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Conformational Analysis of Enantiomers of Chiral Chloroalkanes

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The pairs of compounds that are nonsuperimposable mirror images called enantiomers. There are several classes of enantiomers that are being studied rather extensively because of their industrial and research importance. 2-Chloropentane, 2-chlorohexane and 2-chloroheptane are the most important chiral enantiomers. Conformational analysis is the study of the energies of different conformations. Many reactions depend on a molecule's ability to twist into a particular conformation. Conformational analysis can help to predict which conformations are favoured and which reactions are more likely to take place. Here we apply conformational analysis to these three enantiomers. From these we predict the most stable conformer. Besides that, the successful interpretations of these compounds using various parameters of the molecules have been provided.

Key Words: Conformational analysis, Enantiomers, 2-Chloropentane, 2-Chlorohexane, 2-Chloroheptane.

INTRODUCTION

All the three chiral enantiomers of primary chloroalkanes have one chlorine atom substituted at the second position of carbon chain. Although the same type of compounds have been studied extensively by previous workers[1, 2] largely in the context of using these molecules as model compounds, however, to the best of knowledge of authors, molecular mechanics conformation and optimization of the structures of the above enantiomers has not been made earlier. The structures of all enantiomers are shown in Fig. 1. The optimization problem often comprises a complex series of molecules, their properties and their various types of energies involved such as steric energy, torsional energy, van der Waals' energy, compression energy, bending energy and dipole moment. Conformational analysis can help to predict which conformations are favoured and which reactions are more likely to take place. Conformational analysis is based on the Newman projection angles[3]. The optimization of molecules can be calculated by changing the dihedral angles of all enantiomers from 0 to 360° in steps of 60°. The final steric energies of the enantiomers are calculated and tabulated and compared with one another

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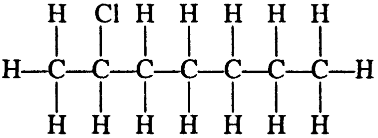
using Table-1. The purpose of the present study is to find the most stable conformers among them which explains the distribution of various energies, moment of inertia and dipole moment of the conformer. Also the best fits for the reactions are more likely to take place.



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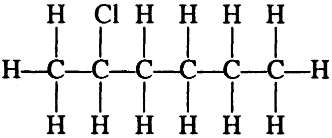
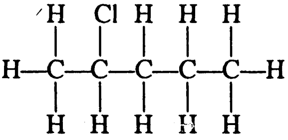
(a) 2-Chloroheptane



$$\begin{array}{ccccccccccccccc} & & H & & Cl & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & C & — & C & — & C & — & H \\ & & | & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & H & & \end{array}$$

(b) 2-Chlorohexane



$$\begin{array}{ccccccccccccc} & & H & & Cl & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & C & — & C & — & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$

(c) 2-Chloropentane

Figure 1. Structures of enantiomers

TABLE-1
CONFORMATIONS OF CHIRAL ENANTIOMERS

Energies in kcal/mole	Totally eclipsed	Gauche	Eclipsed	Anti	Eclipsed	Gauche	Totally eclipsed	Skew
2-Chloropentane	4.3925	6.1554	4.4321	3.5683	4.4329	6.1554	6.1560	—
2-Chlorohexane	748.4226	10.3712	7.9145	74.7359	7.9112	10.3647	1168.92	5.1040 (270°)
2-Chloroheptane	—	145.6025	70.5729	61.9861	69.0474	110.1138	—	8.1076 (30°)

Molecular Mechanics Calculation

There are several classes of molecules that are being studied rather extensively because of their industrial, commercial and pharmaceutical importance. The calculations for the different parameters such as steric energy, torsional energy, Van der Waals' energy, compression energy, bending energy and dipole moment have been performed using MM_2 computer program with pentium III processor. It is written in Microsoft Fortran version 3.20 under MS-DOS or PC-DOS on the IBM-PC or MS-DOS computers either with or without an 8087 floating point math computer and 196 K of RAM is required[4]. The dihedral angles are responsible for the stability of the molecules for optimization of the molecules. The optimization of molecules can be calculated by changing the dihedral angles of all the enantiomers from 0 to 360°. The energies of the enantiomers are calculated for Newman projection[3].

RESULTS AND DISCUSSION

Table-1 summarizes the results of the optimization calculations performed to identify some of the stable conformers based on Newman projections[3]. Seven conformers were found for 2-chloropentane and 2-chlorohexane. In the case of 2-chloroheptane five stable conformers were found. Here, we have been made to locate the global minimum for all the molecules studied. In the following discussion, the structure and atomic positions have been changed based on the Newman projection and various parameters of the enantiomers have been calculated such as steric energy, torsional energy, van der Waals' energy, compression energy, bending energy and dipole moment.

2-Chloroheptane: Even though the five stable conformers have been found for 2-chloroheptane based on the Newman projection, but the most stable conformer was found with a dihedral angle of 30°. The steric energy on this stage is 8.1076 kcal. The force constant of the molecule closely agrees with previous study of the same enantiomer by Jaggi and Jayaswal[1, 2] using MOLVIB computer program.The energy of this enantiomer is comparatively higher than that of other enantiomers studied here. The ellipsoid of inertia has three mutually perpendicular axes, which are denoted[3] by X, Y and Z. The three axes are the principal axes of moment of inertia about these three axes designated as I_x, I_y, I_z. Here the moments of inertia of all conformers of 2-chloroheptane along the three axes are $I_x = 34.2215$, $I_y = 103.6143$ adn $I_z = 110.3749$, so that according to the classification of rotors, the molecule belongs to the asymmetric top. Here the dipole moment of these enantiomers is 1.94 D, because only one halide is attached to the methyl group. This value is in good agreement with available literature value[3]. The heat of formation is comparatively much higher than the other two enantiomers, *i.e.*, 54.08 kcal, so that the boiling point is also high. The bond lengths, bond angles and bond enthalpy constants closely agree with the available literature values[3, 6].

2-Chlorohexane: In case of 2-chlorohexane the most stable conformer is found with the dihedral angle of 30°. The steric energy on this stage is 5.1040 kcal. The force constant of the molecule closely agrees with previous studies of the related compound[1, 2]. The energy of this enantiomer is comparatively less than 2-chloroheptane and higher than that of 2-chloropentane studied here. The moments of inertia of all conformers of 2-chlorohexane along the three axes are $I_x = 24.7073$ kg m^2, $I_y = 80.5800$ kg m^2 and $I_z = 93.5054$ kg m^2. The heat of formation is comparatively much higher than the other two enantiomers, *i.e.*, 50.67 kcal/mole, so that the boiling point is also high. The bond length, bond angles and bond enthalpy constants are closely agree with the available literature values[3].

2-Chloropentane: By comparing the final steric energy of 2-chloropentane, 2-chlorohexane and 2-chloroheptane from Table-2, 2-chloropentane has least energy, *i.e.*, 3.5683 kcal, so that the enantiomer 2-chloropentane is the most stable conformer among them. All the calculated various energies, force constants, bond lengths and bond angles are summarized in Tables 3–6. The above said most stable conformer got from anti form of the Newman projection.

TABLE-2
ENERGIES OF STABLE 3 CHIRAL ENANTIOMERS

Energy in kcal/mol	2-Chloropentane	2-Chlorohexane	2-Chloroheptane
Steric	3.5683	5.1040	8.1076
Compression	0.2982	0.3839	0.4608
Bending	0.7049	1.2690	2.5399
Stretch bend	0.1235	0.1777	0.2599
Van der Waals'	3.0280	3.7491	4.5925
Torsional	–0.1313	0.2145	1.4286

TABLE-3
CONFORMATIONS OF 2-CHLOROPENTANE

Energies in kcal/mol	Totally Eclipsed	Gauche	Eclipsed	Anti	Eclipsed	Gauche	Totally eclipsed
Steric Energy	4.3925	6.1554	4.4321	3.5683	4.4329	6.1554	6.1560
Bending	1.1375	2.1409	1.1711	0.7049	1.1690	2.1377	2.1504
Compression	0.3026	0.2997	0.3091	0.2982	0.3089	0.3003	0.2994
Stretch-bend	0.1515	0.1951	0.1537	0.1235	0.1535	0.1951	0.1952
Van der Waals'	3.0572	3.1769	3.0811	3.0280	3.0831	3.1777	3.1704
Torsional	0.2520	0.9552	0.2506	–0.1313	0.2505	0.9573	0.9476
PFC	2.40	2.40	2.40	2.40	2.40	2.40	2.40
Heat of formation	–44.96	–43.20	–44.92	–45.79	–44.92	–43.20	–43.20
Strainless heat of formation	–46.15	–46.15	–46.15	–46.15	–46.15	–46.15	–46.15
Inherent strain	1.19	2.95	1.23	0.37	1.23	2.95	2.95
Strain energy	1.19	2.95	1.23	0.37	1.23	2.95	2.95
Bond enthalpy	–51.76	–51.76	–51.76	–51.76	–51.76	–51.76	–51.76
Strainless bond enthalpy	–48.55	–48.55	–48.55	–48.55	–48.55	–48.55	–48.55

TABLE-4
BOND LENGTH (Å) FOR ENANTIOMERS

Bond Type	2-Chloroheptane	2-Chlorohexane	2-Chloropentane
C—C	1.5345	1.5348	1.5365
C—H	1.1148	1.1149	1.1149
C—Cl	1.7931	1.7939	1.7942

TABLE-5
BOND ANGLES (°) FOR ENANTIOMERS

Bond Type	2-Chloroheptane	2-Chlorohexane	2-Chloropentane
C—C—C	109.510	109.510	109.510
C—C—H	110.000	110.000	110.000
H—C—H	109.400	109.400	109.400
Cl—C—H	106.900	106.900	106.900

TABLE-6
FORCE CONSTANTS FOR ENANTIOMERS

Bond type	2-Chloroheptane	2-Chlorohexane	2-Chloropentane
C—C	4.4000	4.4000	4.4000
C—H	4.6000	4.6000	4.6000
C—Cl	3.2300	3.2300	3.2300

A graph of the relative torsional energies of 2-chloropentane is as shown in Fig. 2. The anti-conformer has lower energy than any other conformations. The anti-conformation has the lowest energy because it places the bulky methyl groups as far apart as possible. The gauche conformations, with the methyl groups separated by just 60°, are 0.9573 kcal higher in energy than all other conformations because the bulky methyl groups are close enough that their electron clouds begin to repel each other. The heat of formation of 2-chloropentane is much less (*i.e.*, it lies between –44.96 kcal/mol to –43.20 kcal/mol) than all other enantiomers, because 2-chloropentane contains less methylene groups (CH_2) groups per mole. The totally eclipsed conformation has higher steric energy (6.1560 kcal/mol) than other eclipsed conformations because it forces the two end methyl groups so close together that their electron clouds experience a strong repulsion. This kind of interference between two bulky groups is called steric strain. Rotating anti-conformation 60° to an eclipsed conformation is still a more steric strain (6.1560 kcal/mol) than the anti-conformation. Hence, among these conformations,

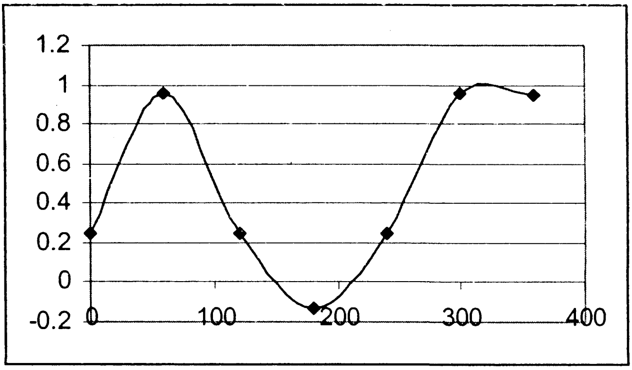


Fig. 2. Torsional Energy for Pentane

the anti-conformation is preserved, since it has the lowest torsional and strain energies –0.1313 kcal/mol and 3.5683 kcal/mol respectively.

The moments of inertia of all conformers of 2-chloropentane along the three axes are different ($I_x = 0.962$ kg m^2, $I_y = 1.393$ kg m^2 and $I_z = 0.947$ kg m^2) and hence the molecule belongs to the asymmetric top.

A molecular dipole moment is the vector sum of the individual bond dipole moments. Molecular dipole moments are not easy to predict, because they depend on the bond angles and other factors that vary with the specific molecule. Here the dipole moment of all the three enantiomers 1.94 D, because only one halide is attached to the methyl in group. This value is good the agreement with available literature value[3].

The heat of formation calculated for this enantiomer is –45.79 kcal/mol, which is much less than the heat of formation of all other enantiomers studied here and hence this enantiomer has less boiling point than that of the other 2-chiral enantiomers[3].

Conclusion

The present study demonstrates the utility of the molecular mechanics computational method to study the structural and spectroscopic properties of enantiomers and research important molecules. Using molecular mechanics method, the structural properties of these enantiomers such as 2-chloroheptane, 2-chlorohexane and 2-chloropentane were predicted and the most stable conformer among them was found out and a theoretical support for it was given. Several stable conformers have been found for 2-chiral enantiomers based on Newman projection structure. In this case 2-chloropentane is the most stable conformer among them, with the anti-conformers. The molecular mechanics yields values for changing dihedral angles that are responsible for the stability of the conformers.

REFERENCES

1. N. Jaggi and R.M.P. Jaiswal, *Indian J. Phys.*, **74B**, 493 (2000).
2. N. Jaggi and R.M.P. Jaiswal, *Indian J. Pure Appl. Phys.*, **40**, 385 (2002).
3. L.J. Wade, (Jr.), Organic Chemistry, 33rd Edn., Prentice-Hall.
4. N.L. Allinger, *QCPE Bull.*, **8** (addendum) (1998).
5. Website address: Computational Chemistry Module Index.
6. Manas Chandra, Atomic Structure and Chemical Bond, 2nd Edn., Tata McGraw-Hill Publishing Company Ltd., New Delhi.

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