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Theoretical Study on Bromofulvene isomers (3-Bromofulvene , 4-Bromofulvene and 6-Bromofulvene) and their positive and negative radical ions . Part A

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Abstract

Gaussian 03 calculations have been done after complete optimization of geometry on bromofulvene isomers (3-Bromofulvene, 4-Bromofulvene and 6-Bromofulvene) and their positive (+1,+2) and negative (-1,-2) radical ions . It was found that only the radical anions of these isomers are stabilizing . Also, both charges, positive and negative, increase the dipole moment. Geometric parameters, ionization potential, orbital energies (Highest Occupied Molecular Orbital "HOMO" and Lowest Unoccupied Molecular Orbital " LUMO "), electron densities of atoms are reported for all these isomers and their charged corresponding states.

الخلاصة

أجريت الحسابات باستخدام برنامج Gaussian 03 متضمّنة الحصول على الشكل الهندسي ذي الطاقة الأقل ، لآيزومرات البروموفولفين (3- بروموفولفين ، 4- بروموفولفين ، 6- برومو فولفين) وجذورها الأيونية الموجبة (+1,+2) والسالبة (-1,-2) . فوجد أن الجذور السالبة فقط لهذه الآيزومرات ، تؤدي الى زيادة استقرار نظيراتها غير المعوضة . أن الشحنات الموجبة والسالبة كلاهما تؤدي الى زيادة عزم ثنائي القطب . كما تم تدوين المتغيرات الهندسية و جهد التأين و الطاقات المدارية (أعلى مدار جزيئي مشغول HOMO وأوطأ مدار جزيئي غير مشغول LUMO) والكثافات الألكترونية للذرات لجميع هذه الآيزومرات و نظيراتها المشحونة .

Introduction

Fulvenes are a cross-conjugated molecules with some unique properties [1] . Their structure and electronic distribution were investigated theoretically and experimentally[2,3] . The halogenated substituted fulvenes were used to improve the octane quality of a fuel for an internal combustion engines[4]. The fluorosubstituted fulvenes is relatively common ligand in the organometallic; the low-valent titanium-pentafulvene complexes had been prepared[5]. Theoretical study on monosubstituted fulvenes that having substituents from first, second[6-9] and third[10] had been reported. However, no experimental and or theoretical studies are found for charged and non-charged bromofulvene isomers. The aim of the present work was done to study the three bromofulvene isomers and their radical ions, where Br is the substituent at C_3 , C_4 and C_6 ,by using the Gaussian03, applying the Density Function Theory (DFT) calculations based on Becke 3-Lee-Yang- Parr (B3LYP) level with CEP-121G basis set.

Results and Discussion :

1-Geometrical properties

Angles and lengths of bonds for the studied molecules and their radical ions were listed in (Table 1). It is obvious that adding and removing one electron or two electrons to the bromofulvene isomers cause an increase in the bond lengths of R(1-2), R(3-4) and R(5-6) , and a decrease in R(2-3) , R(4-5) and R(1-5) , this may be due to an increasing in the delocalization of electrons resulting from the positive and negative charges. Generally, the C-Br bond length increase in radical anions (-1,-2) this may be resulting from the electron repulsion of the non-bonding paired electrons on Br with the negative charge, that delocalized throughout the entire radical anions, and decrease in radical cations (+1,+2) because the decreasing of electrons that may leads to attraction Br (carrying electron pairs) to the carbon atom to which it is attached . Negative charges are found to

increase the bond angle to which Br is attached, but the positive charges decrease this bond angle, and in the order of :

Anion (-2) >Anion (-1) >Neutral >Cation (+1) >Cation (+2)

2-Dipole moment

The dipole moments can be understood as a result from intramolecular charge transfer from exocyclic double bond to five membered ring thereby acquiring pseudoaromatic cyclopentadienide character[6] . The dipole moments is mainly depend on the charges and the distance between the atoms[11] . For the studied molecules and their radical ions ,the dipole moments were listed in (Table 2) . In the bromofulvene molecule, the dipole moment is due to the high electronegativity of Br, and it is obvious that adding and removing one electron or two electrons to the bromofulvene isomers cause an increase in the dipole moment because the increasing in the charges, for 4-Bromofulvene and 3-Bromofulvene , the order is:

Anion (-2) > Cation (+2) > Cation (+1) > Anion (-1) > Neutral

This may be due to the direct attachment of Br to the five membered ring , while 6-Bromofulvene which is on the exocyclic double bond at C_6, is ordered in the following:

Cation (+2) > Anion (-2) > Cation (+1) > Anion (-1) > Neutral

The largest dipole moment value is in 3-Bromofulvene (-2) .

3-Electron densities

The electron densities for the studied molecules and their radical ions were listed in (Table 3) . It was found for all isomers that the radical anions have the largest electron densities at their atoms , followed by the molecules of isomers , and then the radical cations , and in the order of :

Anion (-2) >Anion (-1) >Neutral >Cation (+1) >Cation (+2)

Except the C_5 position which is directly attached to the exocyclic double bond C_5-C_6 , and the substituted position for the three isomers which have different order, that may be attributed to the effect of the substitute .

4-Orbital energies

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the two most important molecular orbitals [12] . Radical cations are more easily to be reduced than that of the molecules, and then the radical anions. The ability for increasing the reduction is in the order of :

Anion (-2) >Anion (-1) >Neutral >Cation (+1) >Cation (+2)

The low energy of LUMO suggests a high reactivity (Table 2). 6-Bromofulvene radical cation is more easily to be reduced than that of the 3-Bromofulvene and 4-Bromofulvene, this is may be due to the low values of the LUMO energies.

5-Ionization potential

The calculated HOMO-LUMO orbital energies can be used to estimate the ionization energy[13]. Koopmans' theorem suggests that the energy of the HOMO is a good approximation to the negative experimental ionization potential (-IP)[12]. The ionization potential for the studied molecules and their radical ions were listed in (Table 2) . For the three bromofulvene isomers , they were found that the ionization potentials are in the order of:

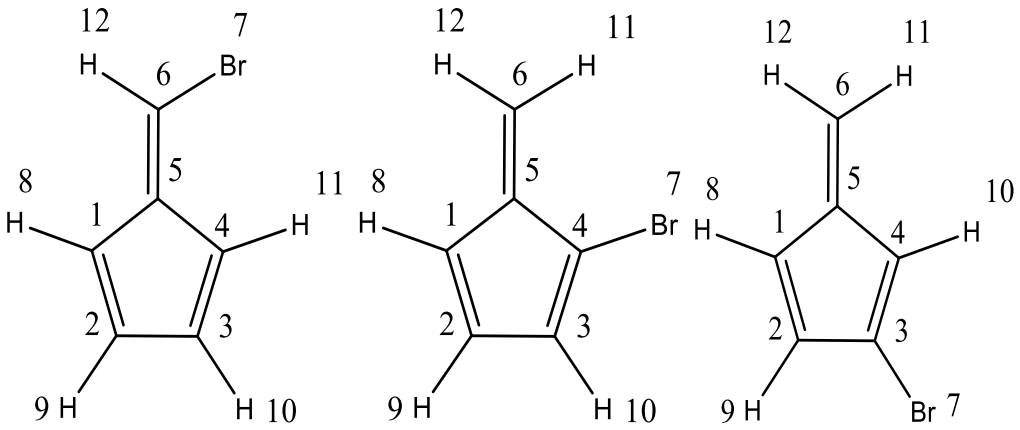
Cation (+2) > Cation (+1) >Neutral > Anion (-1) > Anion (-2)

And the 4- bromofulvene isomer (+2) is more difficulty to be oxidized than that of the 3-Bromofulvene(+2) and 6-Bromofulvene(+2) ,this is may be due to the low values of the HOMO energies.

6-Stabilization by substituents

The stabilizing effect of a substituent is often assessed by using isodesmic reactions (conserved bond type)[14]. A positive energy difference (Δ) (Table 4) indicates stabilization of the reactant by substituent. The results show that only the radical anions of these isomers are stabilizing , this may be attributed to electron withdrawing effect of Br which decrease the electron abundance resulting from acquiring one electron or two, and a small degree in 4-Bromofulvene (+2). It is found that the 3-Bromofulvene is the more stable than that of the 4-Bromofulvene and 6-Bromofulvene in the radical anion (-1) state, while the 6-Bromofulvene is the more one in the radical anion (-2) state. In the molecules and radical cations (+1,+2), the substituent decrease the stabilization of the reactant .

Figure 1.The bromofulvene isomers.



6-Bromofulvene 4-Bromofulvene 3-Bromofulvene

Table 1. Calculated geometric parameters (bond lengths in Angstrom and bond angles in degrees) of the bromofulvene isomers and their radical ions.

Geometrical properties		3-C_6H_5Br (3-Bromo fulvene)				
		Neutral	Anion(-1)	Anion(-2)	Cation(+1)	Cation(+2)
Bond lengths(Angstrom)	R(1-2)	1.372	1.423	1.467	1.414	1.412
	R(1-5)	1.496	1.461	1.461	1.484	1.528
	R(1-8)	1.084	1.089	1.097	1.086	1.090
	R(2-3)	1.491	1.436	1.412	1.435	1.425
	R(2-9)	1.083	1.085	1.089	1.082	1.084
	R(3-4)	1.370	1.411	1.442	1.445	1.536
	R(3-7)	1.945	2.0026	2.091	1.892	1.847
	R(4-5)	1.492	1.463	1.469	1.470	1.412
	R(4-10)	1.082	1.085	1.089	1.085	1.092
	R(5-6)	1.362	1.428	1.466	1.371	1.402
	R(6-11)	1.089	1.091	1.098	1.089	1.093
	R(6-12)	1.089	1.091	1.098	1.088	1.093
Angles(degree)	A(2-1-5)	108.4	109.5	111.2	109.4	110.2
	A(2-1-8)	127.3	125.8	124.1	125.7	125.3
	A(1-2-3)	107.6	105.8	103.8	108.0	107.8
	A(1-2-9)	128.0	127.9	128.2	126.5	126.0
	A(5-1-8)	124.3	124.6	124.6	124.9	124.4
	A(1-5-4)	106.6	106.7	105.3	105.7	105.9
	A(1-5-6)	126.5	126.8	128.0	127.5	128.9
	A(3-2-9)	124.4	126.3	128.0	125.5	126.2
	A(2-3-4)	110.9	111.6	113.1	109.5	108.5
	A(2-3-7)	122.7	123.8	123.5	126.1	128.7
	A(4-3-7)	126.4	124.5	123.3	124.4	122.8
	A(3-4-5)	106.5	106.4	106.6	107.5	107.5
	A(3-4-10)	128.0	127.3	126.9	125.9	124.4
	A(5-4-10)	125.5	126.3	126.6	126.6	128.0
	A(4-5-6)	126.9	126.6	126.7	126.9	125.2
	A(5-6-11)	121.3	121.0	120.9	121.4	121.9
	A(5-6-12)	121.7	121.5	121.5	121.6	121.2
	A(11-6-12)	117.0	117.5	117.6	117.0	117.0
Geometrical properties		4-C_6H_5Br (4-Bromo fulvene)				
		Neutral	Anion(-1)	Anion(-2)	Cation(+1)	Cation(+2)
Bond lengths(Angstrom)	R(1-2)	1.373	1.418	1.452	1.426	1.486
	R(1-5)	1.496	1.465	1.473	1.476	1.444
	R(1-8)	1.084	1.089	1.096	1.085	1.092
	R(2-3)	1.494	1.447	1.429	1.426	1.390
	R(2-9)	1.085	1.089	1.097	1.083	1.086
	R(3-4)	1.370	1.414	1.451	1.433	1.491
	R(3-10)	1.083	1.086	1.090	1.083	1.086
	R(4-5)	1.496	1.453	1.447	1.489	1.508
	R(4-7)	1.947	2.001	2.083	1.885	1.831
	R(5-6)	1.359	1.424	1.456	1.367	1.385
	R(6-11)	1.088	1.091	1.097	1.088	1.092
	R(6-12)	1.088	1.089	1.093	1.088	1.091
A ng	A(2-1-5)	108.5	109.7	111.7	109.1	110.5

	A(2-1-8)	127.7	126.7	125.8	126.2	124.4
	A(1-2-3)	109.5	108.8	108.5	109.2	108.7
	A(1-2-9)	126.6	126.2	125.9	125.5	124.5
	A(5-1-8)	123.8	123.6	122.5	124.7	125.1
	A(1-5-4)	104.7	103.6	100.4	104.5	104.0
	A(1-5-6)	127.5	127.4	128.3	127.4	126.6
	A(3-2-9)	123.9	125.0	125.6	125.3	126.8
	A(2-3-4)	107.7	106.0	104.1	108.2	108.0
	A(2-3-10)	125.0	127.4	129.1	126.4	127.6
	A(4-3-10)	126.8	126.6	126.8	125.3	124.4
	A(3-4-5)	109.7	112.0	115.4	109.0	108.7
	A(3-4-7)	126.3	22.9	24.1	125.0	124.0
	A(5-4-7)	124.0	23.0	22.3	126.0	127.2
	A(4-5-6)	127.8	129.0	131.4	128.2	129.4
	A(5-6-11)	121.1	120.6	120.2	121.2	120.9
	A(5-6-12)	121.4	121.4	121.6	121.7	122.6
	A(11-6-12)	117.4	118.0	118.2	117.1	116.5
Geometrical properties		6-C_6H_5Br (6-Bromofulvene)				
		Neutral	Anion(-1)	Anion(-2)	Cation(+1)	Cation(+2)
	R(1-2)	1.373	1.416	1.455	1.442	1.446
Bond lengths(Angstrom)	R(1-5)	1.500	1.469	1.463	1.470	1.529
	R(1-8)	1.084	1.089	1.097	1.086	1.094
	R(2-3)	1.492	1.448	1.426	1.418	1.392
	R(2-9)	1.085	1.090	1.098	1.084	1.084
	R(3-4)	1.375	1.419	1.457	1.438	1.557
	R(3-10)	1.085	1.090	1.098	1.083	1.089
	R(4-5)	1.487	1.455	1.447	1.472	1.399
	R(4-11)	1.082	1.086	1.092	1.085	1.090
	R(5-6)	1.359	1.418	1.460	1.380	1.425
	R(6-7)	1.9509	2.010	2.147	1.898	1.853
	R(6-12)	1.086	1.084	1.082	1.088	1.092
Angles(degree)	A(2-1-5)	107.6	108.2	109.1	108.4	110.4
	A(2-1-8)	127.9	127.0	126.0	126.0	124.9
	A(1-2-3)	109.0	108.3	107.8	108.7	107.5
	A(1-2-9)	126.3	125.8	125.5	125.2	125.3
	A(5-1-8)	124.4	124.8	124.9	125.6	124.7
	A(1-5-4)	106.4	106.5	105.7	105.8	105.2
	A(1-5-6)	123.5	123.1	123.3	124.6	124.5
	A(3-2-9)	124.7	125.9	126.7	126.1	127.2
	A(2-3-4)	109.3	108.5	107.9	108.9	108.7
	A(2-3-10)	124.6	125.7	126.5	126.0	127.9
	A(4-3-10)	126.1	125.8	125.6	125.2	123.4
	A(3-4-5)	107.7	108.4	109.5	108.3	108.3
	A(3-4-11)	127.8	127.0	126.3	126.1	123.6
	A(5-4-11)	124.5	124.6	124.2	125.6	128.1
	A(4-5-6)	130.1	130.4	131.1	129.7	130.5
	A(5-6-7)	124.4	23.3	23.6	125.1	126.3
	A(5-6-12)	124.2	127.9	135.3	121.9	120.2
	A(7-6-12)	111.3	23.2	23.4	113.0	113.5

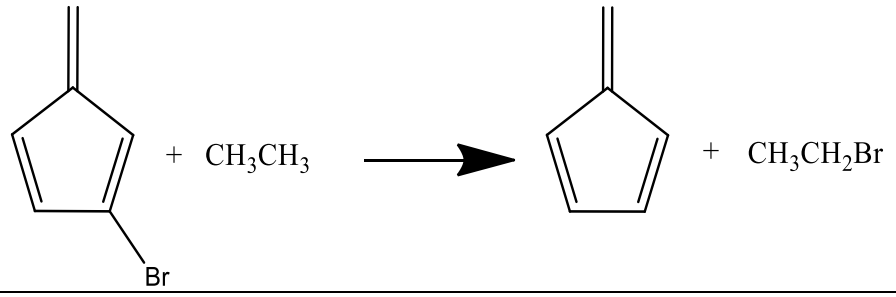
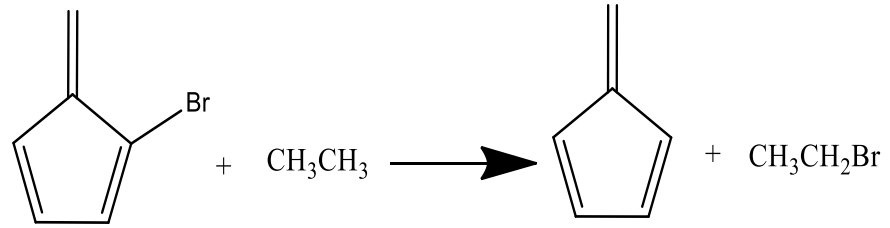
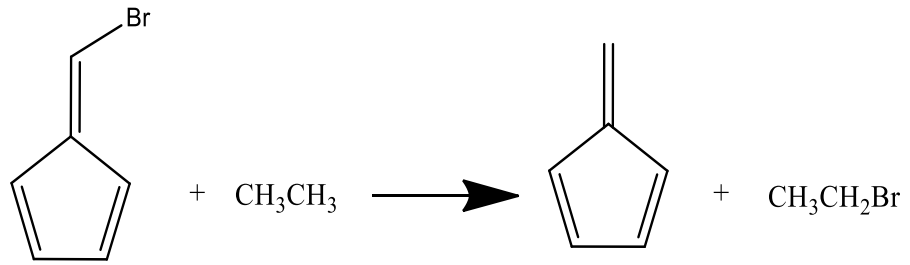
Table 2. Calculated orbital energies (HOMO,LUMO), (in eV),total energies (E_{tot} in au) , dipole moments (in Debye) , orbital energies (IP in eV) for the bromofulvene isomers and their radical ions.

Molecule	HOMO (eV)	LUMO (eV)	E_{tot} (au)	Dipol moment (μ in Debye)	IP(eV)
6-Bromofulvene (neutral)	-6.310	-2.374	-50.168	1.114	6.310
6-Bromofulvene radical anion(-1)	0.920	3.654	-50.196	4.295	-0.920
6-Bromofulvene radical anion(-2)	6.361	8.198	-50.018	7.817	-6.361
6-Bromofulvene radical anion(+1)	-12.242	-8.401	-49.874	6.425	12.242
6-Bromofulvene Radical cation(+2)	-17.707	-15.901	-49.347	10.933	17.707
4-Bromofulvene (neutral)	-6.163	-2.404	-50.166	1.664	6.163
4-Bromofulvene radical anion(-1)	0.889	3.868	-50.194	3.208	-0.889
4-Bromofulvene radical anion(-2)	6.570	8.067	-50.014	8.631	-6.570
4-Bromofulvene radical anion(+1)	-11.971	-8.290	-49.876	5.249	11.971
4-Bromofulvene radical cation(+2)	-18.341	-15.629	-49.368	8.160	18.341
3-Bromofulvene (neutral)	-6.338	-2.377	-50.167	2.435	6.338
3-Bromofulvene radical anion(-1)	0.872	3.986	-50.195	4.267	- 0.872
3-Bromofulvene radical anion(-2)	6.611	7.523	-50.013	13.483	-6.611
3-Bromofulvene radical anion(+1)	-12.148	-8.313	-49.871	6.806	12.148
3-Bromofulvene radical cation(+2)	-17.838	-15.712	-49.356	10.931	17.838

Table 3.calculated electron densities for the bromofulvene isomers and their radical ions.

Atomic properties table (Electronic densities)					
Atoms	Radical anion(-1)	Radical anion(-2)	Neutral	Radical cation(+1)	Radical cation(+2)
3-Bromofulvene					
C_1	4.291	4.401	4.142	4.067	3.969
C_2	4.240	4.284	4.174	4.084	3.983
C_3	4.242	4.110	4.339	4.399	4.468
C_4	4.343	4.465	4.179	4.058	3.994
C_5	3.552	3.444	3.576	3.626	3.683
C_6	4.640	4.782	4.648	4.503	4.294
Br_7	7.081	7.312	6.846	6.557	6.234
4-Bromofulvene					
C_1	4.292	4.400	4.148	4.084	4.030
C_2	4.206	4.189	4.185	4.115	4.048
C_3	4.208	4.261	4.193	4.064	3.971
C_4	4.401	4.394	4.359	4.460	4.500
C_5	3.541	3.473	3.525	3.522	3.521
C_6	4.622	4.761	4.633	4.493	4.323
Br_7	7.064	7.313	6.822	6.523	6.191
6-Bromofulvene					
C_1	4.330	4.411	4.201	4.129	4.006
C_2	4.199	4.199	4.174	4.100	4.024
C_3	4.234	4.224	4.217	4.140	4.059
C_4	4.283	4.390	4.138	4.068	4.053
C_5	3.439	3.364	3.454	3.534	3.598
C_6	4.850	4.878	4.914	4.777	4.612
Br_7	7.094	7.423	6.841	6.607	6.334

Table 4. Evaluation of substituted effects (energies Δ , in kJ/mol) .

Evaluation of substituted effects	energies Δ , in k J /mole	
	Anion(-1)	Cation(+1)
	35.972	-38.865
	Anion(-2)	Cation(+2)
	84.842	-16.507
	Neutral	
	-16.939	
	Anion(-1)	Cation(+1)
	26.707	-38.450
	Anion(-2)	Cation(+2)
	83.915	0.592
	Neutral	
	-21.638	
	Anion(-1)	Cation(+1)
	13.941	-44.521
	Anion(-2)	Cation(+2)
	92.311	-30.291
	Neutral	
	-34.920	

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