



Research Journal of Pharmaceutical, Biological and Chemical Sciences

Quantum Chemical Study of the Chlorofulvene Isomers by DFT Method

JH Ali*

Department of Chemistry, College of Science, Karbala University, IRAQ

ABSTRACT

DFT method within Gaussian 03 program was used to calculate the minimum energy geometries and the $(3N-6=30)$ fundamental vibration frequencies for the molecules: 2-chlorofulvene, 3-chlorofulvene, 6-chlorofulvene, chlorobenzene and the fulvene. It was shown that all the molecules except chlorobenzene, belong to C_s point group symmetry; the more stable isomer is the 2-chlorofulvene. The 3-chlorofulvene has the higher frequency values for the fundamental vibrations associated with the methylene group.

Keys words: DFT calculation, 2-chloro, 3-chloro, 6-chlorofulvenes, chlorobenzene isomers

**Corresponding author*

INTRODUCTION

Fulvenes are cross-conjugated molecules with some unique properties [1-3]. Their structure and electronic distribution were investigated theoretically [4] and experimentally [5]. The 6-chlorofulvene was synthesized from cyclopentadiene and dichlorocarbene [6]. The halogenated substituted fulvenes are used to improve the octane quality of a fuel for internal combustion engines [7]. To the best of our knowledge, there are no reported experimental and or advanced theoretical studies on the vibrational spectra of chlorofulvenes. However, Ali et al [8], applied the MINDO/3-FORCES MO semiempirical method to calculate the equilibrium geometries of the chlorofulvene isomers. In the present paper, the isomers; 2-chloro, 3-chloro, 6-chlorofulvenes along with the chlorobenzene and the unsubstituted fulvene molecules, Fig 1, were investigated theoretically using the Density Functional Theory (DFT) calculation [9] at the B3LYP/6-311G(p,d) level of theory to get the optimised geometry and vibrational wave numbers of the normal modes of the five molecules.

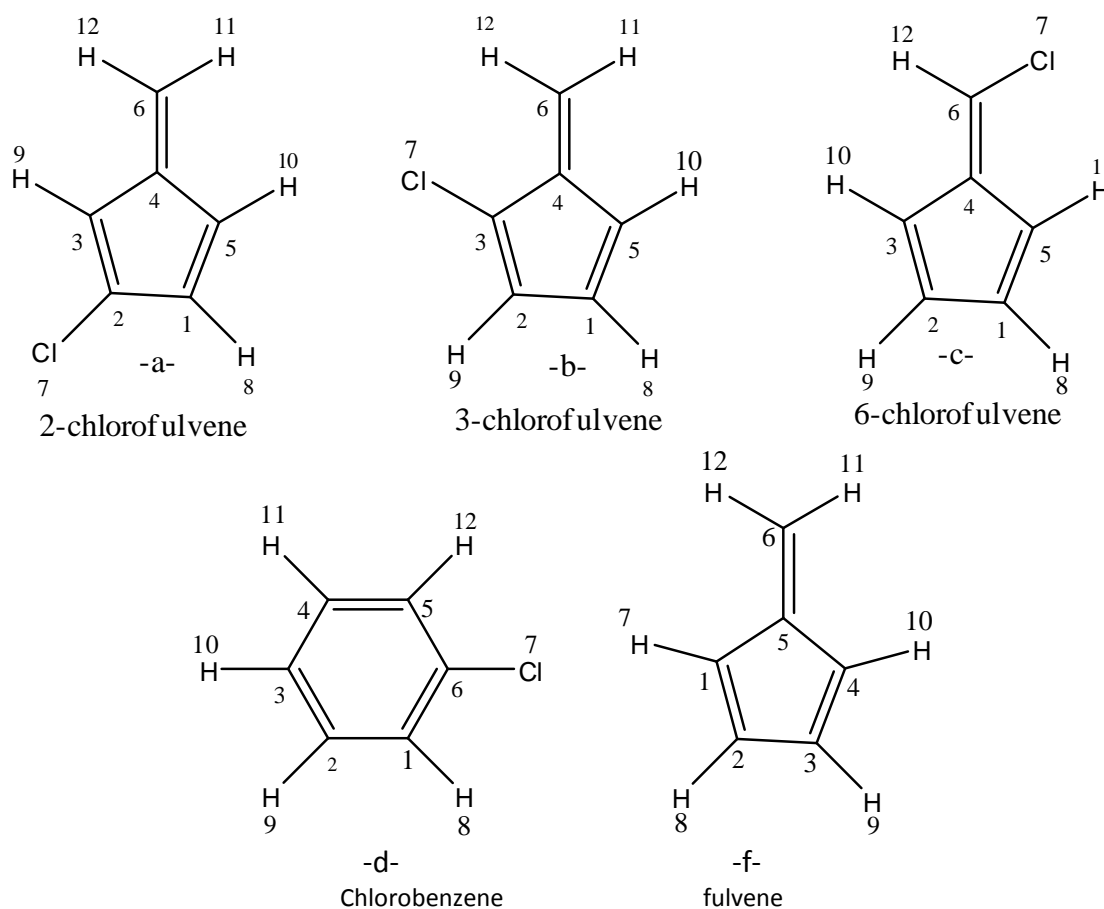


Fig 1 The chlorofulvenes(a,b,c), chlorobenzene(d) isomers, and the fulvene(f) molecules.

MATERIALS AND METHODS

Computational Details

The vibrational wavenumbers were calculated using the Gaussian 03 software package on a personal computer[9]. The density functional theoretical (DFT) computations were performed at the B3LYP/6-311G(p,d) level of theory to get the optimised geometry and vibrational wave numbers of the normal modes of the title molecules. The DFT partitions the electronic energy $E=E_T+E_V+E_J+E_{XC}$, where E_T , E_V and E_J are electronic kinetic energy, electron nuclear attraction and electron–electron repulsion terms, respectively. The electron correlation is taken into account in the DFT via the exchange–correlation term E_{XC} , which includes exchange energy arising from the antisymmetry of quantum mechanical wavefunction and dynamic correlation in the motion of individual electrons, and it makes DFT dominant over the conventional Hartree–Fock (HF) procedure [10]. DFT calculations were carried out with Becke’s three-parameter hybrid model using the Lee–Yang–Parr correlation functional (B3LYP) method. Molecular geometries were fully optimized by Berny’s optimisation algorithm using redundant internal coordinates. All optimized structures were confirmed to be minimum energy conformations. Harmonic vibrational wavenumbers were calculated using analytic second derivatives to confirm the convergence to minima in the potential surface. At the optimized structure of the examined species, no imaginary wavenumber modes were obtained, proving that a true minimum on the potential surface was found. The optimum geometry was determined by minimizing the energy with respect to all geometrical parameters without imposing molecular symmetry constraints. The assignments of the calculated wavenumbers are aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes [11, 12].

RESULTS AND DISCUSSION

Geometry

The chloroene (1-d) has the lower total energy than the others isomers. Therefore, it is the more stable one, Table 2. However, the 2-chlorofulvene is the more stable one among the three chlorofulvene isomers. This may be due to the high resonance effect in this isomer compared with the others chlorofulvene isomers, Table 2. Also, all the isomers except 3-chlorofulvene, the C1 substituent increases the angle to which it attached and decreases or increase one of the adjacent bond lengths (or both of them). The case is more pronounced for the 6-chlorofulvene, Table 1.

Dipole moments

It can be seen from Table 2 that the dipole moments of the four isomers have higher values than the unsubstituted fulvene and benzene. The higher dipole moment value is for 2-chlorofulvene where the dipoles-dipoles is stabilized by the resonance effect. The low value of 6-chlorofulvene may be due to the low of this effect, which may be attributed to the presence of C1 substituent outside the ring. Also, the lone pair of electrons in chlorobenzene is enclosed

through the resonance within the phenyl ring and this may be the reason of its low dipole moment compared with the 2-chlorofulvene isomers.

Electron densities

The C1 substituent decreases the electron density at the atom to which the substituent is attached and increases the density at the two adjacent atoms. The situation is reversed for the 6-chlorofulvene and the C₆ has the higher density, Table 3.

HOMO-LUMO energy

The 3-chlorofulvene is the more reducible isomer compared with the other two chlorofulvene isomers. This may be due to its lower LUMO energy. Also, the more stable isomer 2-chlorofulvene has the higher HOMO-LUMO energy difference, 0.14732 a.u. Table 2. In addition to this and according to Koopman theorem, the negative sign of the HOMO energy is equal to the ionisation energy of the molecule. The values of all studied species were also listed, Table 2.

Vibrational spectra

Each one of the five molecules, Fig.1, has (3N-6=30) fundamental vibration modes. The three chlorofulvenes along with the fulvene molecules belong to C_s point group and the thirty fundamental vibrational frequencies are distributed among the following symmetry species,

$$\Gamma_{30} = 9A^{\bar{}} + 21A^{\bar{}}$$

Where: 21A⁻ are in-plane modes and 9A⁻ are out of plane. Also, all these vibration modes are IR and Raman active. The chloroene has the C_{2v} symmetry and its thirty vibration modes are distributed among the following irreducible representation:

$$\Gamma_{30} = 3A_2 + 6B_1 + 10A_1 + 11B_2$$

Where: 3A₂+6B₁ are out of plane vibration modes and the 10A₁+11B₂ are in plane modes. Also, all these vibration modes are IR and Raman active except the 3A₂ modes, which are Raman active only.

The thirty fundamental vibrations of each one of the molecules were listed, Tables 4. Among these vibrations, seven modes are associated with the methylene group. These are the symmetric and asymmetric CH₂ stretching, the rocking and scissoring in plane bending, and the wagging and twisting out of plane bending modes. The C=CH₂ stretching vibration, Table 6, may also be considered. It is obvious that the 3-chlorofulvene has the highest values for methylene group: twisting, wagging, rocking, CH_{2(s)} stretching and CH₂ (as) stretching and vibration modes, Tables 4 and 6.

Thermodynamics functions

Thermodynamics functions for the studied molecules were listed in Table 5. Compared with the fulvene; the C1 substituent causes an increase in the entropy, S , for the chlorofulvene isomers. Due to the presence of C1 outside the ring, the higher (S) value appeared to be for the 6-chlorofulvene molecules, and the lower one is for 3-chlorofulvene. Moreover, among the four isomers, Fig.1 (a, b, c, and d), chlorobenzene (1-d) has the lowest entropy value due to its stabilization by resonance effect.

Table (1): The geometrical parameter of chlorofulvenes, chlorobenzene isomers and the fulvene molecules. R: bond length in Å and A, bond angle in degrees. See Fig.1 for atom numbering

| 2-chlorofulvene | | 3-chlorofulvene | | 6-chlorofulvene | |
|-----------------|-------|-----------------|-------|-----------------|-------|
| R(1-2) | 1.472 | R(1-2) | 1.473 | R(1-2) | 1.472 |
| R(1-5) | 1.350 | R(1-5) | 1.352 | R(1-5) | 1.354 |
| R(1-8) | 1.080 | R(1-8) | 1.081 | R(1-8) | 1.082 |
| R(2-3) | 1.350 | R(2-3) | 1.349 | R(2-3) | 1.352 |
| R(2-7) | 1.737 | R(2-9) | 1.080 | R(2-9) | 1.081 |
| R(3-4) | 1.470 | R(3-4) | 1.478 | R(3-4) | 1.475 |
| R(3-9) | 1.079 | R(3-7) | 1.737 | R(3-10) | 1.080 |
| R(4-5) | 1.476 | R(4-5) | 1.474 | R(4-5) | 1.466 |
| R(4-6) | 1.342 | R(4-6) | 1.339 | R(4-6) | 1.342 |
| R(5-10) | 1.081 | R(5-10) | 1.080 | R(5-11) | 1.079 |
| R(6-11) | 1.084 | R(6-11) | 1.084 | R(6-7) | 1.737 |
| R(6-12) | 1.084 | R(6-12) | 1.084 | R(6-12) | 1.082 |
| A(2-1-5) | 107.7 | A(2-1-5) | 109.6 | A(2-1-5) | 109.4 |
| A(2-1-8) | 124.2 | A(2-1-8) | 123.9 | A(2-1-8) | 124.6 |
| A(1-2-3) | 110.8 | A(1-2-3) | 107.9 | A(1-2-3) | 108.9 |
| A(1-2-7) | 122.4 | A(1-2-9) | 125.6 | A(1-2-9) | 124.7 |
| A(5-1-8) | 128.0 | A(5-1-8) | 126.5 | A(5-1-8) | 126.0 |
| A(1-5-4) | 108.3 | A(1-5-4) | 108.2 | A(1-5-4) | 107.5 |
| A(1-5-10) | 127.3 | A(1-5-10) | 127.7 | A(1-5-11) | 127.7 |
| A(3-2-7) | 126.8 | A(3-2-9) | 126.5 | A(3-2-9) | 126.4 |
| A(2-3-4) | 106.5 | A(2-3-4) | 109.3 | A(2-3-4) | 107.6 |
| A(2-3-9) | 127.7 | A(2-3-7) | 126.9 | A(2-3-10) | 127.8 |
| A(4-3-9) | 125.8 | A(4-3-7) | 123.7 | A(4-3-10) | 124.7 |
| A(3-4-5) | 106.7 | A(3-4-5) | 105.0 | A(3-4-5) | 106.7 |
| A(3-4-6) | 127.0 | A(3-4-6) | 127.3 | A(3-4-6) | 123.6 |
| A(5-4-6) | 126.3 | A(5-4-6) | 127.7 | A(5-4-6) | 129.7 |
| A(4-5-10) | 124.5 | A(4-5-10) | 124.1 | A(4-5-11) | 124.9 |
| A(4-6-11) | 121.2 | A(4-6-11) | 121.1 | A(4-6-7) | 124.4 |
| A(4-6-12) | 121.6 | A(4-6-12) | 121.4 | A(4-6-12) | 123.0 |
| A(11-6-12) | 117.2 | A(11-6-12) | 117.6 | A(7-6-12) | 112.6 |

| chlorobenzene | | fulvene | |
|---------------|-------|---------|-------|
| R(1-2) | 1.394 | R(1-2) | 1.332 |
| R(1-6) | 1.392 | R(1-5) | 1.477 |
| R(1-8) | 1.083 | R(1-7) | 1.073 |
| R(2-3) | 1.394 | R(2-3) | 1.479 |

| | | | |
|-----------|-------|------------|-------|
| R(2-9) | 1.084 | R(2-8) | 1.074 |
| R(3-4) | 1.394 | R(3-4) | 1.332 |
| R(3-10) | 1.084 | R(3-9) | 1.074 |
| R(4-5) | 1.394 | R(4-5) | 1.477 |
| R(4-11) | 1.084 | R(4-10) | 1.073 |
| R(5-6) | 1.392 | R(5-6) | 1.325 |
| R(5-12) | 1.083 | R(6-11) | 1.076 |
| R(6-7) | 1.761 | R(6-12) | 1.076 |
| A(2-1-6) | 119.0 | A(2-1-5) | 108.2 |
| A(2-1-8) | 121.0 | A(2-1-7) | 127.4 |
| A(1-2-3) | 120.5 | A(1-2-3) | 109.1 |
| A(1-2-9) | 119.3 | A(1-2-8) | 126.5 |
| A(6-1-8) | 120.1 | A(5-1-7) | 124.4 |
| A(1-6-5) | 121.4 | A(1-5-4) | 105.4 |
| A(1-6-7) | 119.3 | A(1-5-6) | 127.3 |
| A(3-2-9) | 120.2 | A(3-2-8) | 124.4 |
| A(2-3-4) | 119.7 | A(2-3-4) | 109.1 |
| A(2-3-10) | 120.1 | A(2-3-9) | 124.4 |
| A(4-3-10) | 120.1 | A(4-3-9) | 126.6 |
| A(3-4-5) | 120.5 | A(3-4-5) | 108.2 |
| A(3-4-11) | 120.2 | A(3-4-10) | 127.4 |
| A(5-4-11) | 119.3 | A(5-4-10) | 124.4 |
| A(4-5-6) | 119.0 | A(4-5-6) | 127.3 |
| A(4-5-12) | 121.0 | A(5-6-11) | 121.6 |
| A(6-5-12) | 120.1 | A(5-6-12) | 121.5 |
| A(5-6-7) | 119.3 | A(11-6-12) | 116.9 |

Table (2): Some physical properties of the 2-chloro, 3-chloro, 6-chlorofulvene, chlorobenzene isomers and the fulvene molecules, Fig.1

| property | 2-chlorofulvene | 3-chlorofulvene | 6-chlorofulvene |
|---------------------------------------|-----------------|-----------------|-----------------|
| E_{LUMO} a.u., | -0.08806 | -0.09006 | -0.08782 |
| E_{HOMO} | -0.23538 | -0.22819 | -0.2339 |
| $\Delta (E_{LUMO} - E_{HOMO})$, a.u. | 0.14732 | 0.13813 | 0.14608 |
| $E(RB+HF-LYP)$, a.u. | -691.87936640 | -691.87729099 | -691.87931441 |
| Dipole moment, Debye | 2.1811 | 1.4977 | 0.93040 |
| Ionization energy, au | 0.23538 | 0.22819 | 0.2339 |
| Point group symmetry | Cs | Cs | Cs |

| property | chlorobenzene | fulvene |
|---------------------------------------|---------------|---------------|
| E_{LUMO} , a.u., | -0.03177 | 0.08495 |
| E_{HOMO} , a.u., | -0.25749 | -0.30761 |
| $\Delta (E_{LUMO} - E_{HOMO})$, a.u. | 0.22572 | 0.39256 |
| $E(RB+HF-LYP)$, a.u. | -691.93421533 | -232.25200527 |
| Dipole moment, Debye | 1.86000 | 0.5762 |

| | | |
|--------------------------|-----------------|----------------|
| Ionization energy, a.u., | 0.25749 | 0.30761 |
| Point group symmetry | C _{2v} | C _s |

Table (3): The electron density of the chlorofulvenes, chlorobenzene isomers and the fulvene molecules. See Fig.1 for atom numbering

| atom no. | 2-chloro | 3-Chloro | 6-chloro | chlorobenzene | fulvene |
|----------|----------|----------|----------|---------------|----------|
| 1 | 4.584593 | 4.083397 | 4.210813 | 4.485826 | 4.130608 |
| 2 | 3.487350 | 4.698217 | 4.212751 | 4.303613 | 4.162821 |
| 3 | 4.630043 | 3.439424 | 4.307792 | 4.124823 | 4.162796 |
| 4 | 3.532828 | 3.815024 | 2.710385 | 4.303613 | 4.130627 |
| 5 | 4.292564 | 4.277488 | 4.468297 | 4.485826 | 3.852748 |
| 6 | 4.543317 | 4.784446 | 5.176004 | 3.258501 | 4.297637 |
| 7 | 6.616076 | 6.598012 | 6.626349 | 6.739687 | 0.147252 |
| 8 | 0.857408 | 0.869286 | 0.872913 | 0.848726 | 0.14851 |
| 9 | 0.864800 | 0.861624 | 0.873917 | 0.865724 | 0.148556 |
| 10 | 0.872707 | 0.875466 | 0.876282 | 0.869210 | 0.147232 |
| 11 | 0.859256 | 0.985717 | 0.859095 | 0.865724 | 0.141658 |
| 12 | 0.859058 | 0.840445 | 0.805402 | 0.848726 | 0.141633 |

Table (4)*: The thirty fundamental vibration frequencies along with their assignments and the corresponding IR absorption intensity of the 2-chloro, 3-chloro, 6-chlorofulvene isomers. See Fig.1 for atom numbering

| Vib. mod | 2-chlorofulvene | | 3-chlorofulvene | | 6-chlorofulvene | |
|--|--|--|--|--|--|--|
| | Frequency, cm ⁻¹ (ir intensity, km mol ⁻¹) | assignment | Frequency, cm ⁻¹ (ir intensity, km mol ⁻¹) | assignment | Frequency, cm ⁻¹ (ir intensity, km mol ⁻¹) | assignment |
| in plane vibration modes, A ⁻ | | | | | | |
| V ₁ | 3243.8 (0.2986) | C ₃ -H st. | 3235.2 (1.9251) | (C ₁ -C ₅ +C ₁ -C ₂) H s. st. | 3244.7 (1.8481) | (C ₁ -C ₅)H s. st |
| V ₂ | 3237.9 (3.1442) | (C ₁ -C ₅)H s. st. | 3234.1 (2.4571) | CH ₂ as st. | 3231.4 (6.9664) | (C ₂ -C ₃)H st +C ₅ H st. |
| V ₃ | 3227.0 (4.7256) | CH ₂ as st. | 3228.5 (5.1706) | (C ₁ +C ₅)H s.st.+C ₂ H st. | 3213.0 (5.3473) | (C ₃ -C ₂)H as.st + (C ₁ -C ₅) H as.st |
| V ₄ | 3216.5 (0.4304) | (C ₁ -C ₅)H as st. | 3207.3 (4.3878) | (C ₁ +C ₅)H as.st.+C ₂ H | 3207.0 (5.8431) | C ₆ H ₁₂ st |
| V ₅ | 3139.7 (3.9479) | CH ₂ s st. | 3145.1 (2.6382) | CH ₂ s.st. | 3202.4 (4.4031) | (C ₃ -C ₂)H as.st + (C ₁ -C ₅)H as.st |
| V ₆ | 1691.5 (0.7949) | C=CH ₂ st+CH ₂ sciss. | 1699.0 (3.9604) | C=CH ₂ +CH ₂ sciss. | 1664.4 (135.8739) | C=CH ₂ st+ δ (C ₃ +C ₅ +C ₆)H |
| V ₇ | 1606.7 (46.8354) | C ₂ -C ₃ +C ₁ +C ₅ as st. | 1617.4 (9.8125) | (C ₂ =C ₃ +C ₁ =C ₅) as st.+ δ CH | 1604.0 (0.0048) | (C ₂ =C ₃ +C ₁ =C ₅) as st. + δ (C ₂ -C ₃ +C ₁ -C ₅) H |
| V ₈ | 1536.1 (2.3565) | (C ₂ =C ₃ + C ₁ =C ₅) s st.+ δ CH | 1529.7 (72.3268) | (C ₂ =C ₃ + C ₁ = C ₅) s st.+ δ CH + CH ₂ sciss. | 1518.1 (29.8032) | (C ₂ =C ₃ +C ₁ =C ₅) s st + δ (C ₂ -C ₃ +C ₁ -C ₅)H |



| | | | | | | |
|--------------------------------|---------------------|--|---------------------|--|---------------------|--|
| V_9 | 1450.8 (2.4912) | CH_2 sciss. | 1446.2 (7.6915) | CH_2 sciss. | 1389.1 (43.4951) | $\delta (\text{C}_2\text{-C}_3 + \text{C}_1\text{-C}_5)\text{H} + \delta \text{C}_6\text{H}$ |
| V_{10} | 1352.2 (28.0650) | $\delta (\text{C}_1 + \text{C}_5)\text{H}$ | 1353.1 (24.3495) | $\delta \text{CH} + \text{CH}_2$ Sciss | 1341.0 (4.8254) | $\delta (\text{C}_2\text{-C}_3) \text{H} + \delta \text{C}_6\text{H}$ |
| V_{11} | 1298.5 (67.5419) | ring(CCC) st.+ δ CH | 1309.4 (14.3459) | $\delta \text{C}_2\text{H} + \text{C}_3\text{-C}_4$ st. | 1297.5 (3.5021) | $\delta (\text{C}_2\text{-C}_3 + \text{C}_1\text{-C}_5) \text{H} + \delta \text{C}_6\text{H}$ |
| V_{12} | 1217.6 (4.3797) | δCH | 1224.2 (0.1532) | $\delta \text{CH} + \rho \text{CH}_2$ | 1170.1 (2.9568) | $\delta (\text{C}_2\text{-C}_3 + \text{C}_5)\text{H} + \delta \text{C}_6\text{H}$ |
| V_{13} | 1107.3 (25.7854) | δCH | 1108.9 (0.9783) | $\delta (\text{C}_1\text{-C}_5)\text{H}$ | 1106.4 (11.0072) | $\delta (\text{C}_2\text{-C}_3 + \text{C}_5 + \text{C}_6) \text{H}$ |
| V_{14} | 1072.6 (49.9407) | δCH | 1053.5 (28.5133) | $\rho \text{CH}_2 + \text{ring}(\delta \text{CCC})$ | 1104.8 (11.3395) | $\delta (\text{C}_2\text{-C}_3 + \text{C}_1\text{-C}_5) \text{H} + \delta \text{C}_6\text{H}$ |
| V_{15} | 965.4 (5.9428) | $\rho \text{CH}_2 + \delta \text{CH}$ | 995.4 (3.2845) | $\delta (\text{C}_1\text{-C}_2)\text{H} + \rho \text{CH}_2$ | 1007.5 (0.8608) | $(\text{C}_1\text{-C}_2) \text{st.} + \delta \text{C}_6\text{H}$ |
| V_{16} | 924.5 (5.9816) | ring(δCCC) | 941.2 (9.0082) | $\delta \text{CCC} + \rho \text{CH}_2$ | 922.6 (1.3975) | ring(δCCC) |
| V_{17} | 876.2 (25.8032) | ring(δCCC)+ δCH | 799.8 (2.1110) | ring(δCCC)+ ρCH_2 | 825.9 (101.4514) | C-Cl st + ring (δCCC) |
| V_{18} | 687.4 (1.5741) | ring elongation | 711.5 (5.8983) | ring elongation | 816.3 (37.0824) | ring elongation |
| V_{19} | 442.5 (8.7608) | δ ring | 476.4 (7.3016) | ring(δCCC) + ρCH_2 | 700.6 (4.7413) | ring (δCCC) + ($\delta \text{C}_4\text{C}_6\text{Br}$) |
| V_{20} | 385.0 (0.9302) | δ ring | 397.5 (1.9387) | δ ring + ρCH_2 | 382.6 (3.5985) | $\delta \text{C}_4\text{C}_6\text{Br}$ |
| V_{21} | 242.7 (0.0303) | δ ring | 226.9 (1.0589) | $\delta \text{C}_3\text{C}_4\text{C}_6$ | 166.9 (0.1556) | $\delta \text{C}_4\text{C}_6\text{Br}$ |
| out of plane vibrations, A'' | | | | | | |
| V_{22} | 962.8 (1.9159) | ωCH_2 | 979.7 (36.3198) | ωCH_2 | 945.0 (0.0316) | $\gamma (\text{C}_2\text{-C}_1\text{-C}_4) \text{H}$ |
| V_{23} | 931.6 (1.2022) | $\gamma (\text{C}_1\text{-C}_5)\text{H}$ | 939.0 (0.2536) | $\gamma (\text{C}_1\text{-C}_5)\text{H}$ | 930.8 (0.5602) | $\gamma \text{C-H}$ |
| V_{24} | 826.6 (36.0627) | $\gamma (\text{C}_1\text{-C}_5)\text{H} + \gamma \text{C}_3\text{-H}$ | 860.4 (14.5961) | $\gamma \text{C}_2\text{-H} + \gamma \text{C}_5\text{-H}$ | 858.6 (35.4354) | $\gamma \text{C}_6\text{-H}_{12} + \gamma \text{C}_2\text{H}$ |
| V_{25} | 774.2 (9.4651) | $\gamma (\text{C}_1\text{-C}_5)\text{H} + \tau \text{CH}_2$ | 775.3 (29.1838) | $\gamma (\text{C}_1\text{-C}_5) \text{H} + \tau \text{CH}_2$ | 784.1 (56.8434) | $\gamma \text{C-H} + \gamma \text{C}_6\text{H}_{12}$ |
| V_{26} | 675.9 (0.0877) | $\gamma \text{C}_3\text{-H} + \gamma \text{C}_5\text{-H} + \tau \text{CH}_2$ | 747.0 (4.0873) | $\gamma (\text{C}_2\text{-H} + \gamma \text{C}_5\text{-H}) + \tau \text{CH}_2$ | 719.0 (2.1196) | $\gamma (\text{C}_2\text{-C}_3) \text{H} + \gamma \text{C}_5\text{H}$ |
| V_{27} | 659.9 (16.4133) | $\gamma \text{C}_3\text{-H} + \gamma \text{C}_5\text{-H} + \gamma \text{C}_6\text{H}$ | 648.4 (26.0263) | $\gamma (\text{C}_1\text{-C}_5)\text{H} + \gamma \text{C}_6\text{H}_{12}$ | 631.0 (41.1915) | $\gamma (\text{C}_2\text{-C}_3) \text{H} + \gamma \text{C}_5\text{H} + \gamma \text{C}_6\text{H}_{12}$ |
| V_{28} | 567.7 (16.3332) | $\gamma (\text{C}_1\text{-C}_5)\text{H} + \gamma \text{C}_3\text{H} \gamma + \tau \text{CH}_2$ | 487.3 (0.4204) | $\gamma \text{C}_2\text{C}_1\text{C}_5$ | 556.4 (2.0854) | $\gamma (\text{C}_1\text{C}_2\text{C}_3)\text{H}$ |
| V_{29} | 281.7 (0.6507) | ring(γCCC)+ $\gamma \text{C}_6\text{H}_{12}$ | 261.2 (7.4743) | γCCC | 292.2 (3.6806) | γ ring |



| | | | | | | |
|----------|-------------------|---------------------|-------------------|---------------------|-------------------|---------------|
| V_{30} | 145.5 (1.9159) | CH ₂ tor | 168.8 (1.2340) | CH ₂ tor | 135.0 (0.3799) | γ ring |
|----------|-------------------|---------------------|-------------------|---------------------|-------------------|---------------|

| Vibration mode | Chlorobenzene** | | Fulvene | |
|-----------------------------|---|---|---|--|
| | Frequency, cm ⁻¹ (ir intensity, km mol ⁻¹) | assignment | Frequency, cm ⁻¹ (ir intensity, km mol ⁻¹) | assignment |
| in plane vibration modes, A | | | | |
| V_1 | 3203.0 (1.1554) | C-H st. | 3229.8 (4.0920) | (C ₁ -C ₂ +C ₃ -C ₄)H s.st |
| V_2 | 3200.6 (5.8329) | (C ₁ -C ₂ +C ₄ -C ₅)H st. | 3224.0 (15.3213) | (C ₁ -C ₂ +C ₃ -C ₄)H as.st |
| V_3 | 3190.8 (13.3976) | C-H st | 3221.3 (7.8220) | CH ₂ as st. |
| V_4 | 3177.9 (8.7412) | (C ₁ -C ₂ +C ₄ -C ₅)H st. | 3206.2 (9.6810) | (C ₁ -C ₂ +C ₃ -C ₄)H as.st |
| V_5 | 3169.2 (0.0839) | C-H st | 3196.3 (3.4366) | (C ₁ -C ₂ +C ₃ -C ₄)H as.st |
| V_6 | 1624.0 (2.6342) | ring(CCC) st+ δ CH | 3136.1 (7.1908) | CH ₂ s st. |
| V_7 | 1620.9 (27.8384) | ring(CCC) st+ δ CH | 1700.0 (2.4464) | C=CH ₂ st. +CH ₂ sciss.+ δ (C ₁ +C ₄)H |
| V_8 | 1506.8 (45.4010) | ring(CCC) st+ δ CH | 1616.4 (0.0007) | (C ₁ -C ₂ +C ₃ -C ₄) as st. + δ (C ₁ -C ₂ +C ₃ -C ₄)H |
| V_9 | 1475.1 (5.3818) | ring(CCC) st+ δ CH | 1532.0 (29.2067) | (C ₁ -C ₂ +C ₃ -C ₄) s.st + δ (C ₁ -C ₂ +C ₃ -C ₄) + CH ₂ sciss. |
| V_{10} | 1342.6 (0.4007) | δ CH+ ring(CCC) st | 1452.9 (0.1919) | CH ₂ sciss. |
| V_{11} | 1317.6 (0.1078) | δ (C ₂ +C ₃ +C ₄)H+ ring(CCC) st. | 1368.6 (25.6261) | ring (CCC st.) + δ (C ₁ -C ₂ +C ₃ -C ₄)H + CH ₂ sciss. |
| V_{12} | 1197.1 (0.0058) | ring(CCC st.) | 1333.8 (0.0833) | ring (CCC st.)+ δ (C ₁ -C ₂ +C ₃ -C ₄)H+ ρ CH ₂ |
| V_{13} | 1182.3 0.0371 | δ CH | 1252.5 (0.3256) | δ (C ₁ -C ₂ +C ₃ -C ₄)H + ρ CH ₂ |
| V_{14} | 1097.4 (44.0107) | δ (C ₁ -C ₂ +C ₄ -C ₅)H | 1104.6 (9.2091) | δ (C ₁ -C ₂ +C ₃ -C ₄)H |
| V_{15} | 1096.2 (5.4187) | δ CH | 1102.1 (1.7753) | δ (C ₁ -C ₂ +C ₃ -C ₄)H |
| V_{16} | 1041.6 (21.5100) | δ CH+ ring(δ CCC) | 999.8 (2.5358) | ring(δ CCC) |
| V_{17} | 1015.0 (3.9320) | ring(δ CCC) | 962.4 (3.1166) | ρ CH ₂ |
| V_{18} | 1197.1 (0.0058) | ring(CCC st.) | 1333.8 (0.0833) | ring (CCC st.)+ δ (C ₁ -C ₂ +C ₃ -C ₄)H+ ρ CH ₂ |
| V_{19} | 1182.3 0.0371 | δ CH | 1252.5 (0.3256) | δ (C ₁ -C ₂ +C ₃ -C ₄)H + ρ CH ₂ |
| V_{20} | 1097.4 | δ (C ₁ -C ₂ +C ₄ -C ₅)H | 1104.6 | δ (C ₁ -C ₂ +C ₃ -C ₄)H |

| | | | | |
|---|--------------------|---|--------------------|--|
| | (44.0107) | | (9.2091) | |
| V_{21} | 1096.2 (5.4187) | δ CH | 1102.1 (1.7753) | δ (C ₁ -C ₂ +C ₃ -C ₄)H |
| Out of plane vibrations, A ⁻ | | | | |
| V_{22} | 1003.8 (0.1855) | γ CH | 961.7 (37.3451) | ω CH ₂ |
| V_{23} | 982.1 (0.0000) | γ CH | 943.3 (0.0002) | γ (C ₁ -C ₂ +C ₃ -C ₄)H |
| V_{24} | 919.8 (3.0527) | γ (C ₁ +C ₅ +C ₃)H | 929.6 (2.4681) | γ (C ₁ -C ₂ +C ₃ -C ₄)H + ω CH ₂ |
| V_{25} | 841.4 (0.0000) | γ (C ₁ -C ₂ +C ₄ +C ₅)H | 790.6 (50.3683) | γ (C ₁ -C ₂ +C ₃ -C ₄)H + ω CH ₂ |
| V_{26} | 757.2 (63.5658) | γ (C ₁ -C ₂ +C ₃ -C ₄ +C ₅)H | 778.4 (0.0000) | τ CH ₂ + γ (C ₁ -C ₂ +C ₃ -C ₄)H |
| V_{27} | 704.8 (26.7375) | γ (C ₂ +C ₄)H | 690.8 (0.0000) | γ (C ₁ +C ₄)H + τ CH ₂ |
| V_{28} | 481.4 (8.8641) | ring(γ CCC) | 636.3 (42.3207) | γ (C ₁ -C ₂ +C ₃ -C ₄)H |
| V_{29} | 415.7 (0.0000) | ring(γ CCC) | 492.1 (0.0000) | γ (C ₂ +C ₃)H + τ CH ₂ |
| V_{30} | 187.0 (0.1672) | γ CCC | 208.4 (4.3409) | CH ₂ tor. |

*Abbreviations and symbols ;st: stretching, δ : in plane bending, s: symmetric, as: ant symmetric, γ : out of plane bending, tor: torsion, ρ :rocking, ω : wagging, τ :twisting, sciss :scissor; **For chlorobenzene under the C_{2v} symmetry, the following sequence of the vibration frequencies is used: the first three ones, V_{1-3} take the A₂ symmetry, the later six modes, V_{4-9} , are with B₁ symmetry, the modes V_{10-19} have the A₁ and finally, the V_{20-30} modes are with the B₂ symmetry.

Table (5): Thermodynamics functions for the 2-chloro, 3-chloro, 6-chlorofulvene, chlorobenzene isomers and the fulvene molecules., Fig.1 .

| Molecule | U ^o | H ^o | S ^o | G ^o | A ^o |
|-----------------|----------------|----------------|----------------|----------------|----------------|
| 2-chlorofulvene | 59.201 | 59.793 | 78.624 | 36.351 | 35.759 |
| 3-chlorofulvene | 59.282 | 59.874 | 78.536 | 36.459 | 35.867 |
| 6-chlorofulvene | 59.471 | 60.063 | 78.821 | 36.563 | 35.971 |
| chlorobenzene | 60.350 | 60.942 | 74.882 | 38.616 | 38.024 |
| fulvene | 64.315 | 64.907 | 71.291 | 43.652 | 43.059 |

* U^o ; H^o; G^o; A^o; Kcal.mol⁻¹; S^o, cal mol⁻¹K⁻¹

Table.6: comparison of frequency, cm⁻¹, and the corresponding IR absorption intensity, km mol⁻¹. in parentheses, for CH₂ twist., CH₂ wag., CH₂ rock., CH₂ sciss., C=CH₂ st., CH₂ s.st., and CH₂ as.st. normal modes of the 2-chloro, 3-chloro, and 6-chlorofulvene isomers and fulvene molecules, Fig.1.

| Molecule | CH ₂ Twist. | CH ₂ Wag. | CH ₂ Rock. | CH ₂ Sciss. | C=CH ₂ st. | CH ₂ s.st. | CH ₂ as.st |
|------------------|------------------------|----------------------|-----------------------|------------------------|-----------------------|-----------------------|-----------------------|
| 2-chloro fulvene | 774.18 (9.4651) | 962.8 (1.9159) | 965.4 (5.9428) | 1450.8 (2.4912) | 1691.5 (0.7949) | 3139.7 (3.9479) | 3227 (4.7256) |
| 3-chloro fulvene | 746.99 (4.0873) | 979.7 (36.3198) | 1053.5 (28.5133) | 1446.2 (7.6915) | 1699.0 (3.9604) | 3145.1 (2.6382) | 3234.1 (2.4571) |
| 6-chloro | ----- | ----- | ----- | ----- | 1664.4 | ----- | ----- |

| | | | | | | | |
|---------|-------------------|--------------------|-------------------|--------------------|--------------------|--------------------|--------------------|
| fulvene | | | | | (135.8739) | | |
| fulvene | 778.4 (0.0000) | 961.7 (37.3451) | 962.4 (3.1166) | 1452.9 (0.1919) | 1700.0 (2.4464) | 3136.1 (7.1908) | 3221.3 (7.8220) |

CONCLUSION

The DFT calculation (within Gaussian 03 program), showed that the fulvene similar to the three chloro fulvene isomers belonged to the C_s and not to the C_{2v} point group. The 2-chlorofulvene is the most stable one and the 3-chlorofulvene showed the highest fundamental vibration frequency values associated with methylene group.

REFERENCES

- [1] <http://en.wikipedia.org/wiki/fulvene>
- [2] M. Neuenschwander. Pure and Applied Chemistry 1986; 58: 55.
- [3] O Deep, S Cogan and S Zillberg. Chemical Physics 2006; 325 (2-3): 251.
- [4] T Oicson and J Sanstrom. Acta chem Scand B 1982; 56: 23.
- [5] Z Yoshida, M Shibata, A Sakai and T Sugimoto. J Am Chem Soc 1984; 106: 6383.
- [6] <http://www.freepatentsonline.com/4264336.html>
- [7] Michael B. D'Amore and Robert G. Bergman Journal of the Chemical Society D: Chemical Communications 1971; 24: 1585.
- [8] JH Ali, KH A Khidhir and KU Gzaar. Iraqi National Journal of chemistry 2011; 328: 43.
- [9] MJ Frisch, GW Trucks, HB Schlegel, GE Scuseria, MA Robb, JR Cheeseman, JA Montgomery, T Vreven, KN Kudin, JC Burant, et al. Gaussian, Inc., Pittsburgh, PA 2003.
- [10] JB Foresman. Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian. Frisch E (ed): Gaussian Inc: Pittsburg, PA, 1996.
- [11] Flukiger, HP Luthi, S Portmann, J Weber. MOLEKEL 4.3. Swiss Center for Scientific Computing: Manno, Switzerland 2000-2002.
- [12] Portmann HP Luthi. Chimia 2000; 54: 766.