A Comparative Theoretical Study of the Effects of First- and Second-row Substituents in α-Substituted Carbanions

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This paper reports the investigations we carried out on substituent effects in the carbanions $H_2\bar{C}$–X (where X = F, Cl, OH, or SH), using an *ab initio* SCF-MO treatment with three different basis sets of at least double zeta quality augmented with a set of diffuse *p* functions on carbon and with or without diffuse *p* functions and *d* polarization functions on the heteroatoms. It was found that with all these substituents the carbanion centre is pyramidal, with inversion barriers that are larger than that of $H_3\bar{C}$, and which decrease in the order Cl > F > OH > SH. We also found that the order of stabilization energies is Cl > SH > F > OH. The 3*d* orbitals play a negligible role in determining the stabilization energies of $H_2\bar{C}$–Cl and $H_2\bar{C}$–SH. However, the 3*d* orbitals have a significant effect on the determination of some structural properties of $H_2\bar{C}$–SH and $H_2\bar{C}$–Cl.

Carbanions are very reactive species and play an important role in the chemical synthesis[1] as well as in physical organic chemistry.[2] One of the most important groups of carbanions is the α-substituted carbanions. In this paper we report the results obtained in a comparative study of the effects of first- and second-row substituents on various properties of the carbanions $H_2\bar{C}$–X. In particular we compare the effects of OH *versus* F and SH *versus* Cl (a comparison along a row of the Periodic Table) and the effects of OH *versus* SH and F *versus* Cl (a comparison down a column of the Periodic Table).

To obtain reliable information on the structure of these carbanions we used three different basis sets of at least double zeta quality augmented with a set of diffuse *p* functions on carbon and with or without diffuse *p* functions and *d* polarization functions on the heteroatoms. The inclusion of the diffuse *p* functions on carbon seems to be essential to obtain a reliable description of the geometry at the carbanion centre.[3,4] One of the main purposes of this paper is, in fact, to compute reliable estimates of the inversion barriers and the pyramidalization angles of the various carbanions, since this type of information is of relevance in stereochemical studies. Also the inclusion of the 3*d* orbitals for the second-row heteroatoms seems to have a significant effect on the description of the C–X bond lengths, according to recent results[5] obtained for $H_2\bar{C}$–SH. This finding seems to contradict, at least partly, the results of a previous investigation[6] where the role of the *d* orbitals on the static, dynamic, and chemical properties of the anion $H_2\bar{C}$–SH was found to be negligible. This conclusion has now been found to be an artifact of the geometry optimization procedure used, which was based on a one-dimensional search for each chosen co-ordinate and which provided C–S bond lengths that were too long to permit the *d* orbital effects to be exerted.

This type of difficulty can be overcome through the use of a variable metric procedure based on the analytical calculated gradient[7,8] to optimize the geometry. Consequently, all the structures discussed in this paper have been fully optimized with a gradient procedure at the *ab initio* SCF level.

Results and Discussion

All computations have been performed with the Gaussian 80 series of programs[9] and the various geometries have been fully optimized with an analytical gradient procedure. The computations have been carried out using the following basis sets:

Table 1. Pyramidalization angles, θ, (°) and inversion barriers, IB, (kcal mol^{-1}) of $H_3\bar{C}$ computed with various basis sets

Basis set	θ	IB
STO-3G[a]	74.60	23.96
4-31G[b]	66.46	8.10
[4*s*2*p*][c]	60.37	4.79
2Z	47.46	1.31
2ZD+	58.03	3.97
Duke[d]	53.78	1.71

[a] Reference 12. [b] Reference 13. [c] Reference 10. [d] Reference 11.

(1) A basis set of double zeta quality[3,10] (denoted here by 2Z) where for C we used a (9*s*5*p*) basis contracted to [4*s*2*p*] with an additional set of diffuse *p* functions, for O and F a (9*s*5*p*) basis contracted to [4*s*2*p*], for S and Cl an (11*s*7*p*) basis contracted to [6*s*4*p*], and for H a (4*s*) basis contracted to [2*s*].

(2) A basis set of the type described in (1) with an additional set of 3*d* orbitals on S and Cl (denoted here by 2ZD);

(3) A basis set of the type described in (2) with an additional set of *d* orbitals on C, O, and F and of diffuse *p* functions[3] on O, F, S, and Cl (denoted here by 2ZD+).

The *d* orbital coefficients used are 0.85 for O, 0.90 for F, 0.52 for S, and 0.35 for Cl and have been optimized for the corresponding carbanions at the optimum 2Z geometry. For C we used the value of 0.75, which has been optimized for $H_3\bar{C}$ at the optimum 2Z geometry. The coefficients of the diffuse *p* functions have been taken from reference 3.

The values of the inversion barriers and pyramidalization angles computed for $H_3\bar{C}$ with these basis sets are reported in Table 1, together with the values obtained with other basis sets. The pyramidalization angle is the supplementary angle to the angle between the C–H axis (or the C–X axis for the α-substituted carbanions) and the HCH plane, while the inversion barrier is the energy difference between the total energy values of the ground state and of the transition state to inversion. The results presented have to be compared with the 'accurate' values of 1.71 kcal mol^{-1} for the inversion barrier and 53.78° for the pyramidalization angle computed by Duke.[11] It can be seen

Table 2. Total energies and geometric parameters of the relevant conformations of $H_2\bar{C}$–H, $H_2\bar{C}$–F, and $H_2\bar{C}$–Cl computed at various computation levels

Carbanion		Planar			Pyramidal		
		2Z	2ZD	2ZD+	2Z	2ZD	2ZD+
$H_2\bar{C}$–H	r(C–H) (Å)	1.091		1.089	1.107		1.111
	$H\hat{C}H$ (°)	120.0		120.0	112.2		108.1
	θ (°)	0		0	47.47		58.1
	E_T (a.u.)	−39.487 02		−39.495 45	−39.489 11		−39.501 77
$H_2\bar{C}$–F	r(C–F) (Å)	1.485		1.412	1.568		1.485
	r(C–H) (Å)	1.079		1.078	1.120		1.116
	$H\hat{C}H$ (°)	133.5		130.7	105.7		104.0
	θ (°)	0		0	73.7		71.3
	E_T (a.u.)	−138.331 12		−138.364 71	−138.357 18		−138.392 55
$H_2\bar{C}$–Cl	r(C–Cl) (Å)	1.971	1.887	1.848	2.244	2.098	2.118
	r(C–H) (Å)	1.076	1.078	1.076	1.114	1.114	1.106
	$H\hat{C}H$ (°)	137.4	132.7	131.8	105.4	105.9	103.9
	θ (°)	0	0	0	85.7	80.4	82.6
	E_T (a.u.)	−498.370 73	−498.381 71	−498.402 41	−498.404 70	−498.409 84	−498.436 68

Table 3. Total energies and geometric parameters of the relevant conformations of $H_2\bar{C}$–OH and $H_2\bar{C}$–SH computed at various computation levels

		Y			TS			W		
Carbanion		2Z	2ZD	2ZD+	2Z	2ZD	2ZD+	2Z	2ZD	2ZD+
$H_2\bar{C}$–OH	r(–O) (Å)	1.541		1.491	1.478		1.432	1.528		1.484
	r(C–H) (Å)	1.118		1.114	1.084		1.084	1.123		1.120
	r(O–H) (Å)	0.958		0.947	0.960		0.950	0.966		0.954
	$H\hat{C}H$ (°)	106.3		104.6	126.7		125.1	106.9		105.0
	$C\hat{O}H$ (°)	105.7		103.8	109.5		107.9	112.5		109.5
	θ (°)	65.8		65.4	−3.2		−2.5	−63.2		−63.0
	E_T (a.u.)	−114.323 51		−114.368 47	−114.304 72		−114.347 08	−114.319 02		−114.363 52
$H_2\bar{C}$–SH	r(C–S) (Å)	2.014	1.828	1.852	1.825	1.760	1.738	1.962	1.793	1.816
	r(C–H) (Å)	1.111	1.102	1.104	1.084	1.089	1.086	1.109	1.101	1.102
	r(S–H) (Å)	1.357	1.352	1.348	1.385	1.369	1.376	1.378	1.375	1.369
	$H\hat{C}H$ (°)	108.2	111.9	107.5	124.2	119.1	120.5	108.9	112.1	108.7
	$C\hat{S}H$ (°)	98.6	101.5	100.8	105.8	105.4	107.2	108.0	109.3	109.3
	θ (°)	69.2	52.2	62.7	8.0	22.1	9.5	−62.9	−45.4	−55.8
	E_T (a.u.)	−436.985 44	−437.015 32	−437.038 59	−436.975 70	−437.014 49	−437.031 87	−436.985 58	−437.019 52	−437.040 66

Table 4. Stabilization energies, SE (kcal mol^{-1}) and inversion barriers, IB (kcal mol^{-1}) for the carbanions $H_2\bar{C}$–X

	SE			IB		
X	2Z	2ZD	2ZD+	2Z	2ZD	2ZD+
H	0		0	1.31		3.97
F	11.92		7.69	16.36		17.47
Cl	29.41	22.48	27.23	21.34	17.65	21.50
OH	2.96		1.79	11.79		13.42
SH	21.03	19.12	21.82	6.20	3.16	5.52

that basis sets that do not contain diffuse *p* functions on carbon, such as STO-3G,[12] 4-31G,[13] and [4*s*2*p*],[10] provide values of the inversion barrier and pyramidalization angle that differ significantly from the reference values, while the basis sets 2Z and 2ZD+, which contain diffuse *p* functions, provide much more accurate results. In particular it was found that the 2Z basis set slightly underestimates the inversion barrier and the pyramidalization angle, while the 2ZD+ basis set, where we have added a set of five carbon *d* orbitals to the 2Z basis set, slightly overestimates these values. It is interesting to point out that in all cases, even at computational levels that provide very small values of the inversion barrier, $H_3\bar{C}$ is strongly pryamidal (for comparison, the pyramidalization angle for $H_3\bar{C}$ with tetrahedral angles is 54.7°).

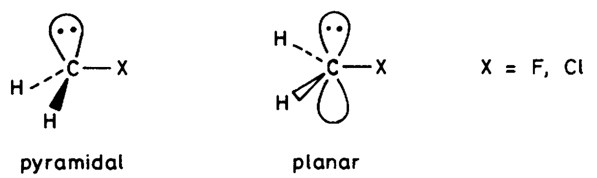
The geometric parameters and total energies for the various minima and transition states found in the study of the various carbanions are listed in Tables 2 and 3, while the computed inversion barriers are listed in Table 4. The transition states to inversion for $H_2\bar{C}$–H, $H_2\bar{C}$–F, and $H_2\bar{C}$–Cl correspond, by symmetry, to the planar structures and therefore the corresponding geometries have been optimized with the constraint of planarity. On the other hand, the transition states to inversion for $H_2\bar{C}$–OH and $H_2\bar{C}$–SH, where there are no constraints of planarity for the carbanion, have been fully optimized: in these cases it has been found that the carbanion centre is non-planar, the effect being particularly significant in $H_2\bar{C}$–SH.

We have also compared the effect of these substituents on the stability of the anions by means of the isodesmic proton-transfer reaction[14] given in equation (1). We defined the stabilization energy of a substituent X as in equation (2). A positive value of SE indicates stabilization of the anion relative to neutral methane. The computed SE values for the various substituents are listed in Table 4. In order to compute these energy differences, we have also fully optimized the species H_3C–X, where X = H, F, Cl, OH, or SH at the 2Z, 2ZD, and 2ZD+ levels. The total energy values together with the optimized C–X bond lengths are listed in Table 5.

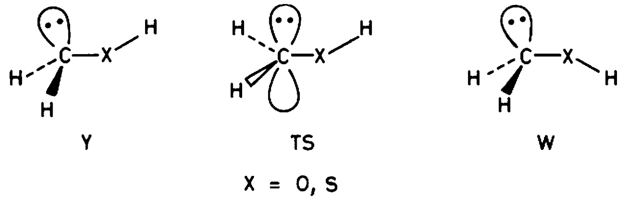
Table 5. Total energies of the optimized structures of the $H_3C–X$ molecules (X = H, F, Cl, OH, or SH) computed at the various computation levels, together with the optimized C–X bond length

	E_T (a.u.)			r(C–X) (Å)			
Molecule	2Z	2ZD	2ZD+	2Z	2ZD	2ZD+	Exp.[a]
$H_3C–H$	−40.177 00		−40.189 27	1.094		1.093	1.094
$H_3C–F$	−139.026 08		−139.067 79	1.423		1.367	1.385
$H_3C–Cl$	−499.045 76	−499.061 91	−499.080 78	1.865	1.827	1.812	1.784
$H_3C–OH$	−115.006 69		−115.053 12	1.436		1.402	1.427
$H_3C–SH$	−437.639 96	−437.676 94	−437.693 39	1.871	1.821	1.819	1.818

[a] See ref. 15.



Scheme 1.



Scheme 2.

$$H_2\bar{C}–X + CH_4 \rightleftarrows H_3C–X + H_3\bar{C} \quad (1)$$

$$SE = E(H_3C–X + H_3\bar{C}) - E(H_2\bar{C}–X + CH_4) \quad (2)$$

The analysis of these results shows the following.

(i) $H_2\bar{C}–F$ and $H_2\bar{C}–Cl$ exist in a stable pyramidal form, while $H_2\bar{C}–OH$ and $H_2\bar{C}–SH$ exist in two different stable pyramidal species, which can be conveniently denoted as Y and W (see Schemes 1 and 2). In $H_2\bar{C}–OH$ the Y conformation is found to be more stable than W (2.82 and 3.11 kcal mol^{-1} at the 2Z and 2ZD+ levels, respectively), while in $H_2\bar{C}–SH$ W is more stable than Y by 0.09, 2.64, and 1.30 kcal mol^{-1} at the 2Z, 2ZD, and 2ZD+ levels, respectively. These results agree with those obtained in previous investigations.[6]

(ii) As expected, the effect of the *d* orbitals on the geometrical parameters of the carbanions containing first-row substituents is small. On the other hand, the *d*-orbital effect is significant when determining the C–X bond length in the carbanions containing second-row substituents.

(iii) The C–X bond length on conversion of $H_3C–X$ into $H_2\bar{C}–X$ increases in all cases, except in the process $H_3C–SH \longrightarrow H_2\bar{C}–SH$ when the computations are performed with explicit inclusion of the sulphur 3*d* orbitals, *i.e.*, at the 2ZD and 2ZD+ levels. It has been previously suggested[5] that a decrease (increase) in the C–X bond length for the process $H_3C–X \rightarrow H_2\bar{C}–X$ should signal conjugative stabilization (destabilization) of the carbanion by X. Therefore, these results suggest that the substituents Cl, F, and OH cause conjugative destabilizations that decrease in the order Cl > F > OH. With SH, the conjugative effect is destabilizing when the basis set does not contain sulphur 3*d* orbitals (2Z level), while it becomes slightly stabilizing when the 3*d* orbitals are taken into account (2ZD and 2ZD+ levels).

(iv) In all of the cases investigated the carbanion is pyramidal. The substitution in $H_3\bar{C}$ of a hydrogen atom with Cl, F, or OH causes an increase of the pyramidalization angle, with the substituent effect following the order Cl > F > OH. The effect of SH is again basis-set dependent: at the 2Z level the pyramidalization angle is larger than that in $H_3\bar{C}$, the effect being of an order of magnitude similar to that shown by OH, while at the 2ZD and 2ZD+ levels the pyramidalization angle in $H_2\bar{C}–SH$ becomes slightly smaller than that in $H_3\bar{C}$.

(v) The substitution in $H_3\bar{C}$ of a hydrogen atom with Cl, F, OH, or SH causes an increase in the inversion barrier, with the substituent effect following the order Cl > F > OH > SH. This order is found at all three computational levels used here and parallels that found for the pyramidalization angle. In turn, both of these trends follow the order shown by the variation of the C–X bond length in the process $H_3C–X \rightarrow H_2\bar{C}–X$ and support the previous suggestion about the conjugative effects of the various substituents.

(vi) The order of stabilization energies (SE) is Cl > SH > F > OH. This order is found at all three computational levels and, therefore, without or with 3*d* orbitals on the heteroatoms. The SE values are positive in all cases, large for Cl and SH, smaller for F and small for OH. Therefore, in the comparative analysis down a column of the Periodic Table, the second-row heteroatom introduces a larger stabilization than the corresponding first-row heteroatom, while in the comparative analysis along a row of the Periodic Table the stabilization increases with increasing electronegativity of the heteroatom. The SE values for F and OH obtained here are significantly smaller than those reported in reference 14, computed with basis sets that do not contain diffuse *p* functions on carbon. On the other hand, the present results agree well with those obtained by Schleyer *et al.*,[16] who use basis sets augmented with diffuse functions.

(vii) The use of a large basis set such as 2ZD+, containing diffuse *p* functions and *d* orbitals on all the atoms except the hydrogens, leads to results that are very similar to those obtained at the 2Z level for carbanions containing first-row substituents and to those obtained at the 2ZD level for carbanions containing second-row substituents.

Conclusions

In recent years α-substituted carbanions have been extensively investigated at the theoretical level, in particular α-oxy- and thio-carbanions.[6,17–20] These studies led to the conclusion that the sulphur 3*d* orbitals do not play a significant role in determining the differences between α-oxy- and thio-carbanions. They also suggested that polarization effects control the stabilization of these carbanions, while the orbital-interaction effects are mainly responsible for the different conformational preferences. In a more recent investigation[5] with full geometry optimization it was found that the 3*d* orbitals play a significant role in determining some of the geometrical parameters of $H_2\bar{C}$–SH. In this paper we re-examined the role of the 3*d* orbitals on various properties not only in $H_2\bar{C}$–SH, but also in $H_2\bar{C}$–Cl. For comparative purposes we extended the investigation to $H_2\bar{C}$–OH and $H_2\bar{C}$–F. We found that the 3*d* orbitals play a negligible role in determining the pyramidalization angle and the inversion barrier of $H_2\bar{C}$–Cl, and the stabilization energies of $H_2\bar{C}$–SH and $H_2\bar{C}$–Cl. However, the 3*d* orbitals have a more pronounced effect on the determination of the C–S bond length, the pyramidalization angle, and the inversion barrier of $H_2\bar{C}$–SH. The nature of the *d*-orbital effect in $H_2\bar{C}$–SH has been previously analysed[5] and it was found that the inclusion of these orbitals makes the conjugative effect stabilizing. This finding is consistent with the present results, since the values of the C–S bond length, the pyramidalization angle, and the inversion barrier decrease with inclusion of the 3*d* orbitals. For $H_2\bar{C}$–Cl the indications are that the conjugative effect remains destabilizing with or without the inclusion of the 3*d* orbitals.

In the present study we also found that these carbanions are all pyramidal with inversion barriers that are larger than that of $H_3\bar{C}$ and that decrease in the order Cl > F > OH > SH. Furthermore, we found that Cl stabilizes the carbanion centre more than SH, while F stabilizes more than OH, and also that Cl and SH stabilize the carbanion centre more than the corresponding first-row substituents F and OH.

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