Theoretical studies of ten selected isomers of $C_7H_7^+$ by computational calculation of their energies

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Abstract: *Various possible isomers for the $C_7H_7^+$ systems are analyzed to predict the relative stability for each species with reference to the energies calculated by the semi-empirical AM1 method as well as the ab initio HF and the density functional theory (DFT) methods using the 6-31G* basis set. A total of ten isomers were chosen for the $C_7H_7^+$ system. They are (a) 3-methyl dicyclopropene cation (**Iso-I**) (b) 3-cycloprop-enyl-cyclobutane cation (**Iso-II**) (c) 3-cycloprop-enyl-cyclobutane cation (**Iso-III**) (d) Spiro [3,3]hepta-1,5-diene cation (**Iso-IV**) (e) bicycle [3.2.0] hepta-dienyl cation (**Iso-V**) (f) bicyclo[3.2.0]hepta-dienyl cation (**Iso-VI**) (g) 3-methyl dicyclopropene cation (**Iso-VII**) (h) polycyclic cation (**Iso-VIII**) (i) Bicyclo[2.2.1]hepta-2,5-diene or norbornyl cation (**Iso-IX**) (j) Cyclohepta-1,3,5-triene or tropylium cation (**Iso-X**). The theoretical studies embodied in this paper concern cationic system of $C_7H_7^+$ isomers of the $C_mH_n^+$ type, which display wide structural diversities among themselves. The $C_7H_7^+$ isomers were studied employing the theoretical computational method based on the Principle of Quantum Mechanical approach viz. The ab initio HF, B3LYP levels of theory and semi-empirical AM1 levels of theory.*

Keywords: *ab initio HF, isomerizations, DFT level of calculation, semi-empirical AM1, $C_7H_7^+$ systems, mechanistic pathways, 6-31G* basis set, semi-empirical AM1 method, B3LYP, Quantum Mechanic approach, theoretical studies, kinetic energy, computational method, 3-methyl dicyclopropene cation, 3-cycloprop-enyl-cyclobutane cation, 3-cycloprop-enyl-cyclobutane cation, Spiro [3,3]hepta-1,5-diene cation, bicycle [3.2.0] hepta-dienyl cation, bicyclo[3.2.0]hepta-dienyl cation, 3-methyl dicyclopropene cation, polycyclic cation, Bicyclo[2.2.1]hepta-2,5-diene or norbornyl cation, tropylium cation, equilibrium geometry. Aromatic resonance, allylic resonance, Multiple pi bond resonance.*

1. INTRODUCTION:

The $C_7H_7^+$ system can have numerous isomers. One typical isomer – the tropylium ion is well known for its high stability which arises out of its aromatic nature. This study is simply an isomeric investigation, estimating the relative stability of the various isomers on the $C_7H_7^+$ energy potential surface. Such isomers are expected to exist as minima having various depths on the energy surface. The stability of each isomer may be assessed relative to the most stable isomer or global minimum. The choice of theoretical studies instead of experimental studies is due to the fact that computation theoretical methods provide precised calculation at low cost compared to the experimental approach. Computational method also gives immense assistance in simulating models of chemical structural patterns which otherwise becomes almost impossible through experimental approach.

2. METHODOLOGY :

The isomers were firstly designed and their geometries were optimized at the semi-empirical AM1 level. Comparison of the AM1 energies or heats of formation could then give an initial idea of their relative stability.

The AM1 structures were then subjected to calculation at the *ab initio* Hartree - Fock SCF-MO level with a 6-31G* basis set (the HF/6-31G* strategy) where full optimization of the structure along with the frequency calculation was carried out. These structures were then calculated and optimized using the density functional theory method at the B3LYP level of theory using the 6-31G* basis set (the B3LYP/6-31G* strategy). They are supposed to be adequate to handle the problem of assigning relative stabilities to carbocationic systems like those studied here. The B3LYP/6-31G(d) strategy was used as the initial computational method to obtain all the energy-minimized equilibrium geometries. Semi-empirical AM1 calculations gave input geometries for B3LYP optimization. All calculations were done using the GAUSSIAN 98 PROGRAM.

3. RESULT AND DISCUSSION:

Ten possible isomers were selected for studies, they are supposed to execute interconversion among themselves by getting activation energy in order to climb up energy barrier for a particular system of interconversion. The selected isomers were designated as Iso-I, Iso-II, Iso-III, Iso-IV, Iso-V, Iso-VI, Iso-VIIa and Iso-VIIb (They are interconvertible

through 180^0 rotation about C-C bond), Iso-VIIIa and Iso-VIIIb (Two resonating structures), Iso-IX and Iso-X respectively given below:
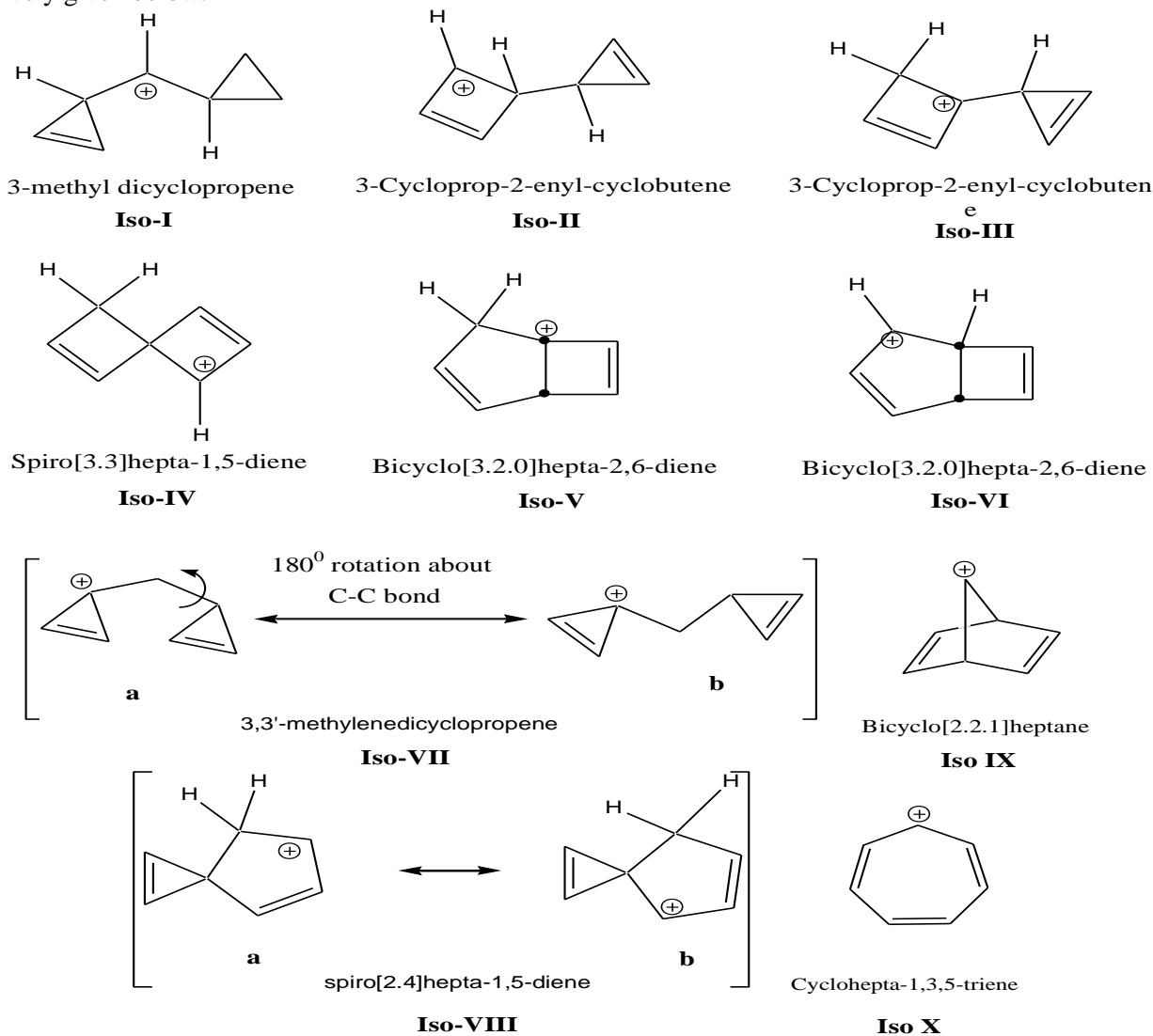

Fig. 1 : Structure of various $C_7H_7^+$ isomers, optimized in the B3LYP/6-31G(d) level

Among the above 10 isomeric structures, the tropyl cation **Iso-X** alone is truly *aromatic*. The norbornyl cation **Iso -IX** is the only isomer that is *non-classical*, it is stabilized by a two-electron three-centre bond, where the pi bond overlaps with the positively charged C7 centre. The first type of delocalization is the *aromatic* kind seen in the *tropyl* cation **Iso-X**, where complete delocalization of positive charge via the six pi bonds leads to an aromatic sextet in the seven-membered symmetrical ring. One may even assume that this aromatic species tropylium, isomer **X**, would most likely represent the global minimum on the $C_7H_7^+$ potential energy surface.   The cations **I, II, II, IV, V, VI, VII and VIII** all contain an allyl cation moiety, and are stabilized by *allylic resonance*. The non-classical cation **IX** is stabilized by overlap of one pi bond with the positively charged C7 centre, but this overlap occurs only on *one* side; the cation is not symmetrical and the C7 hydrogen atom projects over to one side (the non-overlapping side). The cations **I to VIII** contain C=C double bonds within the three- and four- membered carbocyclic moieties.

TABLE : Total energies of the $C_7H_7^+$ isomers along with relative energy (RE in Kcal/mol using Tropylium as a reference which is zero) as calculated by optimization (opt) of semi-empirical AM1 method and by the *ab initio* HF and B3LYP level of theory using a 6-31G* basis set.

Name of Isomers	AM1 opt	RE	HF/6-31G(d) opt	RE	B3lyp/6-31G(d) opt	RE
Isomer I	0.5562149	138.69	-268.7032991	121.77	-270.4870446	120.18
Isomer II	0.5452516	131.81	-268.7261881	107.41	-270.4990947	112.62
Isomer III	0.5219842	117.21	-268.7526063	90.83	-270.5300471	93.21

| Isomer IV	0.5157935	113.33	-268.7654604	82.76	-270.5377188	88.39
Isomer V	0.4691911	84.08	-268.8071026	56.63	-270.5803218	61.65
Isomer VI	0.4370779	63.93	-268.8150397	51.65	-270.5904519	55.30
Isomer VIIa	0.5364326	126.28	-268.7416641	97.69	-270.5051641	108.81
Isomer VIIb	0.533466	124.42	-268.746936	94.40	-270.5088386	106.51
Isomer VIIIa	0.458663	77.48	-268.7966869	63.17	-270.5760556	64.33
Isomer VIIIb	0.4586631	77.48	-268.7966869	63.17	-270.5760556	64.33
Isomer IX	0.4753193	87.93	-268.8207573	48.06	-270.5938123	53.19
Isomer X	0.3351925	0	-268.8973595	0	-270.6785813	0
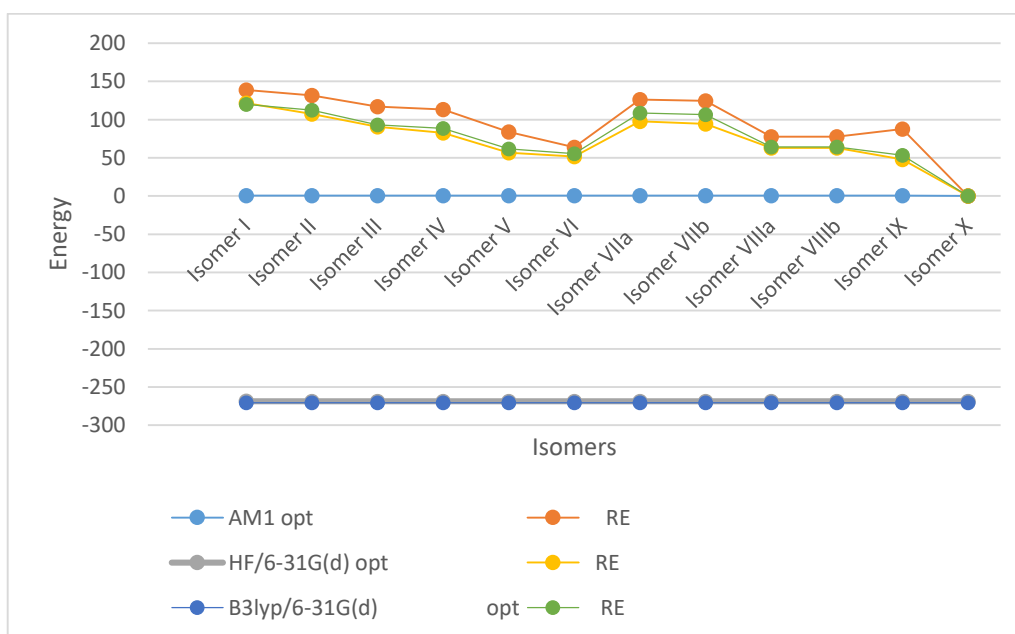
Fig. Graph showing the energies of different isomers calculated by AM1, HF and B3lyp

Within each calculation regime, the relative energies (RE) are also given with respect to the most stable isomer – *tropylium cation* taken as zero. The order of stability of the **10** isomers as calculated by the AM1 method is **X > VI > VIII a = VIII b > V > IX > IV > III > VII(b) > VII(a) > II > I.** This differs from the stability order furnished by the HF/6-31G* method, which emerges as **X > IX > VI > V > VIII a = VIII b > IV > III > VIIb > VIIa > II > I**. The stability order followed by the B3LYP/6-31G* strategy is **X > IX > VI > V > VIII (a) = VIII (b) > IV > III > VIIb > VIIa > II > I** which is quite close to that obtained by the *ab initio* Hartree-Fock SCF method. The only point of disagreement here is that the **IX** and **V** positions are exchanged in AM1 compared to that of the *ab initio* HF and the B3LYP (DFT) levels.

The two higher level methods, however do agree fairly well with each other. One may be led to repose a greater level of confidence on the *ab initio* HF and B3LYP strategy. That the two higher level methods agree well with each other is quite a point to be made in their favour. In any case, the *ab initio* HF and density functional methods are better suited to handle the structural diversities found in the **10** isomers.

Discussion of relative stability is carried out with reference to the three types of delocalization mentioned below:
 (i) *Aromatic resonance:* Only the tropylium cation **X** falls under this heading. All the three methods used here predict this structure as being the *most stable* among the **10** isomers studied. This system owes its remarkable stability due to complete delocalization of six π-electrons within the symmetrical 7-membered ring in an aromatic manner. The unit positive charge is thus equally delocalized among all the seven ring carbons, and this highly stable classical aromatic cation represents a 6π-7C system. Being the most stable equilibrium structure upon the $C_7H_7^+$ potential energy surface, the energies computed for the other isomers are all taken as relative to the tropylium cation, which is itself set at an arbitrary level of zero energy for the sake of comparison.
(ii) *Multiple pi bond resonance* **:** This kind of stabilizing effect is seen in the isomers **IX**. This allow for delocalization of three pi bonds over the cationic framework in conjugation with the positively charged carbon centre. The norbornyl cation **IX** is the *second most stable* $C_7H_7^+$ isomer as mentioned by the three methods qualitatively. The energy of **Iso-IX** relative to the tropyl cation is 53.19 kcal/mol (B3LYP), 48.06kcal/mol (HF) and 87.93 kcal/mol (AM1). Thus, the AM1 method gives a less stable energy for **IX** with reference to the tropyl cation.

(iii) *Allylic resonance* **:**   The simple allyl cation is the prototype case here, where the positive charge is equally distributed over two carbon centers. Isomers I to VIII possesses an allyl cation moiety. All these have an isolated allyl cation moiety which is not in further conjugation with any other multiple-bond system. Their order of stability is given as : **VI > V > VIII a = VIII b > IV > III > VIIb > VIIa > II > I**..

4. CONCLUSION : .

Stability of various isomers of $C_7H_7^+$ depends upon many factors. Of these, electron movement/positive charge distribution within a cation moiety is one of the most important factors that determines stability especially in cationic system. A molecule is said to be stable if it is resonance stabilized which further depends upon the ability of delocalization of electron in the pi-system. Tropylium cation is one of those resonance stabilized cations, the pi electrons in the ring system delocalize in the ring forming aromatic cationic species and is considered as the most stable cation among $C_7H_7^+$ isomers. The stability order of other cations are attributed to multiple pi bond resonance which occurs in multiple bond system and allylic resonance that occurs in allylic bond that determine the stability of carbocation by distributing positive charge in two carbon centers. The main objective of this research is to compare stability of different isomers of $C_7H_7^+$ and it cames out with the conclusion that the stability among various isomers depends on the ease with which electrons delocalize (Resonance) within the ring and among those delocalization the one that contribute for aromaticity will be the most stable.

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