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A theoretical study of substituent effects on the structure of isolated and condensed three-membered rings. A comparison between radicals and parent hydrocarbons

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Abstract. Substituent effects on the structure of radicals and parent hydrocarbons formed by isolated or condensed three-membered rings have been investigated by Hartree-Fock, post-Hartree-Fock and density functional methods. The trends of structural parameters computed for the hydrocarbon systems are in agreement with available experimental data. Substituent effects can be rationalized in terms of interactions between localized orbitals obtained by natural bond analysis. The effects are even larger in free radicals and can be analyzed using the same model.

Key words: Free-radical structure – Three-membered rings – Structural substituent effects – Theoretical calculations

1 Introduction

The chemistry of cyclopropane has received much attention in the past and many cyclopropane derivatives have been studied by microwave spectroscopy [1]. The structural modifications induced by replacement of hydrogens by heteroatoms (X) have been discussed in terms of the interactions between the C-X bond and the characteristic molecular orbitals of small saturated cycles. Hoffmann [2] suggested that conjugation between unsaturated substituents and the delocalized electron system of the ring gives rise to a lengthening of the C-C bond geminal to the substituent and to a corresponding shortening of the C-C bond not involving the substituted carbon atom. These considerations originate quite naturally from the description of the cyclopropane ring according to the Walsh model [3, 4]. A good π-acceptor substituent (e.g. CN) weakens the geminal C-C bonds and the opposite occurs when the

substituent is a good π-donor (e.g. NO_2). Further experimental and theoretical analysis of the structural consequences of cyclopropyl homoconjugation has recently been presented [5, 9]. On the same topic, very few conclusions have been presented concerning bicyclo[1.1.0]butane, which can be considered to be a substituted cyclopropane. As a matter of fact, all the C-C bond lengths in bicyclo[1.1.0]butane are equal within experimental error [8] and this remarkable finding calls for some rationalization.

In a related context, the theoretical prediction of the geometrical structure of free radicals remains a topic of considerable interest since experimental techniques can usually only provide indirect evidence. While quantum mechanical models have reached a sophistication sufficient to provide reliable structural predictions for open-shell species, interpretation of the results in terms of well-defined models is less straightforward and has never been attempted for substituted cyclopropyl and bicyclo[1.1.0]butyl free radicals. Two of us have recently found by refined post-Hartree-Fock computations [10] that the C-C bonds of radicals are significantly different from those of the parent cycloalkanes: in particular, the C-C bond adjacent to the radical center is shortened and the C-C bond opposite the radical center is lengthened correspondingly. This prompted us to use quantum mechanical calculations to investigate the structures of a series of substituted cyclopropyl and bicyclo[1.1.0]butyl radicals and to analyze geometrical trends in terms of orbital interactions. As mentioned above, the Walsh orbitals of the ring have been used in previous studies to rationalize the variations of C-C bond lengths in cyclopropanes. However, in free radicals, one may suppose that interactions involving the vacant β spin orbital mainly localized on the radical center play a role in structural modifications; thus, a model based on localized orbitals appears more suitable than the Walsh approach. As a consequence we have adopted the natural bond orbital (NBO) analysis, which is based on a powerful and fully automated localization technique [11].

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2 Computational details

All calculations were carried out using the GAUSS-IAN94 system of programs [12]. Full optimizations were performed for all minimum-energy and for some symmetry constrained structures at HF, B3LYP and MP2(fc) levels, using the internal 6–311G(d,p) basis set [13]. Vibrational analyses were performed at the B3LYP level in order to confirm the nature of the stationary species. Unrestricted HF (UHF) and Kohn-Sham (UKS) approaches were always used for open-shell systems. Although the single determinant built with UHF or UKS orbitals does not represent a correct spin state, spin contamination is quite small at the UHF level ($< S^2 > < 0.77$) and essentially negligible using UKS orbitals. Under such circumstances we can be confident of obtaining reliable structures and energetic quantities.

Starting from the UHF wave function, a quantitative analysis of delocalization interaction can be obtained using the NBO Fock matrix deletion approach [14]. Although this procedure is not self-consistent, the error in the energy is negligible as long as the interactions that have been dropped from the Fock matrix are not strongly coupled with other interactions [15]. For open-shell systems, elements of the α and β Fock matrices can be deleted independently [16]. Such a procedure is well-adapted to intramolecular interaction analysis and has been successfully applied to the study of anomeric effects in free radicals [17].

3 General considerations

As mentioned in the Introduction, C_2C_3 bond lengths opposite the radical center (see Fig. 1 for atom numbering) in cyclopropyl and bicyclobutyl radicals are longer than in the parent hydrocarbons.
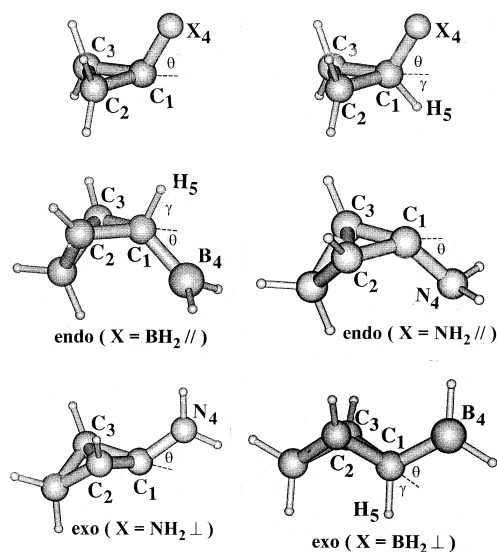

Fig. 1. Structure and atom labeling of α-X cyclopropyl and α-X bicyclobutyl radicals and their parent hydrocarbons

A possible explanation for this lengthening is the presence in the radicals of two interactions, depicted in Scheme 1 for the case of an α-X cyclopropyl radical in this C_s equilibrium geometry:

1. The first interaction referred to as (1) occurs between the localized β spin occupied NBO σ_{C2C3} and the vacant β spin orbital LP*$_{C1}$ centered on the radical center C_1;
2. The second interaction referred to as (2) corresponds to the $\sigma_{C2C3} \rightarrow \sigma^*_{C1X}$ delocalization; although this interaction is operative in the radicals as well as in their parent hydrocarbons, its strength could be quite different in the two classes of compounds owing to

Scheme 1
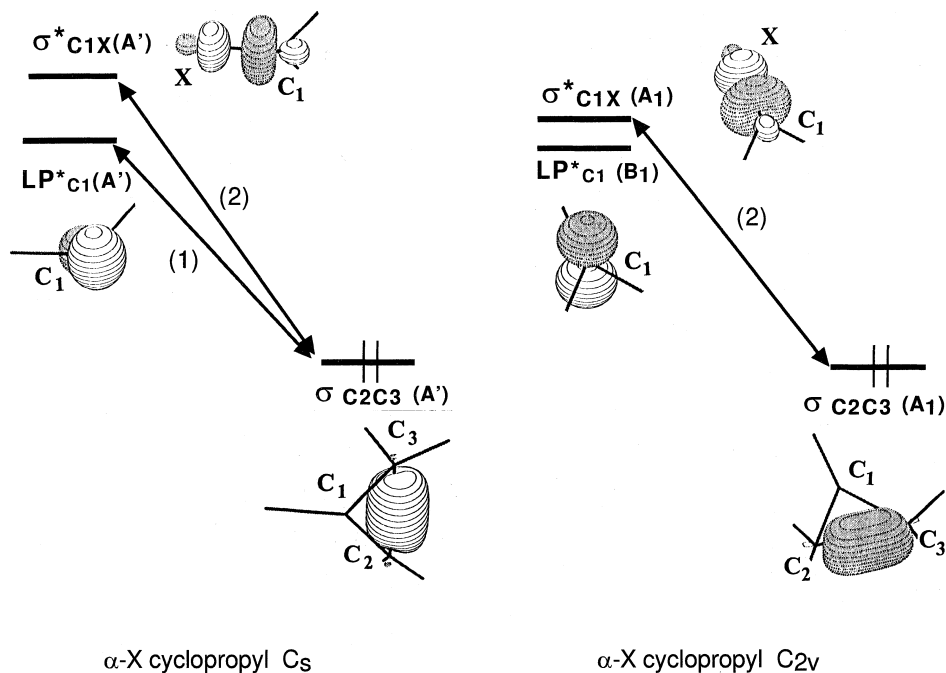
α-X cyclopropyl C_S α-X cyclopropyl C_{2v}

the larger C_1 pyramidalization in cycloalkanes with respect to the corresponding radicals (see θ values in Tables 1 and 2). Such a delocalization from σ_{C2C3} to σ^*_{C1X} produces a lengthening of C_2C_3. Correlatively, the mixing of C_2C_3 with both LP^*_{C1} and σ^*_{C1X} results in an occupied orbital which bonds between C_1 and $C_{2(3)}$; consequently, the $C_1C_{2(3)}$ bond is shortened.

A way to test this hypothesis is to use different substituents at the C_1 atom; for X more electronegative than C_1, the σ^*_{C1X} bond orbital is more concentrated on the C_1 atom and has a lower orbital energy. Since the strength of the $\sigma_{C2C3} \rightarrow \sigma^*_{C1X}$ interaction is roughly proportional to the square of the overlap $<\sigma_{C2C3}|\sigma^*_{C1X}>$ between these two orbitals divided by the difference in their orbital energies, we can expect that, if this interaction has an influence on the C-C bond lengths, the C_2C_3 distance would lengthen and that the $C_1C_{2(3)}$ distance would shorten. Obviously, the reverse situation would be observed for X less electronegative than C_1. Of course meaningful comparisons can be performed only using the same θ angle. A particularly interesting situation is obtained for α-X cyclopropyl radicals enforcing C_{2v} symmetry (see Scheme 1, right side): in this case, the $\sigma_{C2C3} \rightarrow LP^*_{C1}$ interaction vanishes and a convenient analysis of the effect of the $\sigma_{C2C3} \rightarrow \sigma^*_{C1X}$ delocalization upon the structure of cyclopropyl ring can be developed. So, if (2) is a key factor governing C_2C_3 bond lengths, one expects larger

C_2C_3 distances in α-F than in α-Li C_{2v} cyclopropyl radicals.

For symmetry reasons, interaction (1) cannot be completely removed in α-X bicyclobutyl radicals. However, Scheme 2 shows that the σ_{C2C3} NBO is always more concentrated above the $C_1C_2C_3$ plane but the direction of LP^*_{C1} differs in endo and exo conformers. The largest $<\sigma_{C2C3}|LP^*_{C1}>$ overlap and the strongest interaction (1) are expected for the exo radicals; the opposite behavior is predicted for interaction (2). Thus, an analysis similar to that developed for α-X cyclopropyl radicals will be performed for the endo bicyclobutyl radicals.

When the $\sigma_{C2C3} \rightarrow LP^*_{C1}$ interaction is symmetry allowed, its magnitude can be modified by π-donor and π-acceptor X-substituents. Let us consider first a π-donor, e.g. $NH_2//$ (see Fig. 1 for definition); the β spin NBO LP^*_{C1} interacts with the occupied β spin NBO LP_N. As a result, LP^*_{C1} is raised and partially delocalized on the N atom of the amino group and the $\sigma_{C2C3} \rightarrow LP^*_{C1}$ contribution decreases. For $X = NH_2\perp$, the $LP_N \rightarrow LP^*_{C1}$ delocalization is cancelled and comparison of the results obtained for $NH_2//$ and $NH_2\perp$ should provide an estimate of the $\sigma_{C2C3} \rightarrow LP^*_{C1}$ structural effect. In contrast, a π-acceptor substituent such as BH_2 or CN possesses a vacant β spin NBO (LP^*_B or π^*_{CN}) which interacts with LP^*_{C1}; as a result, the energy of LP^*_{C1} is lowered and the $\sigma_{C2C3} \rightarrow LP^*_{C1}$ interaction is enhanced. One may anticipate that substitution by $BH_2//$ and $BH_2\perp$ will

Table 1. Main geometrical parameters (Å and degrees) for the α-X cyclopropyl radicals and their parent hydrocarbons; see Fig. 1 for the atom labeling

X		α-X cyclopropyl radical C_s			α-X cyclopropyl radical C_{2v}		1-X cylopropane			
		C_1C_2	C_2C_3	θ	C_1C_2	C_2C_3	C_1C_2	C_2C_3	θ	γ
	HF	1.471	1.520	40.5	1.457	1.531	1.499	1.499	57.1	57.1
H	B3LYP	1.468	1.535	37.1	1.454	1.543	1.508	1.508	57.1	57.1
	MP2	1.475	1.534	41.0	1.459	1.545	1.509	1.509	57.5	57.5
	HF	1.460	1.545	49.6	1.429	1.585	1.481	1.515	57.8	53.4
F	B3LYP	1.463	1.566	49.7	1.426	1.605	1.491	1.523	57.8	53.5
	MP2	1.468	1.564	50.4	1.431	1.605	1.492	1.526	58.0	54.0
	HF	1.504	1.492	0.0	1.504	1.492	1.525	1.492	49.3	67.6
Li	B3LYP	1.507	1.499	0.0	1.507	1.499	1.534	1.500	49.1	67.7
	MP2	1.512	1.502	0.0	1.512	1.502	1.536	1.501	49.0	68.2
	HF	1.472	1.526	47.7	1.442	1.553	1.495	1.503	58.1	59.5
$NH_2//$	B3LYP	1.476	1.540	47.7	1.439	1.566	1.506	1.511	58.5	59.9
	MP2	1.480	1.541	49.3	1.443	1.569	1.506	1.513	59.2	59.8
	HF	1.468	1.540	37.9	1.453	1.558	1.496	1.515	51.7	59.8
$NH_2\perp$[a]	B3LYP	1.469	1.558	34.5	1.454	1.571	1.509	1.523	51.7	59.8
	MP2	1.475	1.559	38.1	1.457	1.574	1.507	1.526	52.3	59.7
	HF	1.468	1.517	0.0	1.468	1.517	1.504	1.502	50.0	61.4
$BH_2//$[b]	B3LYP	1.468	1.527	0.0	1.468	1.527	1.512	1.514	48.5	61.8
	MP2	1.473	1.529	0.0	1.473	1.529	1.514	1.514	50.4	61.6
	HF	1.495	1.491	39.1	1.480	1.500	1.529	1.474	57.1	61.9
$BH_2\perp$[c]	B3LYP	1.502	1.495	35.9	1.486	1.502	1.548	1.475	57.4	62.5
	MP2	1.506	1.498	41.7	1.487	1.507	1.546	1.480	58.8	62.3
	HF	1.468	1.519	28.4	1.461	1.524	1.507	1.490	56.2	57.4
CN	B3LYP	1.463	1.533	0.8	1.463	1.533	1.521	1.497	55.7	58.3
	MP2	1.459	1.541	0.9	1.459	1.541	1.519	1.502	56.5	58.1

[a] The radical and the hydrocarbon are first order TS
[b] The hydrocarbon is a first order TS
[c] The radical is a first order TS

Table 2. Main geometrical parameters (Å and degrees) for the α-X bicyclobutyl radicals and their parent hydrocarbons; see Fig. 1 for the atom labeling

		α-X bicyclobutyl radical			α-X bicyclobutyl θ fixed			1-X bicyclobutane		
		C_1C_2	C_2C_3	θ	C_1C_2	C_2C_3	C_1C_2	C_2C_3	θ	γ
H	HF	1.454	1.522	48.0 **exo**	1.461	1.516	1.490	1.469	55.4	58.8
	B3LYP	1.459	1.565	47.4	1.466	1.555	1.499	1.492	55.6	58.6
F	HF	1.453	1.539	53.5	1.454	1.534	1.475	1.486	59.1	50.6
	B3LYP	1.464	1.579	53.9	1.465	1.573	1.486	1.510	60.1	50.1
Li	HF	1.481	1.491	6.1	1.494	1.485	1.511	1.469	49.4	65.7
	B3LYP	1.478	1.527	5.4	1.489	1.520	1.519	1.490	48.1	66.1
NH₂//	HF	1.464	1.514	50.6	1.468	1.504	1.489	1.470	59.0	57.8
	B3LYP	1.473	1.549	50.2	1.478	1.536	1.500	1.492	59.4	58.2
NH₂⊥[a]	HF	1.461	1.553	45.8	1.465	1.540	1.491	1.495	55.3	56.4
	B3LYP	1.471	1.601	45.0	1.477	1.586	1.505	1.520	55.0	56.9
BH₂//[b]	HF	1.437	1.549	11.7	1.462	1.525	1.494	1.476	50.7	59.3
	B3LYP	1.441	1.598	12.0	1.467	1.569	1.501	1.500	45.4	60.4
BH₂⊥[c]	HF	1.474	1.490	44.7	1.481	1.481	1.514	1.446	58.3	60.0
	B3LYP	1.478	1.519	42.7	1.488	1.508	1.530	1.456	58.3	60.1
CN	HF	1.451	1.525	38.7	1.462	1.514	1.496	1.461	58.2	54.9
	B3LYP	1.452	1.574	31.5	1.471	1.554	1.509	1.480	57.4	56.1
				endo						
H	HF	1.461	1.500	37.1	1.460	1.501	1.490	1.469	58.8	55.4
	B3LYP	1.454	1.549	29.7	1.457	1.547	1.489	1.492	58.6	55.6
F	HF	1.448	1.522	44.6	1.441	1.526	1.464	1.499	53.6	56.1
	B3LYP	1.451	1.558	43.0	1.444	1.563	1.473	1.524	53.8	55.5
Li	HF				1.491	1.490	1.528	1.458	57.3	68.1
	B3LYP				1.483	1.529	1.535	1.480	58.2	67.3
NH₂//	HF	1.464	1.500	44.0	1.461	1.503	1.486	1.479	53.9	62.1
	B3LYP	1.469	1.530	44.1	1.459	1.533	1.497	1.499	54.9	62.0
NH₂⊥[a]	HF	1.463	1.522	33.9	1.463	1.521	1.488	1.490	48.0	62.0
	B3LYP	1.463	1.576	26.2	1.469	1.567	1.503	1.512	47.9	62.0
BH₂//	HF				1.461	1.518	1.499	1.471	48.7	62.7
	B3LYP				1.468	1.577	1.509	1.495	47.5	62.9
BH₂⊥	HF				1.480	1.472	1.519	1.450	51.1	65.0
	B3LYP				1.484	1.501	1.537	1.460	52.1	65.3
CN	HF				1.460	1.498	1.492	1.464	52.9	59.4
	B3LYP				1.462	1.544	1.506	1.481	53.1	60.0

[a] The radical and the hydrocarbon are first order TS
[b] The hydrocarbon is a first order TS
[c] The radical is a first order TS

Scheme 2

α-X bicyclobutyl endo   α-X bicyclobutyl exo
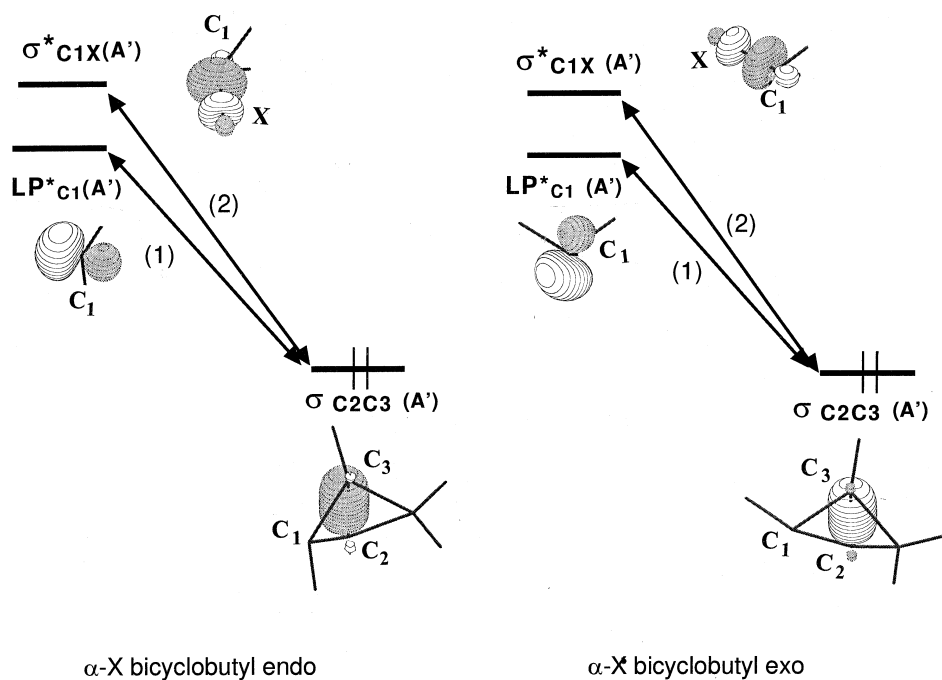
produce structural effects opposite to those produced through substitution by NH_2.

In summary, assuming a relationship between orbital delocalization and C-C bond length, the qualitative analysis presented above suggests significant substituent effects on the ring structure of radicals and parent closed-shell systems.

4 Results and discussion

4.1 Geometries

For consistency reasons, the NBO analysis has been performed using HF geometries. In order to assess the reliability of this computational model, all compounds were also optimized at the B3LYP/6–311G(d,p) level and, for cyclopropane and cyclopropyl derivatives, also at the MP2(fc)/6–311G(d,p) level. The main results are summarized in Tables 1 and 2. In Table 2 optimized C_1C_2 and C_2C_3 bond lengths at fixed θ values for bicyclobutyl radicals are added in order to make the analysis of various electronic effects easier (the overlap between interacting orbitals is θ dependent).

Known experimental C_1C_2 (C_2C_3) bond lengths (Å) for cyclopropane derivatives are: X = H: 1.512 (1.512); X = $NH_2//$: 1.486 (1.513) [18]; X = CN: 1.528 (1.500) [19] and for the difluoro-1,1 derivative: 1.464 (1.553) [20]. Whatever the level of calculation, computed and experimental trends are in good agreement. From a quantitative point of view, we can mention that B3LYP results are in better agreement with experiment than are HF values for the C_1C_2 and C_2C_3 bond lengths in bicyclobutane, which are identical (1.497 Å) [8] within experimental error.

Close comparison of Tables 1 and 2 leads to the following comments:

1. The structures calculated at different levels of theory are fairly well-related; in all cases, HF calculations provide the smallest C_2C_3 distances. However, the three methods of calculation describe well the variations in bond lengths in accordance with the nature of substituent X.

2. The substituents induce significant modifications of the C_1C_2 and C_2C_3 bond lengths: in general, the larger C_2C_3 and the shorter C_1C_2 bonds correspond to the more electronegative substituent. These trends are in line with the qualitative analysis described in the preceding paragraph. In addition, it may be remarked that substituent effects are stronger in *endo* bicyclobutanes than in *exo* ones. Finally, the structural changes in the pairs $NH_2//$, $NH_2\perp$ and $BH_2//$, $BH_2\perp$ are noteworthy: in particular, the replacement of $NH_2//$ by $NH_2\perp$ leads to an increase of the C_2C_3 distance, whereas the C_2C_3 bond becomes shorter with substitution of $BH_2//$ by $BH_2\perp$. These variations are in agreement with our qualitative analysis of the role played by the $\sigma_{C2C3} \rightarrow LP^*_{C1}$ delocalization in determining the C_2C_3 bond length.

3. Another point of interest is the pyramidalization of the radical center as measured by the angle θ (see Fig. 1 for definition). The most pyramidal cyclopropyl radical is the α-F derivative; it is well known that, in acyclic

Table 3. Inversion barriers $\Delta E^{\#}$ (kcal/mol) and energy differences $\Delta E = E_{endo} - E_{exo}$ (kcal/mol)

X	α-X cyclopropyl radical $\Delta E^{\#}$	X bicyclobutane ΔE	α-X bicyclobutyl radical ΔE
H	1.9	–	6.1
F	10.3	−2.9	5.1
Li	0.0	1.9	a
$NH_2//$	8.8	−0.6	3.0
$NH_2\perp$	2.2	−2.1	8.0
$BH_2//$	0.0	1.9	a
$BH_2\perp$	1.4	2.3	a
CN	0.1	0.1	a

[a] The endo conformer is not a stable structure

series, the presence of a fluorine atom directly bonded to the radical center increases the pyramidalization [21]. In contrast, α-Li and α-BH_2 derivatives adopt a C_{2v} equilibrium geometry at both levels of calculation. In addition, Table 1 shows that, going from C_{2v} ($\theta = 0°$) to C_s ($\theta \neq 0°$) structures, the C_1C_2 bond lengths tend to shorten and the opposite occurs for the C_2C_3 distance. The same trend is found in the *exo* form of bicyclobutyl radicals (see Table 2), the largest θ value being obtained for X = F and the smallest for X = Li. For $BH_2//$, $BH_2\perp$, CN and Li derivatives the *endo* forms do not correspond to stationary points on the corresponding potential energy surfaces.

As shown in Table 3, the height of the inversion barrier $\Delta E^{\#}$ of the substituted cyclopropyl radicals parallels the θ angle values, i.e., increases with the electronegativity of the substituent X. An analogous trend has been reported for α-substituted vinyl radicals [22]. These variations are generally attributed to the decrease of the s character of the orbital occupied by the odd electron when the polarity of the C_1-X bond increases [23]. However, further inspection of Table 3 indicates that, in the case of NH_2 and BH_2 substituents, the loss of conjugation leads to opposite effects: for X = BH_2, the energy minimum is reached for the C_{2v} structure when the delocalization of the unpaired electron is allowed ($BH_2//$), whereas a bent structure ($\theta = 35.9°$) is favored when the delocalization is forbidden ($BH_2\perp$); by contrast, for X = NH_2, the larger θ and $\Delta E^{\#}$ values correspond to $NH_2//$. The maximum overlaps $<LP_{C1}|LP^*_B>$ and $<LP_{C1}|LP_N>$ are achieved for a planar radical center. It is tempting to attribute the preferred C_{2v} structure to the two-orbital/one-electron stabilizing interaction between LP_{C1} and LP^*_B. On the other hand, the two-orbital/three-electron interaction between LP_{C1} and LP_N is only slightly stabilizing or even destabilizing: as a consequence the α-aminocyclopropyl radical does not adopt a C_{2v} structure.

The *exo* conformers of α-X bicyclobutyl radicals are more stable than the *endo* ones; the energy difference between the two conformers of the bicyclobutyl radical (6.06 kcal/mol) is in very good agreement with the values calculated at the UQCISD/TZP$^+$//UMP2/TZ2pf level (6.12 kcal/mol) [10]. This agreement is, in a sense, a validation of our results. The energy difference is consistent with the relative magnitude of the

$\sigma_{C2C3} \rightarrow$ LP*$_{C1}$ and $\sigma_{C2C3} \rightarrow \sigma^*_{C1X}$ delocalizations (the first, which predominates in the *exo* form, is more stabilizing than the second, which predominates in the *endo* form; vide infra, for instance Table 5 and Scheme 2).

The substituted hydrocarbons do not exibit such a regular trend: for X = F and NH$_2$//, the *endo* isomer is the most stable, while exactly the opposite is true for the other substituents. This trend can be understood by taking into account the fact that $\sigma_{C2C3} \rightarrow \sigma^*_{C1X}$ contributions predominate in *endo* bicyclobutanes, whereas $\sigma_{C2C3} \rightarrow \sigma^*_{C1H}$ interactions become dominant in *exo* forms. For electronegative substituents the $\sigma_{C2C3} \rightarrow \sigma^*_{C1X}$ contribution becomes more stabilizing and the $\sigma_{C2C3} \rightarrow \sigma_{C1X}$ less destabilizing (the magnitude of this destabilization varies as $<\sigma_{C2C3}|\sigma_{C1X}>^2$) than the $\sigma_{C2C3} \rightarrow \sigma^*_{C1H}$ and $\sigma_{C2C3} \rightarrow \sigma_{C1H}$ contributions, respectively; thus, for X = F and NH$_2$, the *endo* isomer will be preferred.

4.2 Population analysis

Atomic charges obtained from natural population analysis (NPA) [24] using HF/6–311G(*d,p*) wave functions are given in Table 4.

NPA charges reproduce the trends due to electronegativity differences. Thus, going from Li to F substituents, the charge on the C$_1$ atom becomes more positive: for example, the net charge carried by C$_1$ ranges from +0.30 to +0.53 for F derivatives while the corresponding values for Li derivatives range from −0.70 to −0.90. It is well known that C-C bonds are stabilized upon asymmetrical substitution by electronegative atoms [25]. Moreover, Pauling [26] pointed out that bond dissociation energies generally increase when augmenting bond polarities. Thus the increase in C$_1$C$_2$ bond polarity by an electronegative substituent at C$_1$ can

partially explain the shortening of the C$_1$C$_2$ bond; however, one may recall that the predicted effect of the $\sigma_{C2C3} \rightarrow \sigma^*_{C1X}$ contribution to the C$_1$C$_2$ bond length is in line with the polarization effect.

Fortunately the trends in C$_2$C$_3$ bond lengths seem easier to analyze; close examination of Table 4 indicates that C$_{2(3)}$ atomic charges are almost insensitive to the nature of the substituent (nevertheless we notice in many cases a reduced negative charge for CN and BH$_2\perp$ substituents). There is no obvious correlation between (small) variations of the C$_{2(3)}$ charges and the electronegativity of X. One may reasonably suppose that changes in the C$_2$C$_3$ distance cannot be interpreted in terms of coulombic repulsions. In the following analysis, these changes will be tentatively correlated only with the σ_{C2C3} donation (vide infra).

4.3 NBO analysis

As a first step, it is necessary to analyze the magnitude of the interactions likely to vary with substituent X. These interactions are listed and evaluated in Tables 5 (radicals) and 6 (cycloalkanes) for X = F which is representative of the whole set of substituents.

The data shown in Table 5 show that the dominant interactions occur between σ_{C2C3} and LP*$_{C1}$ and/or between σ_{C2C3} and σ^*_{C1X} NBOs. Their strength is comparable in the C_s structure of the α-F cyclopropyl radical, but in the C_{2v} transition structure the first interaction vanishes and the second is considerably increased. In the *endo* form, the $\sigma_{C2C3} \rightarrow \sigma^*_{C1X}$ interaction is the most important. This quantitative analysis confirms our qualitative predictions (vide supra). In addition to these two interactions, noticeable charge transfer between a F lone pair and the σ^*_{C2C3} NBO takes place; the structural consequence of this

Table 4. Calculated NPA charges borne by C$_1$ and C$_{2(3)}$ centers at the HF/6–311G(d,p) level

		H	**F**	**Li**	**NH$_2$//**	**NH$_2\perp$**	**BH$_2$//**	**NH$_2\perp$**	**CN**
α-X cyclopropyl	C$_1$	−0.054	0.534	−0.689	0.333	0.350	−0.153	−0.283	0.318
radical	C$_{2(3)}$	−0.414	−0.446	−0.439	−0.410	−0.434	−0.405	−0.367	−0.354
1-X cyclopropanepan	C$_1$	−0.356	0.300	−0.913	0.019	0.062	−0.610	−0.608	−0.318
	C$_{2(3)}$	−0.356	−0.396	−0.372	−0.364	−0.383	−0.314	−0.321	−0.314
α-X bicyclobutyl	C$_1$	−0.134	0.470	−0.718	0.203	0.257	−0.174	−0.333	−0.064
radical *exo*	C$_{2(3)}$	−0.224	−0.254	−0.263	−0.242	−0.239	−0.180	−0.207	−0.176
1-X bicyclobutane	C$_1$	−0.327	0.319	−0.868	0.039	0.073	−0.568	−0.583	−0.170
exo	C$_{2(3)}$	−0.212	−0.240	−0.241	−0.215	−0.239	−0.200	−0.178	−0.195
α-X bicyclobutyl	C$_1$	−0.086	0.532		0.240	0.311			
radical *endo*	C$_{2(3)}$	−0.245	−0.280		−0.262	−0.261			
1-X bicyclobutane	C$_1$	−0.327	0.290	−0.849	0.031	0.131	−0.562	−0.581	−0.293
endo	C$_{2(3)}$	−0.212	−0.229	−0.242	−0.218	−0.228	−0.202	−0.182	−0.169

Table 5. Main delocalization energies (kcal/mol) involving σ_{C1X}, σ^*_{C1X}, LP$_X$ and LP*$_{C1}$ NBOs of the α-fluoro radicals; see Fig. 1 for the atom labeling

	$\sigma_{C1X} \rightarrow \sigma^*_{C1C2}$	$\sigma_{C1C2} \rightarrow$ LP*$_{C1}$	$\sigma_{C2C3} \rightarrow \sigma^*_{C1X}$	$\sigma_{C1C2} \rightarrow \sigma^*_{C1X}$	$\sigma_{C2C3} \rightarrow$ LP*$_{C1}$	LP$_X \rightarrow \sigma^*_{C1C2}$
α-F cyclopropyl (C_s)	−0.1	−0.6	−11.1	−0.1	−11.2	−9.4
α-F cyclopropyl (C_{2v})	−0.3	0.0	−42.8	−1.0	0.0	−11.9
α-F bicyclobutyl *exo*	−0.2	−1.6	−0.3	−0.1	−46.0	−9.7
α-F bicyclobutyl *endo*	0.0	−0.2	−29.5	−0.2	−1.3	−10.4

interaction is a lengthening of the C_1C_2 bond. Interactions involving an X-centered orbital and giving rise to $C_1C_{2(3)}$ lengthening are operative for all substituents, except for H and Li ($LP_N \to \sigma^*_{C1C2}$ for $X = NH_2\perp$; $\sigma_{NH} \to \sigma^*_{C1C2}$ for $X = NH_2//$; $\sigma_{BH} \to \sigma^*_{C1C2}$ for $X = BH_2//$; $\sigma_{C1C2} \to LP^*_B$ for $X = BH_2\perp$ and $\sigma_{C1C2} \to \sigma^*_{CN}$ for $X = CN$). As a result, these secondary interactions, together with electrostatic effects, make it difficult to rationalize the variations of C_1C_2 bond lengths. The same remark applies to cycloalkane derivatives. Hydrocarbons involve weaker $\sigma_{C2C3} \to \sigma^*_{C1F}$ delocalization energies than the corresponding radicals (–4.4 kcal/mol vs. –11.1 kcal/mol in the α-F cyclopropyl radical; –23.9 kcal/mol vs. –29.5 kcal/mol in the α-F bicyclobutyl radical) due to the larger values of θ in cycloalkanes. In addition, the data in Table 6 show that $\sigma_{C2C3} \to \sigma^*_{C1H}$ contributions cannot be neglected in our analysis.

Let us now examine the variations of the $\sigma_{C2C3} \to \sigma^*_{C1X} + \sigma_{C2C3} \to LP^*_{C1}$ (radicals) and the

$\sigma_{C2C3} \to \sigma^*_{C1X} + \sigma_{C2C3} \to \sigma^*_{C1H}$ (cycloalkanes) interaction energies as a function of the substituent X. The results shown in Tables 7 and 8 deserve the following comments:

1. Except for X = Li, the strongest delocalization energies are obtained for the radicals.
2. The NBO analysis applied to C_{2v} stuctures of α-X cyclopropyl radicals illustrates well the electronegativity effect on the magnitude of the $\sigma_{C2C3} \to \sigma^*_{C1X}$ interaction: the strongest contribution is calculated for X = F (–42.8 kcal/mol) and it decreases regularly in going from X = F to X = Li. This trend gives further support to our qualitative analysis, as depicted in Scheme 1.
3. Another point discussed in the qualitative section is the influence of the delocalization of LP^*_{C1}, effective for X = NH$_2$// or BH$_2$// and absent for X = NH$_2\perp$ or BH$_2\perp$; as predicted, a larger $\sigma_{C2C3} \to LP^*_{C1}$ interaction is calculated for X = NH$_2\perp$ but for X = BH$_2$ the comparison is biased because the cyclopropyl radical

Table 6. Main delocalization energies (kcal/mol) involving σ_{C1X}, σ^*_{C1X}, σ_{C1H}, σ^*_{C1H}, and LP_X NBOs of the 1-fluoro hydrocarbons; see Fig. 1 for the atom labeling

	$\sigma_{C1X} \to \sigma^*_{C1C2}$	$\sigma_{C1H} \to \sigma^*_{C1C2}$	$\sigma_{C2C3} \to \sigma^*_{C1X}$	$\sigma_{C2C3} \to \sigma^*_{C1H}$	$\sigma_{C1C2} \to \sigma^*_{C1X}$	$\sigma_{C2C3} \to \sigma^*_{C1H}$	$LP_X \to \sigma^*_{C1C2}$
1-F cyclopropane	–0.1	–0.2	–4.4	–4.3	0.0	–0.6	–7.6
1-F bicyclobutane *exo*	–0.2	0.0	–0.5	–16.7	–0.2	–0.9	–9.3
1-F bicyclobutane *endo*	0.0	–0.5	–23.9	0.0	–0.2	–0.4	–9.6

Table 7. Variation of the delocalization energies (kcal/mol) involving σ_{C2C3} NBO as function of substituent X for the three membered species

	α-X cyclopropyl radicals			1-X cyclopropane	
	C_s		C_{2v}[a]		
X	$\sigma_{C2C3} \to \sigma^*_{C1X}$	$\sigma_{C2C3} \to LP^*_{C1}$	$\sigma_{C2C3} \to \sigma^*_{C1X}$	$\sigma_{C2C3} \to \sigma^*_{C1H}$	$\sigma_{C2C3} \to \sigma^*_{C1X}$
H	–10.1	–5.4	–24.6	–2.8	–2.8
F	–11.1	–11.2	–42.8	–4.4	–4.3
Li	–1.3	0.0	–1.3	–0.7	–1.5
NH$_2$//	–16.5	–1.1	–34.7	–3.0	–3.9
NH$_2\perp$	–14.4	–7.2	–32.7	–2.8	–5.8
BH$_2$//	–17.3	0.0	–17.3	–2.1	–4.9
BH$_2\perp$	–8.7	–4.1	–16.8	–2.0	–3.2
CN	–17.4	–3.4	–27.5	–3.2	–4.2

[a] For the C_{2v} symmetry the $\sigma_{C2C3} \to LP^*_{C1}$ interaction vanishes

Table 8. Variation of the delocalization energies (kcal/mol) involving σ_{C2C3} NBO as function of substituent X for the four membered species

	α-X bicyclobutyl radical *exo*				α-X bicyclobutyl radical *endo*		1-X bicyclobutane *exo*		1-X bicyclobutane *endo*	
	equilibrium		θ fixed[a]		θ fixed[b]					
X	$\sigma_{C2C3} \to \sigma^*_{C1X}$	$\sigma_{C2C3} \to LP^*_{C1}$	$\sigma_{C2C3} \to \sigma^*_{C1X}$	$\sigma_{C2C3} \to LP^*_{C1}$	$\sigma_{C2C3} \to \sigma^*_{C1X}$	$\sigma_{C2C3} \to LP^*_{C1}$	$\sigma_{C2C3} \to \sigma^*_{C1H}$	$\sigma_{C2C3} \to \sigma^*_{C1X}$	$\sigma_{C2C3} \to \sigma^*_{C1H}$	$\sigma_{C2C3} \to \sigma^*_{C1X}$
H	–0.9	–41.8	–0.2	–47.3	–21.9	–6.2	–12.5	–0.1	–0.1	–12.5
F	–0.6	–46.0	–0.6	–51.7	–35.6	–3.9	–16.7	–0.5	0.0	–23.9
Li	–1.2	–20.1	–0.1	0.0	–1.2	–14.2	–7.0	–0.7	–0.4	–3.6
NH$_2$//	–1.2	–32.7	–0.5	–36.3	–25.0	–0.2	–13.1	–0.1	–0.1	–16.8
NH$_2\perp$	–1.0	–48.1	–0.2	–55.5	–26.7	–3.8	–15.1	0.0	–0.2	–20.0
BH$_2$//	–16.0	–38.8	–1.8	–50.7	–18.1	–11.3	–12.3	–0.4	–0.2	–11.5
BH$_2\perp$	–1.9	–31.9	–0.6	–35.3	–14.8	–5.1	–10.5	–0.2	–0.3	–10.2
CN	–4.2	–39.7	–0.4	–50.1	–24.2	–3.6	–14.0	0.0	0.0	–13.9

[a] θ = 57.1°
[b] θ = 58.8°

substituted by $BH_2//$ has a C_{2v} equilibrium structure. A better comparison of this effect is given by the *exo* conformers of bicyclobutyl radicals with fixed θ angles (Table 8); indeed, we observe an increase of the stabilizing $\sigma_{C2C3} \rightarrow LP*_{C1}$ interaction in going from $NH_2//$ to $NH_2\perp$ (−36.3 vs. −55.5 kcal/mol) and the opposite variation in going from $BH_2//$ to $BH_2\perp$ (−50.7 vs. −35.3 kcal/mol).

4. Delocalization interactions are significantly different in *exo* and *endo* conformers of bicyclo derivatives in accordance with predictions (Scheme 2): in the *exo* forms, the $\sigma_{C2C3} \rightarrow LP*_{C1}$ (radicals) and $\sigma_{C2C3} \rightarrow \sigma*_{C1H}$ (hydrocarbons) predominate, whereas in the *endo* forms the major contribution is the $\sigma_{C2C3} \rightarrow \sigma*_{C1X}$ one (in both radicals and cycloalkanes, except for X = Li).

In order to assess the influence of delocalization interactions on the C_2C_3 distance, we have plotted the C_2C_3 bond lengths against the sum $(\sigma_{C2C3} \rightarrow \sigma*_{C1X} + \sigma_{C2C3} \rightarrow LP*_{C1})$ for radicals or the sum $(\sigma_{C2C3} \rightarrow \sigma*_{C1X} + \sigma_{C2C3} \rightarrow \sigma*_{C1H})$ for hydrocarbons. Examination of the plots (representative plots are given in Fig. 2) shows that, in most cases, the data relative to $BH_2\perp$ deviate from the

others; we also give the R value (hereafter referred to as R') obtained excluding $BH_2\perp$ from the data set.

In our opinion, significant correlations are obtained for cyclopropyl radicals in their C_{2v} structures ($R = 0.940$; $R' = 0.950$), for *exo* bicyclobutyl either in its equilibrium geometry ($R = 0.912$; $R' = 0.953$) or for a fixed θ angle ($R = 0.903$; $R' = 0.939$, Fig. 2c) and for *endo* bicyclobutanes ($R = 0.899$; $R' = 0.966$, Fig. 2d). Fair correlations are observed for *endo* bicyclobutyl radicals at a fixed θ angle ($R = 0.837$; $R' = 0.860$, Fig. 2b) and for cyclopropyl radicals in their equilibrium geometries ($R = 0.831$; $R' = 0.892$). Finally, only marginal correlations are obtained for substituted cyclopropanes ($R = 0.570$; $R' = 0.655$, Fig. 2a) and *exo* bicyclobutanes ($R = 0.371$; $R' = 0.784$, without X = Li). From Tables 7 and 8 one finds that the worst results correspond either to very weak interaction energies (cyclopropane) or to interaction energies almost independent of the substituent (*exo* bicyclobutanes). In these cases, the $\sigma_{C2C3} \rightarrow \sigma*_{C1X}$ interaction does not play the dominant role in determining C_2C_3 bond lengths and other factors such as coulombic repulsions or secondary interactions must be taken into account. By contrast, better C_2C_3 distance-delocalization energy correlations are obtained
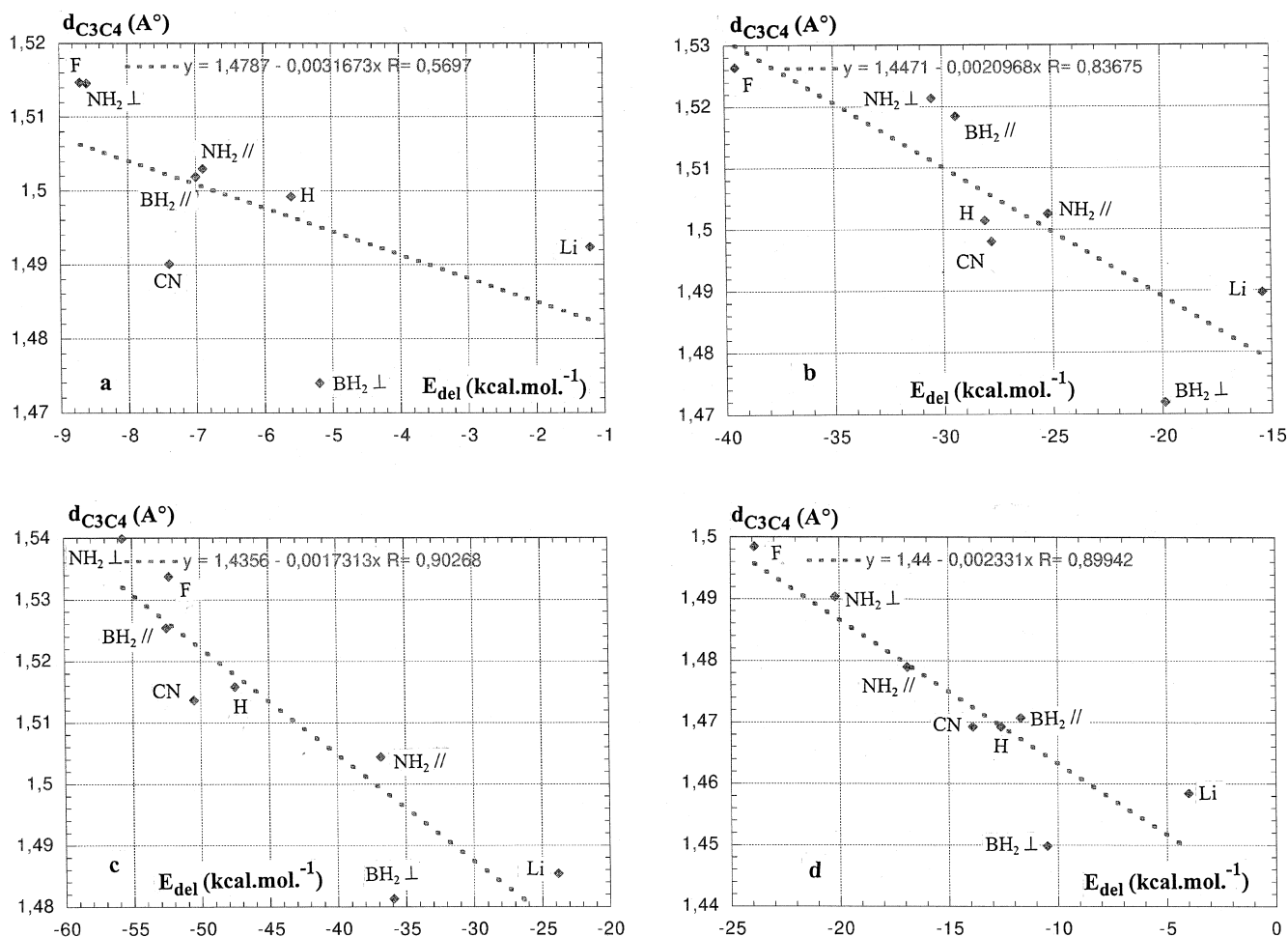

Fig. 2a–d. Plot of d_{C2C3} distance (Å) against energy E_{del} (see text for the definition of E_{del}); **a** 1-X cyclopropanes; **b** α-X bicyclobutyl radicals *endo* (θ fixed); **c** α-X bicyclobutyl radicals *exo* (θ fixed); **d** 1-X bicyclobutanes *endo*

for strong $\sigma_{C2C3} \to \sigma^*_{C1X}$ and/or $\sigma_{C2C3} \to LP^*_{C1}$ contributions, which in these cases become the dominant factors.

5 Conclusion

We have analyzed the variations of structural characteristics of two representative strained radicals as a function of the nature of substituents at the radical center. This analysis has been extended to their parent hydrocarbons. Calculations have shown that C-C bond lengths are dependent on the electronegativity or electron donor-acceptor properties of the substituents. This dependence is emphasized in radicals. Population analysis indicates that internal coulombic interactions contribute to the modification of the C(X)-C adjacent bonds but are less important in determining the C-C distance of the opposite (substituted C) bond.

The most striking difference between radicals and parent hydrocarbons results from the interaction between the vacant β spin orbital localized at the radical center and the σ_{CC} orbital of the opposite bond. This delocalization, which is only operative for pyramidal cyclopropyl radicals or *exo* bicyclic radicals, results in a significant lengthening of the C-C bond.

Although intramolecular delocalization does not appear to play an important role in strengthening or lengthening the C-C bonds of cyclopropane and bicyclobutane *exo* derivatives, it is probably a significant structural factor in other species such as α-substituted cyclopropyl and bicyclobutyl radicals or bicyclobutane *endo* derivatives.

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