	176.3	123.8	65.4	129.9	0.21	0.03
	BClF	MP2	−1064.272627	154.8	259.7	176.5	206.8	42.5	117.0	55.0	−0.04	0.06
	BCl2	MP2	−1064.279966	131.6	286.1	211.2	211.2	109.4	49.9	49.9	0.11	0.27
	TCCl2	MP2	−1064.281323	134.6	195.9	192.1	192.1	173.7	78.1	78.1	0.26	0.03
	TCl2F	MP2	−1064.278836	148.5	236.8	192.4	192.4	53.8	64.9	64.9	−0.27	0.00
				C–F	C–Li	C–H	C–Br	F–C–Li	H–C–Li	Br–C–Li		
CHBrFLi (**7**)	BCBr[a]	HF	−2715.276022	129.7	211.0	108.9	276.6	123.4	124.7	54.1	0.24	0.27
	BBrF[a]	HF	−2715.258636	137.7	265.5	109	289.3	43.6	105.1	48.0	0.16	0.21
	BCBr	MP2	−2715.706772	139.9	200.6	109.3	215.8	117.5	138.0	70.2	0.15	−0.02
				C–F	C–Li	C–Br	C–F	F–C–Li	Br–C–Li	F–C–Li		
$CBrF_2Li$ (**8**)	BCBr[a]	MP2	−2814.757899	130.9	216.9	297.1	130.9	124.3	49.2	124.3	0.43	0.51
	BBrF[a]	MP2	−2814.747402	142.2	274.6	299.2	129.0	43.4	46.1	112.0	0.59	0.60
	TBrF2	MP2	−2814.161360	145.7	232.8	220.5	145.7	57.2	64.6	57.2	0.23	0.31
				C–F	C–Li	C–Br	C–Br	F–C–Li	Br–C–Li	Br–C–Li		
CBr_2FLi (**9**)	BCF	HF	−5284.620496	148.1	195.5	193.5	193.5	62.1	125.1	125.1	0.10	−0.14
	BCBr[a]	HF	−5284.647585	127.0	219.1	321.3	187.0	123.5	44.5	122.7	0.30	0.25
	BBrF[a]	HF	−5284.632388	132.7	297.4	385.8	186.4	34.5	35.1	113.0	0.27	0.22
	BBr2[a]	HF	−5284.644484	123.8	314.6	303.1	210.4	107.7	42.9	53.0	0.45	0.32
	BCF	MP2	−5285.179132	156.1	198.1	194.2	194.3	61.3	125.1	125.1	0.00	−0.18
	BCBr	MP2	−5285.189127	135.8	201.4	219.4	197.2	137.0	70.0	116.6	0.28	−0.02
	BBr2	MP2	−5285.188114	131.4	298.8	227.9	227.9	109.9	51.0	51.0		
	TCBr2	MP2	−5285.189420	133.7	199.3	211.8	211.8	175.2	77.0	77.0	0.33	0.03
	TBr2F	MP2	−5285.186771	147.3	243.4	210.9	210.9	52.7	65.7	65.7	0.04	−0.02
				C–F	C–Li	C–Br	C–Cl	F–C–Li	Br–C–Li	Cl–C–Li		
CBrClFLi (**10**)	BCF	HF	−3174.157316	148.2	195.6	194.5	176.8	62.0	121.3	128.5	−0.04	−0.13
	BCCl	HF	−3174.178640	126.8	220.6	186.7	328.1	123.3	123.0	39.2	0.33	0.28
	BClF[a]	HF	−3174.164368	132.5	298.8	186.5	380.8	34.0	112.8	32.9	0.28	0.22
	BBrCl[a]	HF	−3174.178153	124.8	316.0	325.0	186.0	108.6	40.9	51.6	0.26	0.31
	BCF	MP2	−3174.730259	156.5	197.8	196.1	175.7	61.2	115.8	133.5	−0.15	−0.16
	BCBr	MP2	−3174.741023	135.4	203.7	235.0	175.4	125.0	64.4	128.2	0.25	0.03
	BCCl	MP2	−3174.733914	136.3	199.0	197.8	198.3	138.1	115.6	70.7	0.24	−0.02
	BBrF	MP2	−3174.727772	154.4	265.4	225.0	176.3	40.9	56.6	114.6		
	BBrCl	MP2	−3174.734059	131.6	291.9	230.1	208.9	109.9	51.8	49.0		
	TBrClF	MP2	−3174.732513	145.0	239.9	212.2	190.9	53.2	65.6	65.3	−0.09	−0.01

[a] In these cases the distances between the halogen and lithium atoms exceeded the sums of van der Waals diameters and hence these compounds should be regarded more as complexes of the corresponding carbenes with lithium halides.

3.2. *Fluoromethyllithium (**1**)*

Only two equilibrium structures have been found for fluoromethyllithium (**1**), both at HF and at MP2 levels (see Fig. 3) in agreement with previous calculations[1] [13–15]. Without an inclusion of the electron correlation, the role of fluorine–lithium coordination seems to be overestimated, and the calculated lithium–fluorine bond length is too short. The umbrella-type structures **1 TH2F** have higher potential

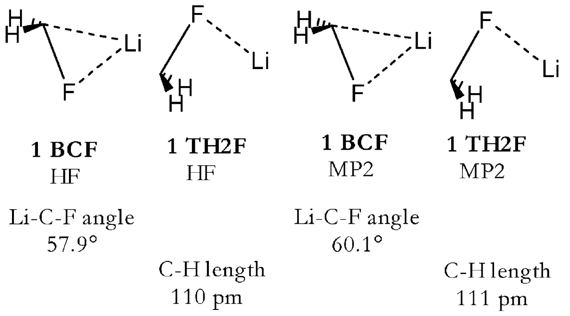


Fig. 3. Equilibrium structures of fluoromethyllithium (**1**).

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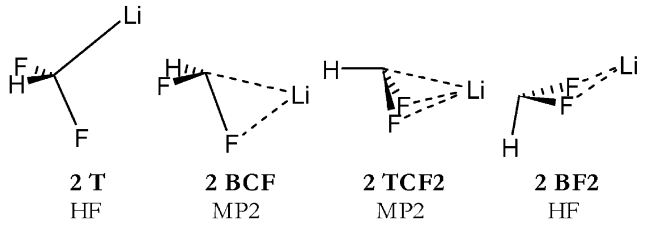
[1] Only structures with carbanion character have been included into this paper. Complexes of carbenes with lithium halides, e.g. $H_2C\cdots LiF$, are hence omitted and will be discussed in the next paper dealing with decomposition pathways of fluorolithiomethanes.

energy then the global minimum **1 BCF** structures and resemble carbene–LiF complexs. The C–H bonds in the **TH2F** structure are little longer, probably due to some level of the interaction with lithium. As can be shown in Fig. 3, structures for compound **1** both at the HF and the MP2 levels are analogous. As we have found that this is common for structures **1–10**, only the MP2 structures will be given further providing that the HF structures do not differ significantly.

3.3. Difluoromethyllithium (2)

We have found four minimum structures for difluoromethyllithium (**2**) at the HF level, viz. **2 T**, **2 BCF**, **2 BF2** and **2 TCF2** (see Fig. 4). Two of these structures have been reported previously [11,12]. On the other hand, the existence of the umbrella-type structure (**2 THF2**) previously found by the calculations at a lower level [13–15] was not confirmed by our calculations. By optimizations including correlation energy, two of four original minima vanished and only structures **2 BCF** and **2 TCF2** were recognized. The energy differences between the minimum structures were much smaller than in the case of fluoromethyllithium (**1**) (see Table 1), probably due to a mobility of positively charged lithium enhanced by the presence of more electron-withdrawing substituents.

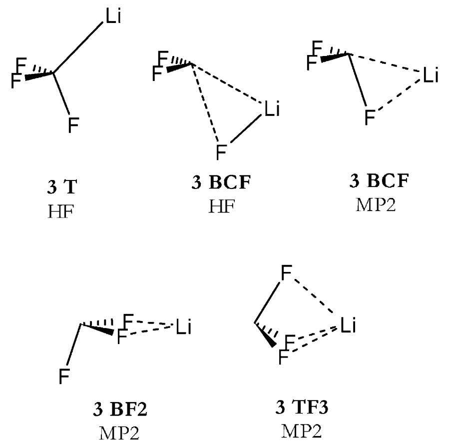


2 T HF | **2 BCF** MP2 | **2 TCF2** MP2 | **2 BF2** HF

Fig. 4. Equilibrium structures of difluoromethyllithium (**2**).

3.4. Trifluoromethyllithium (3)

Two minima (**3 BX2** and **3 TX3**) have been computed for trifluoromethyllithium (**3**) in [16–18] using a similar level to that employed here. We have found two additional minimum structures, viz. **3 T** and **3 BCF** (see Fig. 5). Although the former minimum vanished when electron correlation was included, the latter is the most stable structure for trifluoromethyllithium (**3**). Again, as a result of the presence of more fluorine atoms, the energy differences among individual conformational minima were smaller in agreement with difluoromethyllithium (**2**). In comparison with difluoromethyllithium (**2**), an energy minimum for structure **3 TCF2** was not obtained, probably due to the repulsion between positively charged lithium and positively charged carbon (see Table 2). The difference in geometry between **3 BCF** structures is remarkable: when calculated at the HF level, it resembles a difluorocarbene–lithium fluoride complex, but at the MP2 level it acquires carbanion-like geometry.



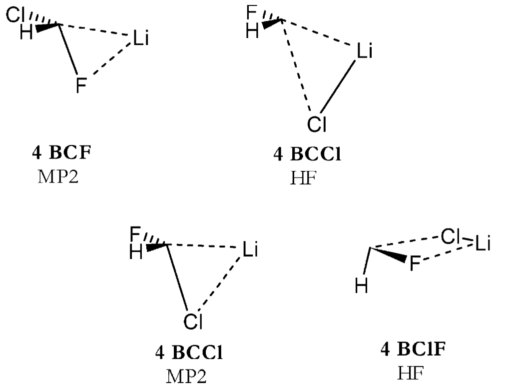
3 T HF | **3 BCF** HF | **3 BCF** MP2

3 BF2 MP2 | **3 TF3** MP2

Fig. 5. Equilibrium structures of trifluoromethyllithium (**3**).

3.5. Chlorofluoromethyllithium (4)

The presence of two different halogens in the carbenoid **4** makes possible the existence of two different bridged BCX structures. This was indeed observed both at the HF and at the MP2 levels. Although both **4 BCF** structures have carbanion geometry, the **4 BCCl** structure at the HF level more resembles a fluorocarbene–lithium chloride complex in analogy to trifluoromethyllithium (**3**). Only one more equilibrium structure at the HF level was found, viz. **4 BClF**, but again a long carbon–chlorine distance points to the fluorocarbene–lithium chloride complex. At the HF level, the difference between the energies of **4 BCCF** and **4 BCCl** structures is quite large (30 kJ/mol), the latter structure being more stable. At the MP2 level, this difference became quite negligible (3 kJ/mol) (see Fig. 6).



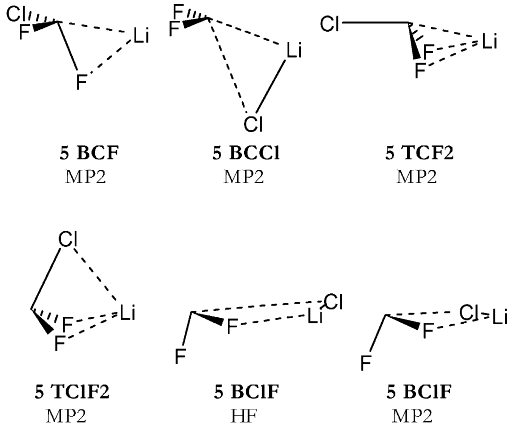
4 BCF MP2 | **4 BCCl** HF

4 BCCl MP2 | **4 BClF** HF

Fig. 6. Equilibrium structures of chlorofluoromethyllithium (**4**).

3.6. Chlorodifluoromethyllithium (5)

At the HF level, only one stable carbanion structure was found, viz. **5 BCF**. Optimizations started from other conformations led to splitting to difluorocarbene and lithium chloride. Another structure found, **5 BClF**, should again be regarded as a difluorocarbene–lithium chloride complex. Computations at the MP2 level led to strikingly different results and all characteristic structures were found as minima. Two structures, **5 BCCl** and **5 BClF**, are hybrids between a carbanion and carbene–lithium halide complex structures. Interestingly, **5 TCF2** structure is a minimum structure at the MP2 level, but a transition state at the HF level, as was found by vibration analysis. **5 BCCl** is the structure with minimal energy at the MP2 level and in contrast to trifluoromethyllithium (**3**) the energy differences among individual structures **5** are higher (maximum 56 kJ/mol between the **5 BCCl** and **5 TCF2** structures (see Fig. 7).

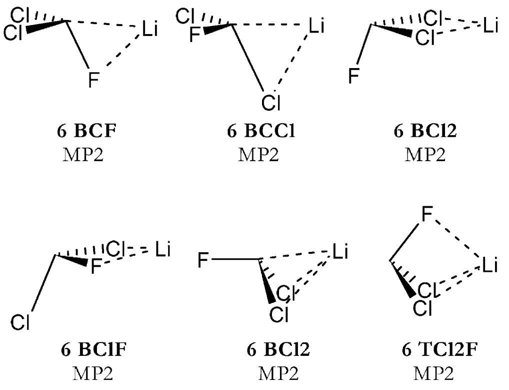

5 BCF MP2 **5 BCCl** MP2 **5 TCF2** MP2

5 TClF2 MP2 **5 BClF** HF **5 BClF** MP2

Fig. 7. Equilibrium structures of chlorodifluoromethyllithium (**5**).

3.7. Dichlorofluoromethyllithium (6)

Computation results analogous to chlorodifluoromethyllithium (**5**) were obtained for dichlorofluoromethyllithium (**6**). At the HF level, splitting to carbene and lithium halide is a usual case and only two equilibrium structures were detected, *viz.* **6 BCF** and **6 TCl2F**. When electron correlation was included, six equilibrium structures were calculated with pure carbenoid structures. Again, the structures **6 TCCl2** and **6 BCl2** represent energy minima at the MP2 level, but transition states at the HF level. The energy differences among individual conformational minima are smaller (maximum 34 kJ/mol) then in chlorodifluoromethyllithium (**5**) (see Fig. 8).


6 BCF MP2 **6 BCCl** MP2 **6 BCl2** MP2

6 BClF MP2 **6 BCl2** MP2 **6 TCl2F** MP2

Fig. 8. Equilibrium structures of dichlorofluoromethyllithium (**6**).

3.8. Bromofluoromethyllithium (7)

A number of equilibrium structures found for bromofluoromethyllithium (**7**) is low both at the HF and at the MP2 levels. While at the HF level most starting geometries led to splitting to fluorocarbene and lithium bromide, at the MP2 level all geometries converged to the **7 BCBr** structure. The only other structure found at the HF level was type **7 BBrF**. Moreover, both equilibrium structures found at the HF level are again borderline cases between a carbenoid structure and carbene–lithium bromide complex (see Fig. 9).

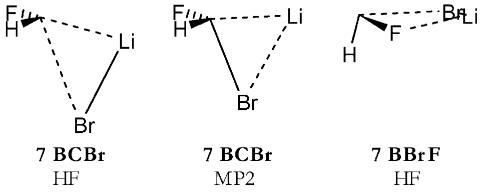

7 BCBr HF **7 BCBr** MP2 **7 BBrF** HF

Fig. 9. Equilibrium structures of bromofluoromethyllithium (**7**).

3.9. Bromodifluoromethyllithium (8)

The tendency of bromofluoromethyllithium structures to split as calculated at the HF level is most strikingly demonstrated for bromodifluoromethyllithium (**8**): no carbanion structure minima were found. At the MP2 level, three energy minima were detected, viz. **8 BCF**, **8 BBrF** and **8 TBrF2**, but the first two are again the borderline case between the carbenoid structure and a difluorocarbene–lithium bromide complex (see Fig. 10).

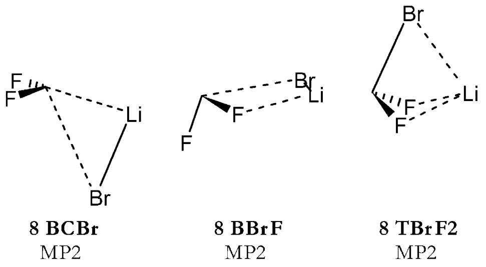
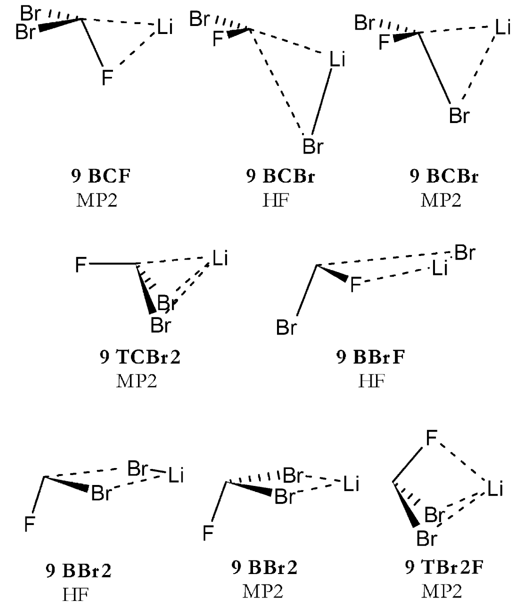

8 BCBr MP2 **8 BBrF** MP2 **8 TBrF2** MP2

Fig. 10. Equilibrium structures of bromodifluoromethyllithium (**8**).

3.10. Dibromofluoromethyllithium (9)

From the four minimum structures calculated at the HF level, only the **9 BCF** type has a carbenoid structure. Two other, viz. **9 BCBr** and **9 BBrF**, should be regarded as complexes of bromofluorocarbene with lithium bromide. The last one, **9 BBr2**, is the borderline case. In contrast to this, five carbanion structures, viz. **9 BCF**, **9 BCBr**, **9 TCBr2**, **9 BBr2** and **9 TBr2F** were found by calculations at the MP2 level. At the HF level, the energy differences between individual conformers are higher than at the MP2 level, dihalocarbene–lithium bromide being the most stable structures (see Fig. 11).

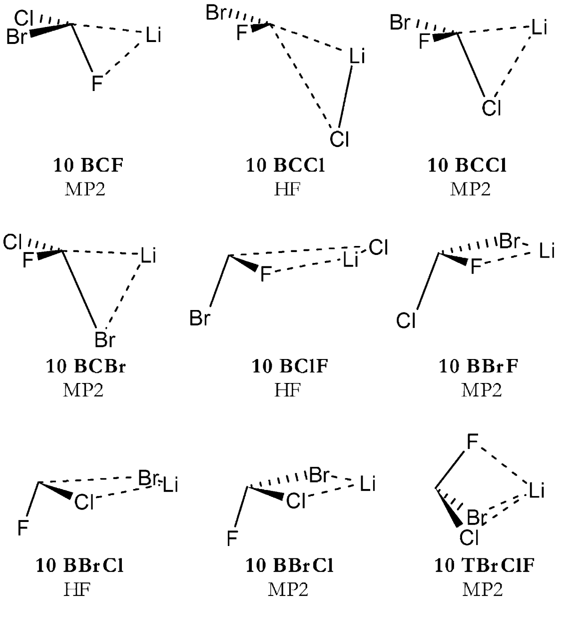


9 BCF MP2; **9 BCBr** HF; **9 BCBr** MP2; **9 TCBr2** MP2; **9 BBrF** HF; **9 BBr2** HF; **9 BBr2** MP2; **9 TBr2F** MP2

Fig. 11. Equilibrium structures of dibromofluoromethyllithium (**9**).

*3.11. Bromochlorofluoromethyllithium (**10**)*

At the HF level, only **10 BCF** structure with relatively high energy can be regarded as a carbanion, three other structures **10 BCCl**, **10 BClF** and **10 BBrCl** correspond more to complexes of halocarbenes with lithium halides. This is a contrast to the more reliable calculations at the MP2 level, where all three possible triangular **BCX** structures (**10 BCF**, **10 BCBr**, **10 BCCl**) were found to have carbanion character. Moreover, three other stable minimum structures, viz. **10 BBrF**, **10 BBrCl** and **10 TBrClF** were calculated. Among the **BCX** structures, **BCBr** is the most and **BCF** the less stable structure in agreement with other calculated structures (see Fig. 12).



10 BCF MP2; **10 BCCl** HF; **10 BCCl** MP2; **10 BCBr** MP2; **10 BClF** HF; **10 BBrF** MP2; **10 BBrCl** HF; **10 BBrCl** MP2; **10 TBrClF** MP2

Fig. 12. Equilibrium structures of bromochlorofluoromethyllithium (**10**).

4. Conclusions

In (halogenated) fluorolithiomethanes, several conformational minima could be formed in most cases. The presence of more halogen atoms at the carbon atom results in more complex PES with more conformational minima, the energy differences between them being smaller. Although the calculations of transition states leading to splitting to (halo)-carbene and lithium halide were not performed (but will be the subject of our further study), the data from minimization computations indicate that the most unstable carbenoids are chlorodifluoromethyllithium (**5**) and bromodifluoromethyllithium (**8**). On the other hand, the presence of more heavier halogen atoms in the molecule (carbenoids **6**, **9**, **10**) seems to stabilize the carbenoid structure in agreement with experimental data [6].

Acknowledgements

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