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Molecular Mechanics Studies on Chamazulene

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The molecular mechanics studies have been undertaken to identify the presence of stable conformers. The attached methyl and ethyl groups are rotated one by one for various dihedral angles and minimum conformational energy of the molecule is recorded. Various parameters such as compression energy, bending energy, torsional energy and van der Waal's energy of the molecule are recorded. The final steric energy and related thermodynamic quantity are found. The heat of formation and related strain energy are also noted.

Key Words: Chamazulene, Steric energy, Dipole moment.

INTRODUCTION

Molecular modelling uses computational methods to study various chemical and biological systems. One of the major advantages of computer modeling over experiment is that the interaction energy and its variation with structure may be investigated at the atomic and molecular levels[1,2]. The expression, molecular mechanics is currently used to define a computational method, designed to give accurate structures and energies of the molecules. In the present investigation, a bio molecule Chamazulene was taken. Chamazulene is deep blue oil extracted from chamomile flower. It is a natural, anti-inflammatory agent used in herbal remedies and cosmetic products. The attached methyl and ethyl groups are rotated separately at different dihedral angles to study the conformational energies, enthalpies and thermodynamic properties, *etc*.

RESULTS AND DISCUSSION

Molecular mechanics method is a natural outgrowth from older ideas of bonds between atoms on molecules and of van der Waal's and electrostatic forces between non-bonded atoms. The computational method employs to evaluate structures, energies and the fundamental formulations of vibrational spectroscopy. Frierson *et al.*[3,4] introduced the electronegativity effect in the molecular force fields is used to produce changes in the bond lengths. It is confirmed that the electronegativity correction is essential to reduce the errors and to increase the correctness of bond lengths. The molecular structural parameters have been carried out for all possible parametric computations. The calculated bond length and bond angles are summarized in Table-1 and compared with available experimental values of similar types of molecules. The calculated and observed values are finding in close agreement with each other.

TABLE–1
DIPOLE MOMENTS VARIOUS CONFORMERS OF CHAMAZULENE

Bond type	Bond angles (°)	Bond lengths (Å)
C–C	–	1.5365
C–H	–	1.1149
C–Cl	–	1.7942
C–C–C	109.51	–
C–C–H	110.00	–
H–C–H	109.40	–
Cl–C–H	106.90	–

In molecular mechanics, when one calculates steric energy which is the energy of a molecule taking into account of bending, stretching, *etc.* related to some particularly defined zero point, one has information to calculate heats of formation of molecules of all types correctly[5]. The calculated steric energy and its components are summarized in Tables 2 and 3. From these values, the variations in the values of van der Waal's compression and bending energies are studied as when the total energies increased.

TABLE-2
ENERGIES OF VARIOUS CONFORMERS OF CHAMAZULENE BY METHYL GROUP ROTATION (kcal)

Dihedral angle (°)	Compression	Bending	Stretch bend	van der Waal's 1,4 energy	Final steric energy
0	-683.27	635.01	-71.98	1304.56	3507.12
60	84.56	302.33	-8.03	217.81	888.54
120	81.65	397.46	-5.38	310.39	1220.63
180	-226.88	684.27	-68.58	1105.89	3106.19
240	97.07	183.34	-2.22	237.05	8166.06
300	19.69	159.96	-3.95	67.01	440.29

Most of the strain needed to calculate reasonable heats of formation by adjusting properly the bending and torsional potentials. Hence to calculate the heat of formation, the force fields are not parameterized and restricted for comparisons of energies between the conformational isomers and also reliable than the structure of the compounds. In the present investigations,

TABLE-3
ENERGIES OF VARIOUS CONFORMERS OF CHAMAZULENE BY ETHYL GROUP ROTATION (kcal)

Dihedral angle (°)	Compression	Bending	Stretch bend	van der Waal's 1,4 energy	Final steric energy
0	-771.68	1011.41	-72.35	1172.54	2921.78
60	89.53	406.60	5.33	594.96	1889.40
120	81.65	397.46	3.97	640.29	1737.61
180	133.96	339.86	7.69	480.00	1533.24
240	195.58	340.60	-8.78	254.15	1448.47
300	19.69	249.23	3.38	122.69	762.10

the heats of formation and the corresponding inherent strain energies are computed and presented in the Tables 4 and 5. From the observations, it is noted that the inherent strain and strain energy are the same and increasing with the increase of conformational steric energies in both the rotations. When the heats of formation and inherent strain energies are compared between the methyl group and ethyl group rotations, the quantities are found more in ethyl group rotations. This may be due to increase in strain, bending and torsional energies when the attached ethyl group is rotated in its position.

TABLE-4
DIPOLE MOMENTS VARIOUS CONFORMERS OF CHAMAZULENE

Dihedral angle (°)	Dipole moment (debye)	
	Ethyl group	Methyl group
0	0.378	0.297
60	0.771	0.269
120	0.706	0.625
180	0.703	0.582
240	0.770	0.539
300	0.656	0.377

For many organic compounds, there is not very much stretching, bending (or) torsional deformations, the most important quantities for determining their molecular structure, are non bonded interactions for non polar hydrocarbons, the only non bonded interactions among carbons and hydrocarbons in the formulations, bulk of these interactions are still among these atoms, therefore the selection of adequate van der Waal's functions for these atoms are very important in molecular mechanics calculations[6]. The energy minimization involves inter atomic adjustment and the selection of a minimum number of geometrical parameters becomes important. For Chamazulene, the computed thermodynamic quantities such as compression, bending and stretch bending are increased for the both rotations where as van der waal's heats of formation, torsional, straineless heats of formation, inherent strain, strain energy values are decreased. Properties like translation and rotation remain unchanged. The reasons, being the compounds are belonging to the cychohexane group and have been confirmed with the twist-boat chain as stable confirmation[7]. The energy associated with the rotation as one atom (or) group of atoms is called torsional potential energy. As the bond rotates the energy increases until the eclipsed confirmation is reached when the energy is at a maximum. Torsional energy varies continuously with degree of rotation as the methyl and ethyl group. The methyl groups ($C–CH_3$) in two positions are rotated while ethyl group $C–CH_2–CH_3$ remains stable position each rotations, the energy components are calculated and summarized in Table-5. Now keeping $C–CH_3$ groups stationary, ethyl group rotation is studied and presented in Table-6. The calculated energies are not varied uniformly in both rotations due to the variation of bond length and bond angles.

TABLE-5
HEATS OF FORMATION AND STRAIN ENERGIES OF VARIOUS CONFORMERS OF CHAMAZULENE BY METHYL GROUP ROTATION (kcal)

Dihedral angle (°)	Torsional energy	Heat of formation	Strain energy	Inherent strain
0	163.70	3699.06	3505.72	3505.72
60	209.27	1079.99	886.65	886.65
120	257.30	1412.56	1219.22	1219.22
180	232.43	3298.13	3104.79	3104.79
240	207.00	1008.00	814.66	814.66
300	183.69	632.22	438.88	438.88

TABLE-6
HEATS OF FORMATION AND STRAIN ENERGIES OF VARIOUS CONFORMERS OF CHAMAZULENE BY ETHYL GROUP ROTATION (kcal)

Dihedral angle (°)	Torsional energy	Heat of formation	Strain energy	Inherent strain
0	306.23	3113.71	2920.37	2920.37
60	209.47	2081.33	1887.99	1887.99
120	289.11	1929.55	1736.20	1736.20
180	264.06	1725.17	1531.83	1531.83
240	137.99	1640.41	1447.06	1447.06
300	240.48	954.04	760.69	760.69

Molecular mechanics methods show shortcomings in the evaluation of dipole moments, which range from one estimation to series of underestimations due to the presence of induced dipoles and dipole-dipole interaction[6,7] as tabulated in Table-4. The dipole moments, which mainly depend on the electrostatic interactions, are computed by additional adjustment to bond dipoles. The calculated values as dipole moments change non-uniformLy due to increase as final steric energy. When the dipole moments are compared, the values find no variations in their magnitudes for the increases of final conformational energies as summarized Tables 5 and 6.

Conclusion

From the study, molecular mechanics models have been extremely useful to predict the conformational and stereo chemical preferences of chemical structure. The computational methods have provided an improved means for carrying out conformational analysis and rotational molecular design. The accuracy in the calculations realized at present by molecular mechanics reveals in many cases that achieved by experimental methods so we concluded that the applications of molecular mechanics for the study of structures become a standard approach to conformational analysis.

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