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# Electronic Interactions and Their Influence on the Conformational Stability of *trans*-2-Halocyclopentanol

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Conformational preferences and electronic interactions of *trans*-2-fluorocyclopentanol (**1**), *trans*-2-chlorocyclopentanol (**2**), and *trans*-2-bromocyclopentanol (**3**) were analyzed using experimental and theoretical $^3J_{HH}$ coupling constants, theoretical calculations, and natural bond orbital (NBO) analysis. The conformational equilibria of compounds **1**−**3** can be represented by their diaxial and diequatorial conformers as supported by theoretical calculations. From $^3J_{HH}$ coupling constant values, it can be found that the diequatorial conformer is present in the equilibrium as 55% for compound **1** and as 60% for compounds **2** and **3**. This behavior is in agreement with orbital interaction analyses obtained from NBO.

## Introduction

The conformational analysis of six-membered rings, mainly cyclohexanes, are widely studied.[1] Recently, in this series, the 2-halocyclohexanones[2−7] and 2-halocyclohexanols[8,9] have been extensively studied. However, the same attention has not been given to five-membered ring systems (cyclopentanes). In Eliel and Wilen's comprehensive textbook on stereochemistry, six-membered ring conformational analysis takes up to 60 pages while five-membered rings just four pages.[1]

The difficulty in establishing the stable forms for the cyclopentane system, in analogy to cyclohexane, is due to its rapid interconversion among many conformers, which often precludes detailed analysis and leads directly to the concept of pseudorotation.[1] The conformational equilibrium in cyclopentane derivatives has been usually reported in the literature,[1] as occurring between two stable symmetrical puckered conformations, the envelope $C_s$ and the half-chair $C_2$ (Figure 1a). The energy barrier between these two conformations is very small and the cyclopentane ring has been described as it is 'in a conformational flux between the two above forms and also among other in-between structures'.[1]

Several spectroscopic studies for the chlorocyclopentane,[10−13] methylcyclopentane,[14] cyclopentanol,[15] and for *cis*- and *trans*-3-methyl- and 1,3-dimethylcyclopentanols[14] have already been reported.

The most recent study[16] on the conformational analysis of cyclopentanol and *cis*- and *trans*-cyclopentane-1,2-diol was done by Abraham et al.[16] Here, the authors concluded that for the cyclopentanol there are two stable forms, where one of them has the hydroxyl group in the axial and the other one in equatorial position at the flap of the envelope. For the *cis*-1,2-cyclopentanediol there are two different envelope conformations, both with one equatorial and one axial hydroxyl group. An envelope conformation with two axial hydroxyl groups and a half-chair conformer with the diequatorial hydroxyl groups were observed for *trans*-1,2-cyclopentanediol.[16]

Another important aspect related to the five-membered rings is that these systems are present in some of the most common natural products, which include many steroids, prostaglandins, sugars, and nucleotides.[1,17] Therefore, it becomes very important to describe the conformational preferences and the electronic interactions that are present in five-membered rings systems.

The interpretation of molecular structure and reactivity usually takes into account steric and electrostatic interactions, and increasingly, stereoelectronic effects, in special hyperconjugative processes.[18−20] These interactions may influence conformational equilibrium, modify reactivity, and determine selectivity.[21] Hyperconjugative effects are proposed to be important components of intermolecular interactions, both in ground and transition states.[18] A hyperconjugative process comes from a two electron-two orbital interaction between an occupied, high-energy donor orbital and an empty, low-energy acceptor orbital.[20]

In the present work, 2-fluorocyclopentanol (**1**), 2-chlorocyclopentanol (**2**), and 2-bromocyclopentanol (**3**) (Figure 1b) were chosen as probes to perform the conformational analysis and to describe the interactions involved in the most stable forms of these compounds. To this end, the experimental and theoretical $^3J_{HH}$ spin−spin nuclear coupling constants are used in analysis of their conformational equilibria. The experimental data are supported by DFT calculations, in conjunction with the natural bond orbital (NBO)[22] analysis.

## Computational Details

All structures were fully optimized (Table 1) at the MP2/aug-cc-pVDZ level using the Gaussian98 program.[23] The aug-cc-pVDZ[24] basis set was chosen for the correct description of fluorine, chlorine, and bromine atoms. This basis set includes additional diffuse functions (prefix aug-), which were used to take into account the relatively diffuse nature of the lone pairs.

Electronic structures of the compounds **1**−**3** were studied using NBO analysis.[22,25] The NBO energies were calculated at the B3LYP/ cc-pVTZ levels using the geometries optimized at the MP2/aug-cc-pVDZ level. These delocalization energies are the stabilizing energies calculated by second-order perturbation theory analysis.

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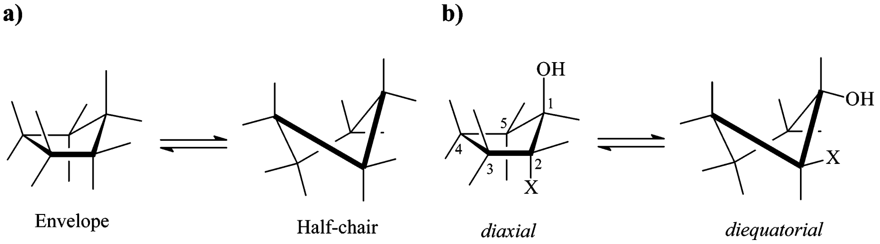

**Figure 1.** Stable conformers: (a) cyclopentane; (b) 2-halocyclopentanol (halo = F, Cl, and Br).

**TABLE 1: Calculated Parameters[a] for 1−3 at the MP2/aug-cc-pVDZ Level**

| parameter | 1 diequatorial | 1 diaxial | 2 diequatorial | 2 diaxial | 3 diequatorial | 3 diaxial |
|---|---|---|---|---|---|---|
| $r_{C-O}$ | 1.426 | 1.439 | 1.423 | 1.442 | 1.422 | 1.443 |
| $R_{C-X}$ | 1.415 | 1.421 | 1.807 | 1.816 | 1.955 | 1.966 |
| $r_{C1-H1}$ | 1.108 | 1.103 | 1.107 | 1.102 | 1.107 | 1.102 |
| $r_{C2-H2}$ | 1.103 | 1.099 | 1.101 | 1.097 | 1.101 | 1.097 |
| $r_{O-H}$ | 0.968 | 0.967 | 0.969 | 0.967 | 0.970 | 0.968 |
| $-_{C2-C1-O}$ | 115 | 104 | 114 | 109 | 115 | 109 |
| $-_{C1-C2-X}$ | 111 | 107 | 112 | 108 | 112 | 109 |
| $-_{H1-C1-C2}$ | 108 | 112 | 107 | 112 | 108 | 112 |
| $-_{H2-C2-C1}$ | 109 | 113 | 109 | 113 | 109 | 113 |
| $\theta_{X-C-C-O}$ | 73 | 168 | 71 | 167 | 71 | 166 |
| $\theta_{H-O-C1-C2}$ | 65 | 172 | 64 | 173 | 65 | 173 |
| $\theta_{H1-C1-C2-H2}$ | 168 | 70 | 169 | 70 | 169 | 71 |
| $E_{rel}$ (kcal mol$^{-1}$) | 1.1 | 0.0 | 0.2 | 0.0 | 0.0 | 0.0 |
| $\mu$ (D) | 1.70 | 1.25 | 1.88 | 1.28 | 2.00 | 1.37 |

[a] $r$ in Å; − and $\theta$ in degrees.

Calculations of all four terms, Fermic (FC), spin-dipolar (SD), paramagnetic spin-orbital (PSO), and diamagnetic spin-orbital (DSO) of $^3J_{HH}$ spin−spin coupling constants (SSCCs) were carried out using the B3LYP functional, which corresponds to the Lee et al.'s correlated functional,[26] and the exchange part is treated according to the Becke's three parameters approach.[27] The EPR-III basis set was used,[28] which is of a triple-$\zeta$ quality and includes diffuse and polarization functions.

The CP−DFT[29] perturbative approach was used for calculating all three second-order terms of spin−spin couplings, i.e., FC, SD, and PSO; the DSO term is treated as a first-order quantity. All DFT calculations were carried out using the Gaussian03 package of programs.[30]

## Experimental Section

**NMR Experiments.** The solvents were commercially available and used without further purification. $^1$H NMR spectra were recorded on a spectrometer equipped with 2.5 mm gradient probe operating at 500.13 MHz for $^1$H. Measurements were carried out at a probe temperature of 25 °C, using solutions of ca. 10 mg cm$^{-3}$ in different solvents. [$^2H_6$]-Benzene was used as deuterium lock signal for the $CCl_4$ solutions. The $^1$H spectra were all referenced to TMS. Typical conditions for $^1$H spectra were: 16 transients, spectral width 3000 Hz with 64k data points, giving an acquisition time of 6.8 s and zero filled to 128k to give a digital resolution of 0.01 Hz.

**Syntheses.** *trans*-2-Fluorocyclopentanol (**1**) was obtained by treating cyclopentene oxide (9.64 g, 0.114 mol) with 42% HF/pyridine (20 mL).[31] The reaction mixture was worked up, and the product was distilled through a Vigreux column to give pure *trans*-2-fluorocyclopentanol (7.7 g, 65%); bp 100 °C/10 mmHg.[32] *trans*-2-Chlorocyclopentanol (**2**) and *trans*-2-bromocyclopentanol (**3**) were prepared through the reaction of cyclopentene with the corresponding *N*-halosuccinimide in water solution, according to a literature procedure,[33] to give a yield of 12.6 g (62%) of *trans*-2-chlorocyclopentanol (bp 85 °C/5 mmHg) and a yield of 15.4 g (55%) of *trans*-2-bromocyclopentanol (bp 108 °C/5 mmHg).

**TABLE 2: Experimental $^3J_{H_1H_2}$ Coupling Constants (Hz) for 1−3 in Different Solvents**

| solvent | 1 | 2 | 3 |
|---|---|---|---|
| $CCl_4/C_6D_{12}$ | 5.26 | 6.83 | 6.20 |
| $CDCl_3$ | 5.46 | 6.35 | 6.47 |
| $CD_2Cl_2$ | 5.36 | 6.43 | 6.53 |
| acetone-$d_6$ | 5.26 | 5.90 | 6.11 |
| $CD_3CN$ | 5.25 | 6.12 | 6.28 |
| DMSO-$d_6$ | 5.18 |  | 5.91 |

## Results and Discussion

The experimental $^3J_{H_1H_2}$ couplings constants for compounds **1**−**3** (Table 2), in solvents of different polarities, show that there are no changes in their values on changing the solvent. This experimental aspect indicates that there is no change on conformer populations.

It has been predicted for cyclopentane[34] from an extended Karplus relationship that the $^3J_{HH_{cis}}$ and $^3J_{HH_{trans}}$ (cis means the position of the hydrogen atoms on the same side of the ring) present almost the same values $^3J_{HH_{cis}} = 7.7$ Hz and $^3J_{HH_{trans}} = 6.3$ Hz. It has been also experimentally observed[35] for *trans*-1,2-dichlorocyclopentane (DCC) and *trans*-1,2-dibromocyclopentane (DBC) values for $^3J_{H_1H_2}$ around 2.8 Hz for DCC and 1.7 Hz for DBC. These small values for $^3J_{H_1H_2}$ coupling constants indicating a preference for the diaxial conformation for both compounds.[35] The observed $^3J_{H_1H_2}$ coupling constant is 4.0 Hz, for the *trans*-cyclopentane-1,2-diol,[16] leading the authors to conclude that the diequatorial conformer (hydroxyl group in pseudo-equatorial position) is the most stable form in solution and that the stabilization of diequatorial conformation is due to the attractive gauche interaction between the two vicinal oxygen atoms.[16] However, a recent interpretation of gauche effect has been done, involving vicinal anti donor−acceptor stabilizing interactions as the determining factor for

**TABLE 3: Theoretically Calculated, at B3LYP/EPR-III Level, $^3J_{H_1H_2}$ Coupling Constants (Hz) for 1−3**

| | 1 | | 2 | | 3 | |
|---|---|---|---|---|---|---|
| $^3J_{H_1H_2}$ | diequatorial | diaxial | diequatorial | diaxial | diequatorial | diaxial |
| $J^{FC}$ | 8.22 | 1.64 | 9.31 | 1.31 | 9.57 | 1.17 |
| $J^{SD}$ | 0.05 | 0.06 | 0.04 | 0.06 | 0.04 | 0.06 |
| $J^{PSO}$ | 2.23 | 0.50 | 2.22 | 0.53 | 2.20 | 0.54 |
| $J^{DSO}$ | −2.56 | −0.47 | −2.44 | −0.33 | −2.13 | 0.02 |
| $J^{total}$ | 7.94 | 1.73 | 9.13 | 1.57 | 9.68 | 1.79 |

conformational preference, which provides a rationale for gauche effect in general.[36−38]

Theoretical calculations, at high level of theory, were performed to describe the conformational equilibrium for compounds **1**−**3**. The calculations at the MP2/aug-cc-pVDZ level gave two stable conformers (Table 1), diaxial and diequatorial (Figure 1b), for each of the studied compounds (**1**−**3**). A comparison of the optimized structures and data presented in Figure 1b and Table 1, respectively, with those for 2-halocyclohexanols,[9] shows that both systems present the same pattern for the molecular fragment which contains halogen, hydroxyl group, $H_1$, and $H_2$. Thus, it can be expected that compounds **1**−**3** exhibit a similar behavior to 2-halocyclohexanols.[9] However, the results for 2-halocyclohexanols (X = F, Cl, and Br) demonstrated that they occur as a single conformer, the diequatorial, due to the strong hydrogen bond between the hydroxyl group and halogens. Experimental evidence for the diequatorial preference comes from the analysis of $^3J_{H_1H_2}$ values, which show large values (∼10 Hz), indicating an axial−axial relationship between the vicinal hydrogen atoms.[9] This is not the case of compounds **1**−**3**, here described, because they presented intermediate values (∼6 Hz) for the $^3J_{H_1H_2}$ coupling constant, which indicates an equilibrium between the diaxial and diequatorial forms for these 2-halocyclopentanols.

The hydrogen bond interaction has been invoked to explain the conformational preference of the diequatorial form for 2-halocyclohexanol.[8] In the NBO analysis[25] the hydrogen bond would occur between LP(X) → $\sigma^*_{OH}$, but this interaction was not observed from second-order perturbation energies from NBO analysis for 2-halocyclopentanol, indicating the absence of hydrogen bond interaction for compounds **1**−**3** studied here.

Furthermore, the individual $^3J_{H_1H_2}$ values for each conformer (diaxial and diequatorial), which are required for a conformational analysis of compounds **1**−**3**, are unknown (diaxial and diequatorial). Thus, non-empirical theoretical spin−spin coupling constants were calculated, at a high level of theory, to get with accurated individual $^3J_{H_1H_2}$ coupling constants for both conformers.

Experimental data (Table 2) shows that there is no significant variation on $^3J_{H_1H_2}$ values on changing the solvent polarity from $CCl_4$ to DMSO, which suggests that there are no changes on conformer populations. The theoretically calculated individual coupling constants (Table 3) together with the experimental data from Table 2 allowed the determination of the amount of each conformer in the equilibrium. This shows that the diequatorial conformer is present as ca. 55% for 2-fluorocyclopentanol, in all solvents studied here, increasing to 60% for 2-chlorocyclopentanol and 2-bromocyclopentanol.

**Conformational Preferences and Orbital Interactions.** Electronic interactions can be invoked to explain the conformational stability for the diaxial and diequatorial conformers of **1**−**3**. The most important orbital interactions from NBO analysis that stabilizes the diequatorial conformers involve C−C, C−O, C−X, and C−H bonds (Table 4). The $\sigma_{C2-C3} \rightarrow \sigma^*_{C-O}$ is more energetic than the $\sigma_{C4-C5} \rightarrow \sigma^*_{C-O}$, while the $\sigma_{C2-C3} \rightarrow \sigma^*_{C-O}$ increases from F to Br derivatives while the $\sigma_{C4-C5} \rightarrow \sigma^*_{C-O}$ interaction decreases.

The other important hiperconjugative interactions observed for diequatorial conformers involving $\sigma_{C1-H1} \rightarrow \sigma^*_{C2-H2}$ and $\sigma_{C2-H2} \rightarrow \sigma^*_{C1-H1}$ presents almost equal energy values. The interactions between $\sigma_{C5-H} \rightarrow \sigma^*_{C-O}$ and $\sigma_{C3-H} \rightarrow \sigma^*_{C-X}$ are responsible for the stability of diaxial conformers. The orbital interactions involving lone pairs from oxygen and halogen (F, Cl, and Br) and O−H bond are almost equal for both conformers as can be observed from Table 4.

The orbital interactions listed in Table 4 clearly show that the stabilization interactions for the diequatorial are slightly more effective than for diaxial conformer in the gas phase. However, the conformer energies (Table 1) indicate an opposite trend, since the diaxial is more stable than diequatorial by 1.1 kcal $mol^{-1}$ for the fluorine derivative (**1**), while for chlorine (**2**) and bromine (**3**) both compounds have almost the same energies. In solution, a reverse behavior is observed, as the diequatorial conformers for **1**−**3** are slightly more stable than the diaxial, as observed from $^3J_{HH}$ coupling constants (see above).

Probably, in vapor phase, there is an electrostatic repulsive interaction between the halogen and oxygen atoms in the diequatorial conformer, which makes the diaxial more stable, as predicted by theoretical calculations (Table 1), superseding the stabilization effects due to orbital interactions.

In solution, the electrostatic repulsive interaction is decreased by the solvent, leading a stabilization of the diequatorial conformers, for compounds **1**−**3**, as found from experimental data and NBO analysis.

## Conclusions

The conformational analysis for 2-halocyclopentanols (**1**−**3**) revealed that they occur in almost equal populations of diaxial and diequatorial conformers, in solution. Moreover, in the vapor

**TABLE 4: Energies (kcal mol$^{-1}$) for the Most Important Orbital Interactions in 1−3, Calculated at the B3LYP/cc-pVTZ Level**

| diequatorial | | | | diaxial | | | |
|---|---|---|---|---|---|---|---|
| orbital interactions | 1 | 2 | 3 | orbital interactions | 1 | 2 | 3 |
| $\sigma_{C1-H1} \rightarrow \sigma^*_{C2-H2}$ | 2.47 | 2.88 | 2.99 | $\sigma_{C5-H} \rightarrow \sigma^*_{C-O}$ | 4.42 | 3.85 | 3.73 |
| $\sigma_{C2-H1} \rightarrow \sigma^*_{C1-H1}$ | 2.33 | 2.53 | 2.60 | $\sigma_{C2-X} \rightarrow \sigma^*_{C-O}$ | 1.33 | 2.65 | 3.24 |
| $\sigma_{C2-C3} \rightarrow \sigma^*_{C-O}$ | 3.37 | 3.40 | 3.44 | $\sigma_{C1-O} \rightarrow \sigma^*_{C2-X}$ | 1.84 | 2.77 | 3.17 |
| $\sigma_{C4-C5} \rightarrow \sigma^*_{C-O}$ | 2.91 | 2.74 | 2.68 | $\sigma_{C3-H} \rightarrow \sigma^*_{C2-X}$ | 5.88 | 5.87 | 6.49 |
| $\sigma_{C1-C5} \rightarrow \sigma^*_{O-H}$ | 1.57 | 1.59 | 1.60 | $\sigma_{C1-C2} \rightarrow \sigma^*_{O-H}$ | 1.68 | 1.64 | 1.64 |
| $\sigma_{C1-C5} \rightarrow \sigma^*_{C2-X}$ | 3.73 | 1.79 | 2.17 | $\sigma_{O-H} \rightarrow \sigma^*_{C1-C2}$ | 2.61 | 3.06 | 3.17 |
| $\sigma_{C3-C4} \rightarrow \sigma^*_{C2-X}$ | 3.61 | 1.66 | 2.05 | $n_O \rightarrow \sigma^*_{C4-C5}$ | 7.24 | 7.35 | 7.32 |
| $\sigma_{O-H} \rightarrow \sigma^*_{C1-C5}$ | 3.54 | 3.64 | 3.65 | $n_X \rightarrow \sigma^*_{C2-C3}$ | 5.63 | 4.40 | 4.27 |
| $n_O \rightarrow \sigma^*_{C1-C2}$ | 8.97 | 9.26 | 9.34 | $n_X \rightarrow \sigma^*_{C1-C2}$ | 5.55 | 4.23 | 3.24 |
| $n_X \rightarrow \sigma^*_{C2-C3}$ | 6.35 | 5.43 | 4.71 | | | | |
| $n_X \rightarrow \sigma^*_{C1-C2}$ | 6.03 | 5.03 | 4.32 | | | | |

phase, the diequatorial conformers are slightly more stabilized by orbital interactions than the diaxial conformers (NBO analysis), but an electrostatic repulsive interaction, between the halogen and oxygen atoms in the diequatorial conformer, reduces, probably, the stability of the former conformers and makes the diaxial conformers more stable by 1.1 kcal mol$^{-1}$ for **1**, 0.2 kcal mol$^{-1}$ for **2**, and 0.0 kcal mol$^{-1}$ for **3**, according to the theoretical calculations.

The comparison between these two series of cyclic compounds (2-halocyclohexanol[9] and 2-halocyclopentanol) leads to the conclusion that small changes in structure can cause profound changes in the electronic interactions and, consequently, in conformational preferences.

The results from the present work provide evidence that the stabilization of diequatorial conformers is due to hyperconjugative interactions involving $\sigma_{C-C} \rightarrow \sigma^*_{C-O}$, $\sigma_{C-C} \rightarrow \sigma^*_{C-X}$, and $\sigma_{C-H} \rightarrow \sigma^*_{C-H}$ orbital interactions

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