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# LONG RANGE STEREOELECTRONIC EFFECTS AND THE W ARRANGEMENT. AN AB INITIO STUDY OF β-HALOANIONS.

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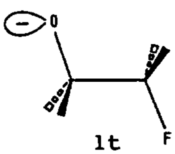
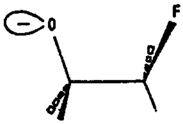
*Abstract : The effect of conformation on properties of β-haloanions is studied.*

We report the results of ab initio calculations on the *gauche* (g) and *trans* (t) conformations of the $^{-}O-CH_2-CH_2-X$ (X=F in 1, X=Cl in 2) and $^{-}CH_2-CH_2-CH_2-X$ (X=Cl) (3) anions [1]. They show marked stereoelectronic effects (SE's) on the protonation energies and on the C-X bond properties in the conformations which can be characterized by a "W" arrangement of a $sp^3$ lone pair (on $O^-$ or $H_2C^-$) and the C-X bond. These SE's are apparent from the changes in the optimized C-X bond lengths (BL's), the atomic charges on X, and the relative total energies (ΔE) summarized in the figure.


1t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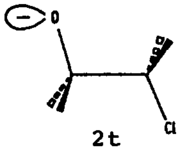
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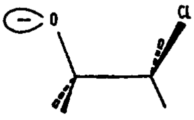
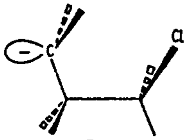

2g

| | | | | | |
|---|---|---|---|---|---|
| C-X BL | 1.403 | 1.390 | 1.874 | 1.828 | Å |
| X charge | -0.516 | -0.484 | -0.345 | -0.270 | e |
| $\Delta E_{g-t}$ (3G) | 0.0 | 3.0 | 0.0 | 9.3 | kcal/mole |
| (4-31G) | 0.0 | 8.0 | | | kcal/mole |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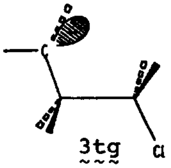
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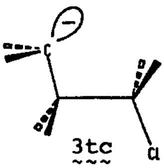
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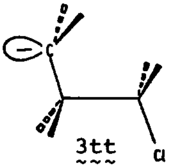

3tt

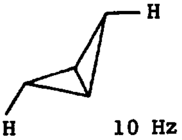
| | | | | | |
|---|---|---|---|---|---|
| C-X BL | 1.827 | 1.852 | 1.865 | 1.881 | Å |
| X charge | -0.256 | -0.308 | -0.330 | -0.344 | e |
| ΔE | 12.9 | 4.6 | 3.6 | 0.0 | kcal/mole |

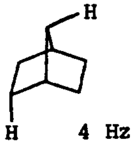
PROTONATION ENERGIES. (i) The 3G protonation energies (difference between the most stable conformers of 1, 2, 3 and the conjugate acids 1H, 2H, 3H in the same conformation) increase in the order 2 (511) < 1 (524) < 3 (536 kcal/mole). Although these numbers are basis set dependent [2], they indicate that β-chloroalkohols are intrinsically more acid than β-fluoroalcohols in the same conformation. This substituent effect, qualitatively similar to that observed in fluoro- and chloro acetic acid [3], could be reduced or even reversed by solvation. (ii) The *trans* conformers 1t, 2t, and 3tt are more stable than the corresponding *gauche* conformers 1g, 2g, and 3gt; this t-g energy difference is markedly greater than the t-g energy difference for 1H (0.7 kcal/mole, 3G; 0.9 kcal/mole, 4-31G), 2H (0.7 kcal/mole, 3G) and 3H (1.1 kcal/mole, 3G) [4]. Thus conformationnally rigid β-halo-substituted alcohols X-C-C-OH are intrinsically more acidic by several pK units in the *trans* than in the *cis* or *gauche* conformation. Similarly, a C-H bond in a planar "W" relationship to a β C-X bond is intrinsically more acidic than in the other conformations (see 3tt). These results should also hold when X is a different electronegative or polarizable substituent.

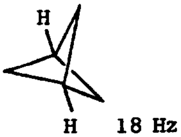
STEREOELECTRONIC EFFECTS. In addition to the dipole-dipole interactions, long range SE's may account for the stabilization of the t conformers of 1-3. A two-electron interaction between a $^-$C or $^-$O lone pair orbital and the empty $\sigma^*_{C-X}$ orbital is stabilizing; it also lengthens the C-X bond and increases the charge on the X atom. The overall structural and electronic parameters summarized in the above figure are in agreement with a conformation dependent delocalization of the negative charge into the $\sigma^*_{C-X}$ orbital: in the t conformers, the C-X bond is longer ($\Delta$=0.013 for 1, 0.046 for 2, 0.054 for 3), the C-X overlap population (OP) is weaker ($\Delta$=-0.009 for 1, -0.039 for 2, -0.045 e for 3), the X atom is more charged ($\Delta$=0.033 for 1, 0.075 for 2, 0.088 e for 3) and the HOMO energy is lower ($\Delta$=0.14 eV for 1, 0.62 eV for 2, 0.68 eV for 3) than in the g conformers. As in the case of α-substituted carbanions C-X-C$^-$ (X=O, S, Se), the stabilization energy which results from the conformation dependent charge delocalization into the $\sigma^*_{C-X}$ bond orbital increases with the polarizability of the C-X bond (compare C-F with C-Cl) [5]. Furthermore, the comparison of the rotamers of 3t where the C$^-$ lone pair is respectively *trans* (3tt), *gauche* (3tg) and *cis* (3tc) with respect to the C-CH$_2$X bond shows an increase of the SE's in the "W" conformation 3tt. If one considers three localized sp$^3$ lone pairs on the oxygen atom of 1 and 2, the *trans* conformations 1t and 2t also contain by a "W" arrangement of a lone pair and of a C-X bond.

These results can account for the easy halide elimination for 2, 3 and related systems to form epoxydes or cyclopropanes respectively [6]. The internal SN displacement which requires a *trans* relationship between the C-X and the C-O$^-$ or C-C$^-$ bonds is facilitated because (i) this conformation is the most stable, (ii) the C-Cl bond is the most weakened with respect to the protonated form and (iii) the halogen atom has enhanced halide character. Our calculations suggest also that the chlorine NQR frequencies should shift to lower values when the C-Cl bond is in a "W" relationship with an heteroatom lone pair, as observed in vicinal dichloro compounds [7].

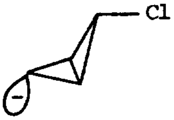
LONG RANGE STEREOELECTRONIC EFFECTS IN OTHER SYSTEMS. IMPORTANCE OF THE "W" ARRANGEMENT. The "W" arrangement of a lone pair orbital and a C-X bond described above has some analogy with the conformation requirements for other long range interactions in rigid systems. For instance, long range hyperfine interactions in bicyclic free radicals depend critically on the geometry at the radical site, and are stronger in the "W" arrangement than in the other conformation [8]. In NMR spectroscopy, long range interproton $^4$J spin-spin couplings are observed when the four σ bonds are in a "W" arrangement [9,10]. We thus decided to study SE's in systems derived from some hydrocarbons where large $^4J$ have been reported:



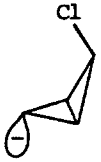




The chloro bicyclo [1.1.0]butyle (4), 7-chlorobicyclo[2.2.1]heptyle (5) and 1-chlorobicyclo [1.1.1]pentyle (6) anions and the corresponding acids 4H-6H were considered; the C-Cl bond length has been optimized in 4, 4H, 6, 6H.

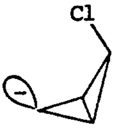


4a



4b

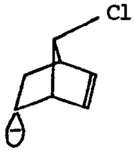
4c



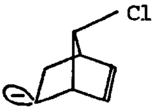
4d

| | 4a | 4b | 4c | 4d | |
|---|---|---|---|---|---|
| ΔE | 0.0 | 6.0 | 19.5 | 15.8 | kcal/mole |
| E prot | 506. | 515. | 526. | 525. | kcal/mole |
| C-Cl BL | 1.863 | 1.862 | 1.829 | 1.880 | Å |
| ΔBL (4H → 4) | 0.077 | 0.042 | 0.043 | 0.060 | Å |
| Cl charge | -0.337 | -0.316 | -0.295 | -0.328 | e |
| Δ charge (4H → 4) | 0.189 | 0.126 | 0.147 | 0.138 | e |

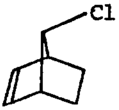
Among the five isomers of 4 reported, 4a and 4d correspond respectively to a "W" and a "anti W" arrangement of the $^-$C lp and the C-Cl bond. The results clearly show that 4a is more stable and much less basic than 4b-4d; its HOMO is also the most stable. Although its C-Cl bond is not the longest, it exhibits the most important lengthening on deprotonation of 4H. Furthermore, the charge on Cl and its increase on deprotonation are more important in this "W" conformation than in 4b-4d.



5a



5b



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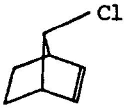
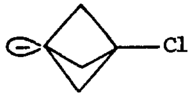


5H



6

A "W" arrangement is also present in the *endo* anion 5a where the charge is more delocalized in the $\sigma^*_{C-Cl}$ orbital than in the *exo* anion 5b: the C-Cl overlap population is weaker, and the Cl charge is greater in 5a than in 5b (respectively 0.173, 0.193 e; -0.372, -0.345 e). The SE's in this bicyclic system are related to the well known *anti* electronic assistance by a double bond in the elimination of $X^-$ at $C_7$ as illustrated by the relative C-Cl OP's and the Cl charge in 5c compared to 5H (respectively 0.219, 0.226 e; -0.183, -0.168 e) [11].

Since in the above systems the most important SE's are observed in the arrangement for which significant $^4J$ proton-proton coupling constants in the parent hydrocarbons have been reported, it is of interest to consider the bicyclo[1.1.1]pentane system where $^4J$ is very large, and the bridgehead C-H bond orbitals interact strongly [12]. The calculations show that the bridgehead C-H bond of **6H** is more acidic ($E_{prot}$=493 kcal/mole) than the C-H bonds of **4aH**-**4dH**, or of **5H** (502 kcal/mole); **6** has the most stable HOMO, the longest C-Cl bond (1.983 Å) and the highest charge on Cl (-0.479 e) of all these species; it shows the largest increase of the C-Cl BL (0.186 Å) and of the Cl charge (-0.295 e) on deprotonation of **6H**.

Although there is no quantitative relationship between the long-range proton-proton coupling constants and the SE's in the derived β-halo substituted anions, this study shows that they follow the same trends both within a molecule, and from a molecule to another. Long-range NMR interactions (even beyond $^4J$) may thus be a guide to characterize arrangements where SE's are present. These results should also hold with other C-X polarizable bonds into which electrons can be delocalized.

## REFERENCES

1 The calculations have been performed with the 3G and 4-31G basis sets of the GAUSSIAN 70 program (QCPE n°236). Ideal geometries with tetrahedral angles have been assumed; the bond lengths (Å) are: C-C: 1.56 in **1**, **2**, 1.54 in **3**, C-H: 1.09, O-H: 0.97, C-OH: 1.42 (assumed); C-O$^-$: 1.417 (optimized in **2g** and **2t**). All C-Cl and C-F BL's have been optimized at the 3G level; C-F: 1.388 in **1H**; C-Cl: 1.809 in **2H**, 1.813 in **3H**.

2 For other protonation energies calculated with the same method, see for instance: (a) L. Radom, J. Chem. Soc. Chem. Comm. 403 (1974); (b) W.J. Hehre, R.T. McIver, Jr., J.A. Pople and P.v.R. Schleyer, J. Amer. Chem. Soc. 1974, *96*, 7162; (c) J.E. Williams, Jr. and A. Streitwieser, Jr., J. Amer. Chem. Soc. 1975, *97*, 2634.

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10 Compare for example the bridgehead C-H bonds, or the *endo* $C_5$-H and $C_6$-H bonds of bicyclo[2.1.1]hexane to the *exo* C-H bonds: J.M. Lehn and G. Wipff, Theor. Chim. Acta 1973, *28*, 223 and references cited therein.

11 Similar long range SE's should operate in the 2-Chloro-7-thiabicyclo[2.1.1]heptanes: the *endo* isomer which displays a "W" relationship between a S lp and the C-Cl bond solvolyses about $10^9$ times faster than the *exo* isomer: I. Tabushi, Y. Tamaru, Z. Yoshida and T. Sugimoto, J. Amer. Chem. Soc. 1975, *97*, 2886.

12 J.M. Lehn and G. Wipff, Chem. Phys. Lett. 1972, *15*, 450.

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