Asian Journal of Chemistry Vol. 10, No. 4 (1998), 784–789

Rotational Studies on Isomers of Benzene Containing Bicyclopropenyl Rings

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Molecular orbital calculations have been carried out at the AM1 level with isomers of benzene having two cyclopropenyl rings. Rotational study of the single bond connecting the two cyclopropenyl moieties resulted in the variation of the total energy of the molecule. Based on these variations, two isomers were found to have interaction between the two classical π-bonds, namely, 1,1′-bicyclopropenyl and 3,3′-bicyclopropenyl. These molecules have relatively larger rotational barrier compared to 1,3′-bicyclopropenyl. An analysis of the wave functions and the charge densities of these show an accumulation of electronic charge in the p_z orbital of the methylene (or methine) carbon C3 in the cyclopropenyl.

INTRODUCTION

The dipole moment of cyclopropene is unusual in its direction and magnitude. Its "reversed polarity" is the result of net electron donation from the π_{CC} to $\sigma^*_{CH_2}$ "component orbitals" imposed by the molecules' symmetry.[1] The magnitude of the dipole moment (0.46 debye) originates in the extensive mixing between these component orbitals.[2] The AM1 calculated value for the dipole moment of cyclopropene is 0.36 debye, which is comparable to the experimental value reported above.

The appreciable π-electron density at the C3 of cyclopropene raises the interesting question of the interaction between two cyclopropenyl rings. In the present study, AM1 molecular orbital calculation[3] has been applied to study the structure and energy of the isomers of benzene possessing two cyclopropenyl groups. The electronic interaction between the cyclopropenyl rings has been studied as a function of conformation. As the single bond attached to either C1 or C3 of cyclopropene is rotated, the variations in the energy and the molecular orbitals are studied.

EXPERIMENTAL

The semi-empirical molecular orbital method AM1 has been employed in all the computations. The energies of the molecules have been computed as a

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function of the dihedral angle about the single bond connecting two cyclopropenyl moieties. The atoms are numbered as shown in Figure 1, where ∠2345 is the dihedral angle. Dihedral angles such as 0°, 30°, 45°, 60°, 90°, 120°, 135°,150° and 180° have been investigated and all the structural parameters (bond lengths, bond angles and dihedral angles) have been fully optimised. The single bond rotational studies of three isomers of benzene have been carried out and their results given below.

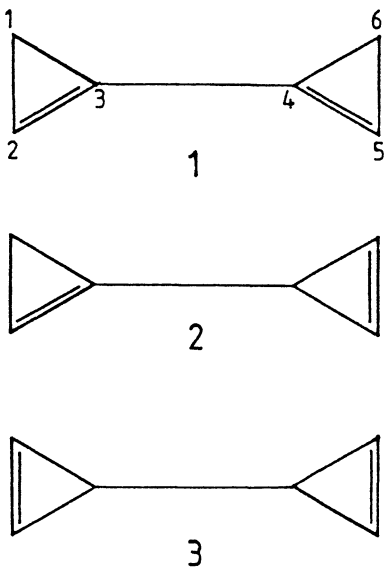

Fig. 1 Structures of bicyclopropenyls

RESULTS AND DISCUSSION

The isomers of C_6H_6 having bicyclopropenyl rings have large strain[4] and hence low stability. The three bicyclopropenyls—1,1′-bicyclopropenyl, 1,3′-bicyclopropenyl and 3,3′-bicyclopropenyl—have been synthesized only in the last ten years.[5] Because of their short lifetimes, the nature and properties of these strained molecules can only be theoretically investigated. The AM1 molecular orbital procedure is well suited for computations on hydrocarbons and has been applied earlier successfully to study strained C_6H_6 isomer and related systems.[6]

The structure of 1,1′-bicyclopropenyl, 1,3′-bicyclopropenyl and 3, 3′-bicyclopropenyl are shown in Figure 1.

1,1′-Bicyclopropenyl

AM1 calculations are performed on 1,1-bicyclopropenyl, as one cyclopropenyl group is roated about the single bond. The results of the calculations are given in Table-1. As the dihedral angle is increased from 0° to 180°, at various intermediate angles the twenty nine other molecular parameters are completely optimised.

TABLE-1
CALCULATED TOTAL ENERGIES (eV) AND RELATIVE ENERGIES (kcal/mol) FOR CONFORMERS OF 1,1′-BICYCLOPROPENYL

θ, degree	Total E	Relative E
0	-844.92709	0.00
30	-844.91208	0.35
45	-844.89622	0.71
60	-844.87790	1.13
90	-844.85808	1.59
120	-844.87847	1.12
135	-844.89651	0.71
150	-844.91205	0.35
180	-844.92646	0.01

The π-electron framework of 1,1′-bicyclopropenyl resembles that of 1, 3-butadiene. 1,1′-Bicyclopropenyl can also exist in *s-cis* and *s-trans* forms, where greater delocalisation of π-electrons is possible. In addition, rotamers with lower symmetry are also possible. The *s-cis* and *s-trans* forms are more stable as indicated by the lower energy values. The *s-cis* and the *s-trans* forms possess almost the same amount of energy and hence should be equally stable. At carbons C1 and C1′, the sp^2 hybrid angle is large and is 151.6°. This compensates for the small angles inside the cyclopropenyl ring. Because of the large angle outside the ring, the amount of crowding is less and the *trans* form is not particularly more stable than the *cis* form.

The length of the single bonds in the cyclopropene moiety is 1.49 Å and the length of the double bond is 1.32 Å. The length of C1–C1′ bond varies around 1.38 Å and does not show large variation as the dihedral angle is varied form 0° to 180°. The bond length is minimum at 0° (and also at 180°) due to delocalisation. But the length does not increase comparable to that of a single bond even at a dihedral angle of 90°.

As the dihedral angle is varied, the total energy of the system also varies. The relative energies of the conformers fit well into the equation

$$V(\theta) = -0.02717 + 1.554 \sin^2 \theta \quad (1)$$

where θ is the dihedral angle (in degrees) and V(θ) is the relative energy (in kcal/mol). The linear fit is excellent with a correlation coefficient greater than 0.99. The energy of the system is lowest at an angle of 0° (and also at 180°), and is highest at 90°. The barrier rotation is computed to be 1.6 kcal/mol. The corresponding value for the experimental rotational barrier in 1,3-butadiene is reported[7] to be 2.3 kcal/mol. When a single bond attached to multiple bonds is rotated, the rotational barrier is generally smaller[8] compared to rotational barriers about a single bond in compounds containing no multiple bonds, like an ethane.[9] The net electronic charges on the various atoms do not show any appreciable variation with changes in dihedral angle.

An analysis of the wave functions shows that in the planar state, eight molecular orbitals (four in the bonding level and four in the anti-bonding level) have only the p_z orbital of the six participating carbon atoms. Of these six carbon atoms, four carbon atoms have alternate double and single bonds as in 1,3-butadiene. The other two carbon atoms, though not a part of the classical π-system, have high electron density at the p_z orbitals. It is also seen that these two methylene carbon atoms have the highest p_z charge. The π-electron delocalization is over the entire carbon framework. The methylene hydrogens show weak interaction with the π-framework.

1,3′-Bicyclopropenyl

1,3′-Bicyclopropenyl is the least symmetrical molecule considered in this study. The total energy and the relative energy, calculated as a function of the dihedral angle, are presented in Table-2. The lowest heat of formation of 150.3 kcal/mol is at dehedral angle of 30° and the largest value of 151.0 kcal/mol at an angle of 125°. The rotational barrier is small for this system, being only 0.68 kcal/mol. The single bond connecting the two cyclopropenyl rings which undergo rotation also does not show any noticeable change in the bond length as the dihedral angle is varied. The analysis of the wave function also reveals that the two classical π-bonds do not appreciably interact with each other at all dihedral angles.

TABLE-2
CALCULATED TOTAL ENERGIES (eV) AND RELATIVE ENERGIES (kcal/mol)
FOR CONFORMERS OF 1,3′-BICYCLOPROPENYL

θ, degree	Total E	Relative E
0	–844.76885	0.15
30	–844.77524	0.00
45	–844.77383	0.03
60	–844.76950	0.13
90	–844.75538	0.46
120	–844.74558	0.68
135	–844.74628	0.67
150	–844.75099	0.56
180	–844.76557	0.22

3,3′-Bicyclopropenyl

3,3′-Bicyclopropenyl is formed when the C3 atoms of the two cyclopropene rings are joined by a single bond by removing the two hydrogens at these carbon atoms. When the molecule is rotated about the C3–C3′ single bond, the energy of the molecule is continuously varied. The total energy and the relative energy as a function of the dihedral angle are presented in Table-3. The energy of the molecule is lowest in the *anti* position, having a heat of formation value of 153.0

kcal/mol and highest in the *syn* position (ΔH_f of 154.7 kcal/mol). The value of the relative energy as a function of dihedral angle is fitted in the equation

$$V(\theta) = 0.7278 + 0.8325 \cos^3 \theta \quad (2)$$

where $V(\theta)$ is the relative energy in kcal/mol and θ is the dihedral angle in degrees, the correlation coefficient for the fit is greater than 0.99.. The rotational barrier is found to be 1.6 kcal/mol, which compares well with value of 2.0 kcal/mol obtained by *ab initio* STO-3G calculations.[10] The C3–C3′ single bond distance also varies with the variation in the angle of rotation. Though the change in the bond length is marginal, it is lowest at the *syn* position. The bond length is found to be largest at a dihedral angle of 30°.

TABLE-3
CALCULATED TOTAL ENERGIES (eV) AND RELATIVE ENERGIES (kcal/mol) FOR CONFORMERS OF 3,3′-BICYCLOPROPENYL

θ, degree	Total E	Relative E
0	–844.58508	1.66
30	–844.60212	1.27
45	–844.61333	1.01
60	–844.62170	0.81
90	–844.62833	0.66
120	–844.63359	0.54
135	–844.64007	0.39
150	–844.64791	0.21
180	–844.65700	0.00

Since there is appreciable π-electron density at C3 of cyclopropene, joining of two such rings at these positions raises the interesting question of interaction between these rings. It is seen that the two classical π-bonds in 3,3′-bicyclopropenyl interact strongly. Among the four wave functions of the classical n-bonds, the lower two have interchanged positions. Therefore, the lower energy π-wave function has the sign $++--$ and the higher function has the sign $++++$. The energy of the 4π-electrons varies mostly between –39.7 and –39.9 eV with change in dihedral angle, but at 90° it attains a low value of –42.6 eV.

Conclusion

Three isomers with the formula C_6H_6 are possible, each containing two cyclopropenyl groups attached by a single bond. Rotation about the single bond has been studied by the AM1 method. The compound cyclopropene has high π-electron density at the carbon atom C3 and shows interesting behaviour when two cyclopropenyl rings connected by a single bond are rotated. The species with the lowest energy is 1,1′-bicyclopropenyl, while 3,3′-bicyclopropenyl has the largest energy. The rotational barrier in the case of 1,1′-bicyclopropenyl and 3,3′-bicyclopropenyl have been computed to be 1.59 kcal/mol and 1.66 kcal/mol respectively. The corresponding value for 1,3′-bicyclopropenyl is found to be only

0.68 kcal/mol. The larger the π-electron interaction between the connected carbon atoms, the larger is the value of the rotational barrier. Thus 1,1′-bicyclopropenyl and 3,3′-bicyclopropenyl having larger π-bond interaction between the rings have larger rotational barrier when compared to 1,3′-bicyclopropenyl. In the case of 1,1′-bicyclopropenyl, in the planar state, methylene carbons have the highest electron density in the p_z orbital and delocalisation of the π-electrons is observed over the entire carbon framework. It is also observed that the energy levels of the occupied classical π-functions in 3,3′-bicyclopropenyl are observed in the reverse.

ACKNOWLEDGEMENT

One of the authors (JJ) gratefully acknowledges the partial assistance for this research provided by the University Grants Commission, New Delhi in the form of a Minor Research Project.

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(*Received*: 19 January 1998; *Accepted*: 27 April 1998) AJC-1484