A Theoretical Study of Fulvene Radical Cations

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MINDO-Forces calculations have been performed, after complete optimization of geometry, on fulvene molecule, fulvene and X-fulvene radical cations, where X is OH, NH_2, CH_3, NO_2, CN and F. A twisted structure with angle 5° was found for fulvene radical cation. The substituents OH, NH_2, CH_3, CN and F are stabilizing. NO_2 is slightly stabilizing. Geometrical parameters, heats of formation, dipole moments and electron densities are reported.

Introduction

Fulvenes are non-aromatic cyclic polyolefins which undergo a gamut of radical, electrophilic, nucleophilic and concerted reactions [1–3]. The electronic spectra of most fulvenes show transitions in the visible region resulting from a small HOMO-LUMO gap [4]. The comparatively large dipole moment of the parent fulvene molecule (0.42 D) [5] indicates the importance of zwitterionic character in the ground state. Substituents can affect the degree of this zwitterionic character, and such perturbations manifest themselves as shielding effects in NMR spectra [6].

The aim of present work is to study the parent fulvene, the new concept of fulvene radical cations [7], and the effect of the substituents OH, NH_2, CH_3, NO_2, CN and F at the carbon atoms C6, C1 and C2 of fulvene radical cations.

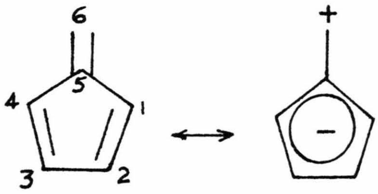
There exist no advanced calculations on fulvene and monosubstituted fulvene radical cations. This paper reports the geometry, heat of formation, dipole moment and electron density of fulvene and monosubstituted fulvene radical cations from calculations by the semiempirical MINDO-Forces method [8]. The molecular energy of the radical cation obtained from the semiempirical MINDO/3 method [9] was completely minimized according to the Murtagh-Sargent minimization Technique [10]. The derivative of the energy was calculated according to Pulay's Force method [11]. A full description of the program and its application is given in [8a].

Results and Discussion

1. *Fulvene Molecule*

The calculated heat of formation of the parent molecule, after complete optimization of geometry, was found to be 67.797 kcal/mole, which is almost in agreement with that found by Dewar et al. [12]. Its geometrical parameters are given in Fig. 1, and the calculated electron densities are given in Table 1. The calculated dipole moment was found to be 0.412 D, which is in a better agreement with the experimental value (0.42 D) [5] than that given by Dewar et al. (0.69 D) [12].

The dipole moment can be understood as resulting from intramolecular charge transfer from the exocyclic double bond to the five-membered ring thereby acquiring pseudoaromatic cyclopentadienide character. This may explain the high electron density at carbon atoms C1 and C4 as compared with that at C6 (Table 1).



2. *Fulvene Radical Cation*

In order to find whether the radical cation of fulvene is planar or twisted [7], we have calculated the heat of formation as function of the dihedral angle ϕ (angle between the plane of the CH_2 group and the plane of the five-membered ring). The results are given

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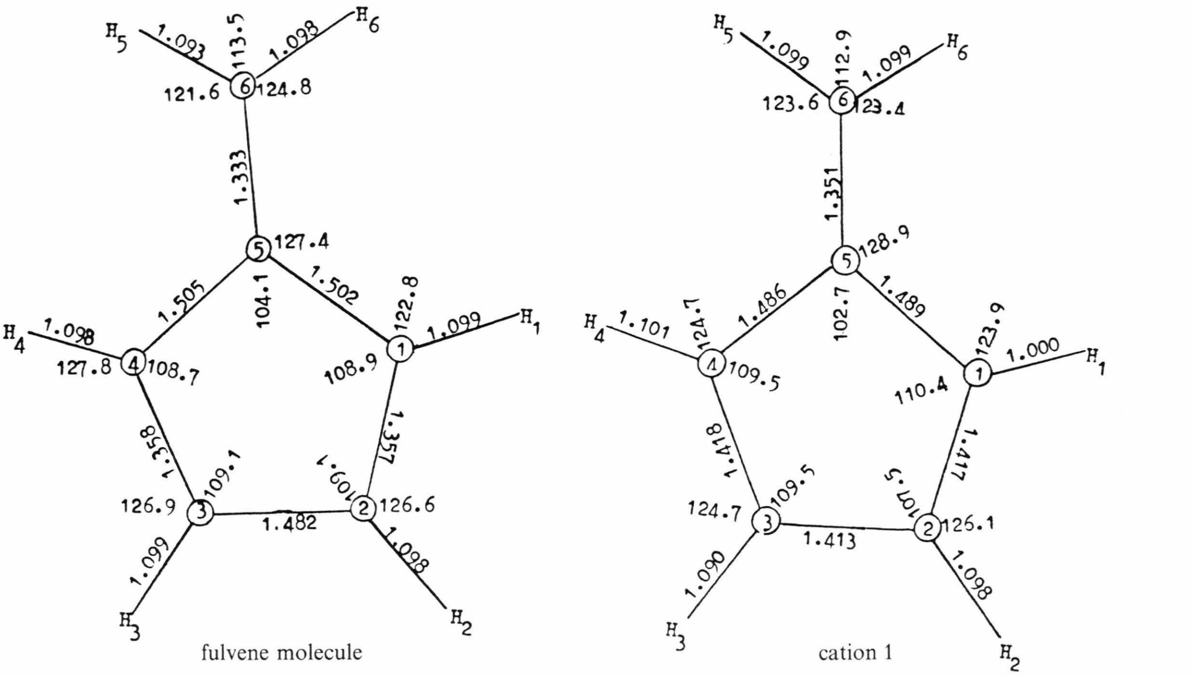


fulvene molecule

cation 1

Fig. 1. Optimized geometry for fulvene molecule and cation 1 ($\phi = 5°$). Bond lengths are in Angstroms and bond angles in degrees.

Atom	Fulvene	Cat. 1
C1	4.038	3.789
C2	3.996	3.965
C3	3.995	3.957
C4	4.037	3.794
C5	3.956	4.105
C6	4.004	3.797
H1	0.994	0.941
H2	1.000	0.909
H3	1.000	0.915
H4	0.993	0.938
H5	0.996	0.944
H6	0.990	0.945

Table 1. See Fig. 1 for numbering. Calculated electron densities of fulvene and fulvene radical cation.

Angle (ϕ)	ΔH_f of the Cation
0	248.176
5	248.125 (cation 1)
10	248.693
20	250.495
40	257.547
60	272.313
80	276.891
90	282.943

Table 2. Calculated heats of formation (ΔH_f in kcal/mole) for fulvene radical cations as function of the dihedral angle (ϕ).

in Table 2. In these calculations the energy is minimized with respect to all geometrical parameters. It can be seen from Table 2 that the most stable cation corresponds to $\phi = 5°$. This cation was called cation 1 and represents the ground state of the fulvene radical cation. This is in agreement with CIDNP results (7) which suggest that there is some degree of twisting in the tert-butyl (dimethylamino) fulvenes. All the substitutions were performed on this cation. It can be seen from Fig. 1 that removing an electron from the fulvene molecule causes an increase in the bond lengths of C1–C2, C3–C4, C6–C5, a decrease in C1–C5, C5–C4, C2–C3 and a twist of the CH_2 group out of the molecular plane by 5° to form cation 1. This result shows a decrease in the degree of cross conjugated structure of the fulvene radical cation.

The rotation of the CH_2 group from 0° to 90° out of the molecular plane causes the following changes in the geometry of the fulvene radical cation:

(a) an increase in the C2–C3 bond length,
(b) a decrease in the C1–C2 bond length,
(c) a slight increase in the C5–C6 bond length,
(d) an increase in the C1–C5–C4 bond angle,
(e) a decrease in the C2–C1–C5 and C3–C4–C5 bond angles.

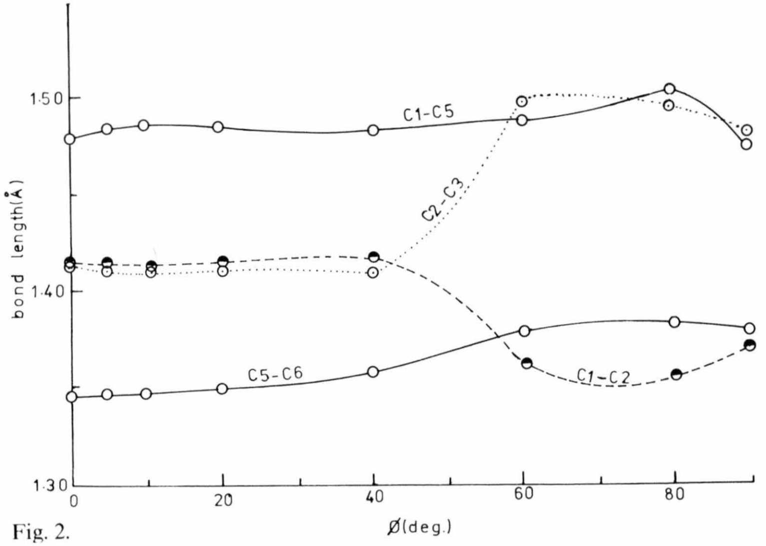


Fig. 2.

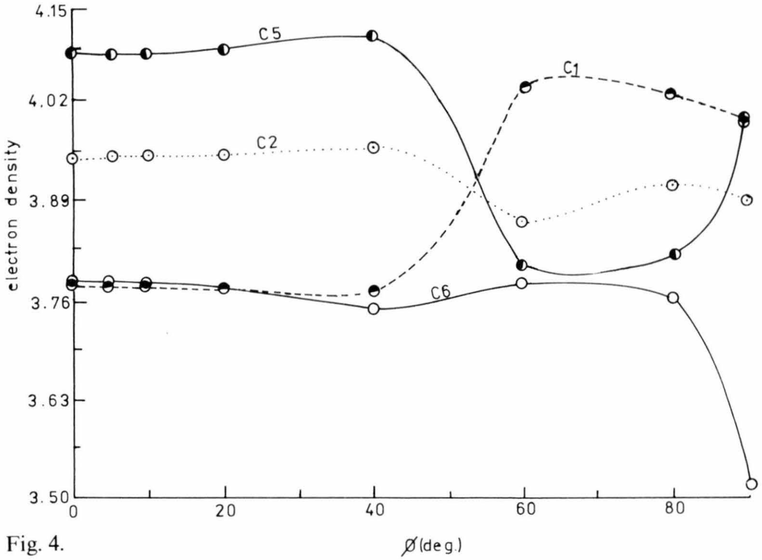


Fig. 4.

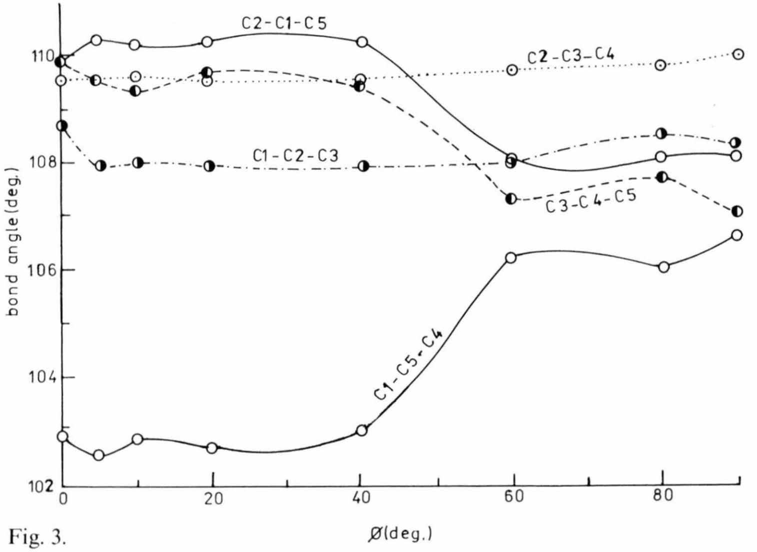
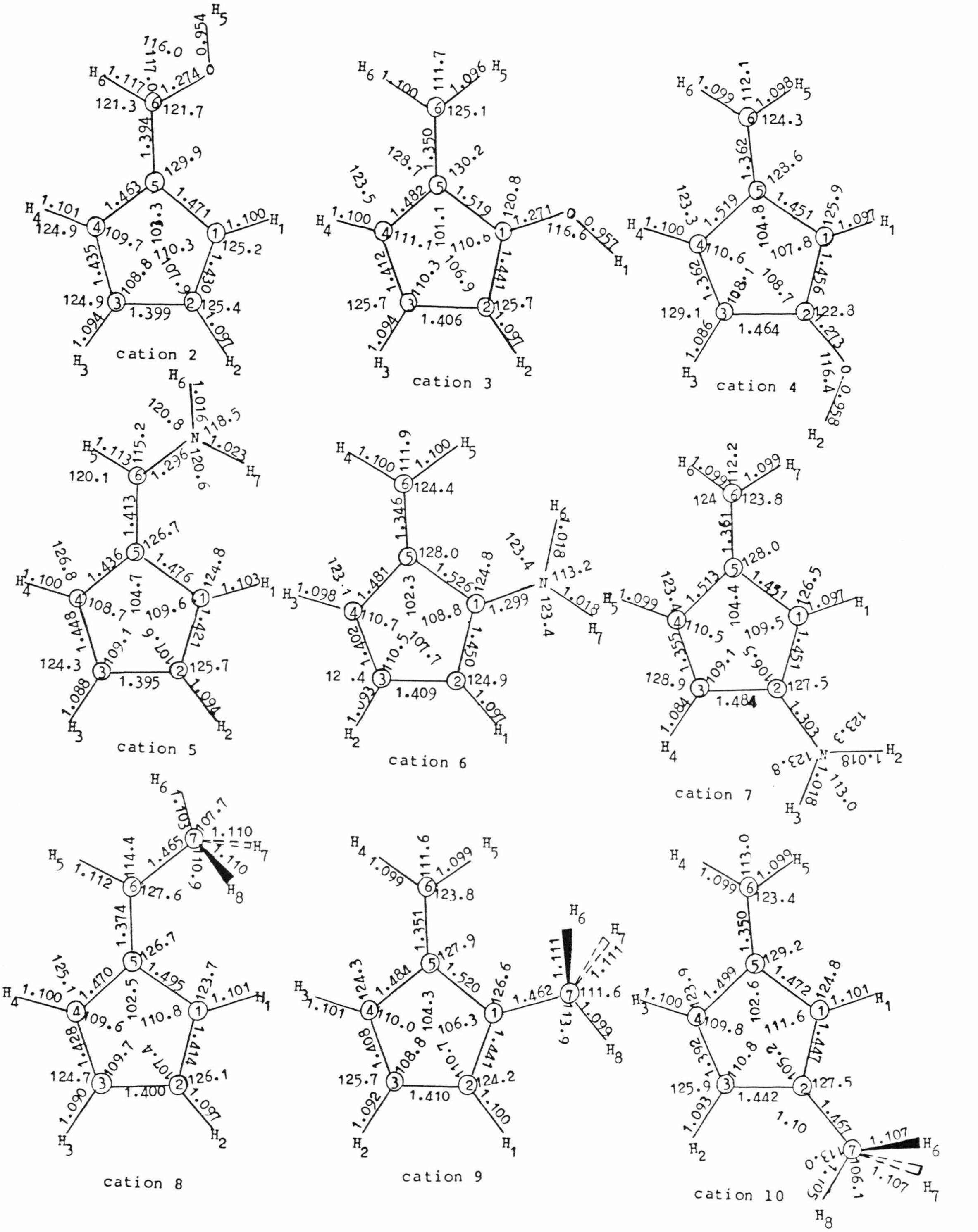


Fig. 3.

Fig. 2. Changes in the C – C bond lengths as functions of the dihedral angle (ϕ) for fulvene radical cations.

Fig. 3. Changes in the bond angles as functions of the dihedral angle (ϕ) for fulvene radical cations.

Fig. 4. Changes in the calculated electron densities as functions of the dihedral angle (ϕ) for fulvene radical cations.



cation 2

cation 3

cation 4

cation 5

cation 6

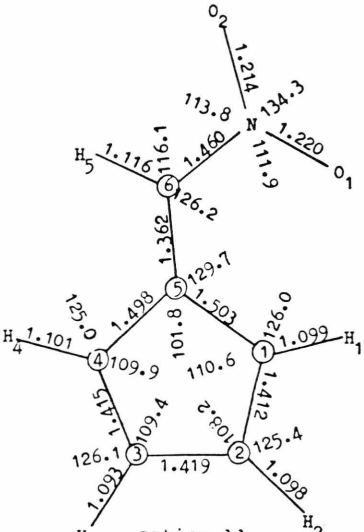
cation 7

cation 8

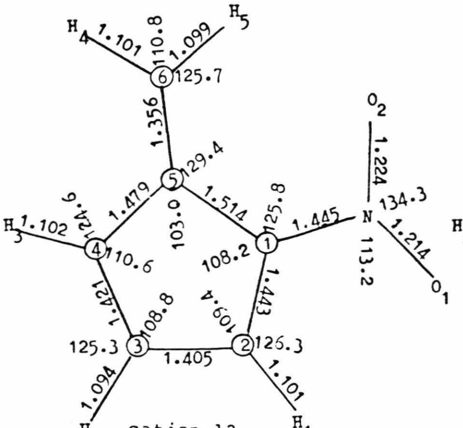
cation 9

cation 10

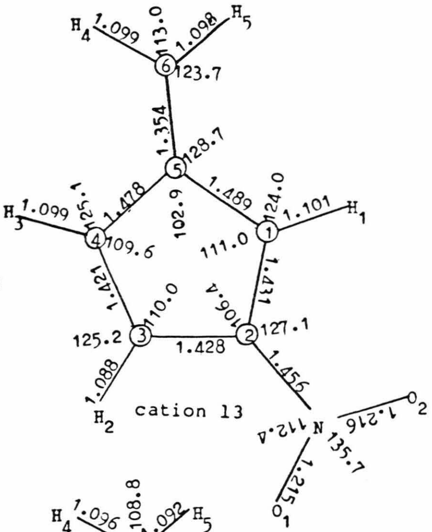
Fig. 5. Optimized geometries for monosubstituted fulvene radical cations. Bond lengths are in Angstroms and bond angles in degrees.



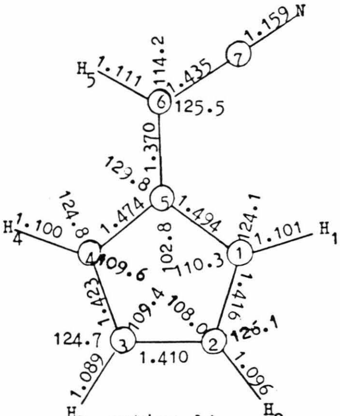
cation 11



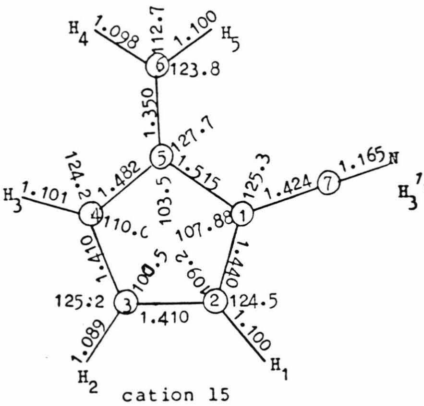
cation 12



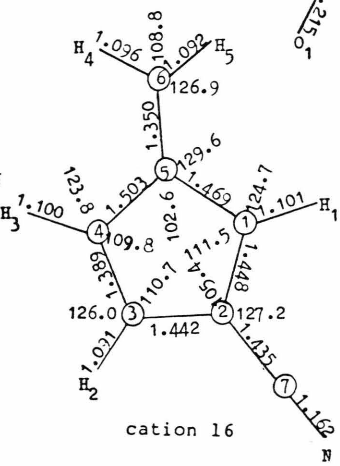
cation 13



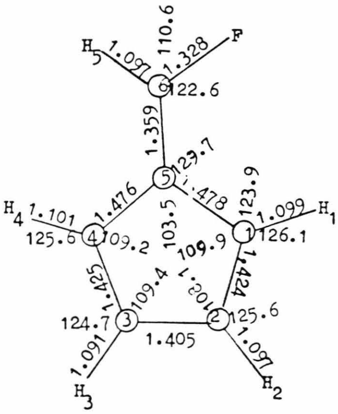
cation 14



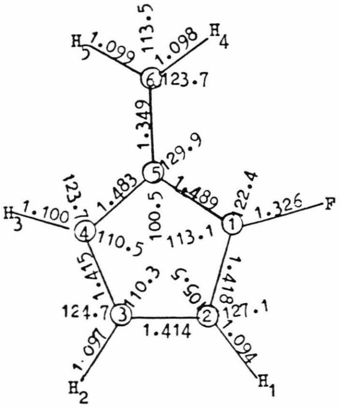
cation 15



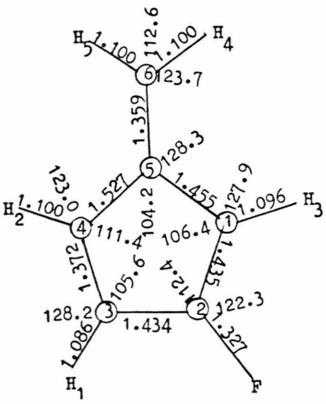
cation 16



cation 17



cation 18



cation 19

Fig. 5. Continued.

The changes in the other bond lengths and bond angles are negligible. Figures 2 and 3 show the changes in the bond lengths and bond angles, respectively, of the fulvene radical cation as function of the dihedral angle (ϕ). In the rotation transition state ($\phi = 90°$), it can be seen that the degree of cross-conjugated structure is increased as compared with cation 1 (ground state $\phi = 5°$). The internal rotational barrier of the CH_2 group was calculated to be 34.818 kcal/mole.

The calculated electron densities of the carbon atoms in the fulvene radical cation with different ϕ values are plotted in Figure 4. On rotating the CH_2 group towards the perpendicular transition state ($\phi = 90°$), the electron density is decreased sharply on C6, decreased slightly on C2 and C5, and increased on C1.

Cation	ΔH_f	μ
1	248.125	13.482
2	177.366	17.359
3	172.925	13.707
4	178.983	11.450
5	216.223	19.314
6	209.133	16.649
7	212.420	12.395
8	233.323	15.048
9	234.932	14.557
10	236.051	13.219
11	248.704	9.978
12	246.124	11.504
13	242.533	15.677
14	264.650	13.311
15	266.150	13.315
16	267.457	13.897
17	191.662	13.305
18	189.903	13.189
19	196.324	14.390

Table 3. Calculated heats of formation (ΔH_f in kcal/mole) and dipole moments (μ in Debyes) for fulvene and monosubstituted fulvene radical cations.

3. *Effect of Substituents*

The calculated heats of formation and the dipole moments of monosubstituted fulvene radical cations after complete optimization of geometry are given in Table 3. It can be seen from this Table that the substituents NH_2, OH and CH_3 at C6 increase the dipole more than that at the ring carbon atoms. This may suggest that these substituents are increasing the degree of zwitterionic character. NO_2 substituent shows the opposite effect to that found for NH_2, OH and CH_3, while CN and F substituents leave the dipole moment almost unchanged.

The calculated electron densities are given in Tables 4 and 5. The geometrical parameters of the monosubstituted fulvene radical cations are given in Figure 5.

Structural Details:

OH substituted on the carbon atom C6 may be perpendicular to or in the plane of H6–C6–0. Also, the latter position has two possibilities, either H5 is trans with H6 or cis (Figure 5). It was found that the most stable structure is the one (cation 2). Similarly for cations 3 and 4.

Introduction of a substituent into fulvene radical cation increases the adjacent bond lengths. For example, in the case of cation 2, C1–C5 and C1–C2 are longer than for cation 1 (Figure 1). This effect of increasing the adjacent bond lengths is more pronounced in the case of NH_2 substituent and almost absent in the case of F substituent. All substituents are found to produce a small decrease in bond angle to

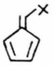
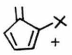
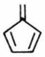
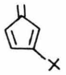
Atom	Cat. 2	Cat. 3	Cat. 4	Cat. 5	Cat. 6	Cat. 7	Cat. 8	Cat. 9	Cat.10
C1	3.763	3.472	3.999	3.803	3.777	3.987	3.791	3.796	3.830
C2	4.006	4.126	3.483	4.046	4.041	3.777	3.992	3.963	3.863
C3	3.977	3.921	4.172	3.938	3.945	4.087	3.948	3.977	4.043
C4	3.789	3.887	3.856	3.834	3.906	3.911	3.796	3.809	3.816
C5	4.263	4.121	4.021	4.220	4.066	3.997	4.151	4.105	4.084
C6	3.386	3.806	3.822	3.678	3.870	3.847	3.738	3.820	3.811
C7							4.006	3.997	3.981
H1	0.955	0.691	0.909	0.982	0.921	0.939	0.957	0.926	0.948
H2	0.916	0.900	0.690	0.921	0.927	0.951	0.911	0.916	0.918
H3	0.921	0.922	0.901	0.934	0.937	0.945	0.922	0.943	0.942
H4	0.959	0.932	0.937	0.958	0.936	0.924	0.944	0.945	0.949
H5	0.684	0.944	0.944	0.962	0.968	0.938	0.981	0.958	0.949
H6	1.029	0.944	0.944	0.853	0.873	0.945	0.947	0.944	0.953
H7				0.864	0.863	0.951	0.959	0.944	0.952
H8							0.956	0.956	0.965
O	6.351	6.334	6.325						
N				5.007	4.971	4.965			

Table 4. Calculated electron densities of monosubstituted (OH, NH_2, CH_3) fulvene radical cations. See Fig. 5 for numbering.

Table 5. Calculated electron densities of monosubstitued (NO_2, CN, F) fulvene radical cations. See Fig. 5 for numbering.

Atom	Cat. 11	Cat. 12	Cat. 13	Cat. 14	Cat. 15	Cat. 16	Cat. 17	Cat. 18	Cat. 19
C1	3.805	4.016	3.707	3.789	3.800	3.810	3.751	3.370	3.924
C2	3.952	3.880	4.199	3.984	3.934	3.858	3.986	4.091	3.392
C3	3.935	3.992	3.886	3.949	3.991	4.035	3.966	3.935	4.155
C4	3.816	3.745	3.806	3.800	3.801	3.826	3.778	3.851	3.837
C5	3.997	4.084	4.117	4.131	4.101	4.087	4.270	4.170	4.040
C6	4.057	3.780	3.768	3.740	3.812	3.802	3.318	3.770	3.798
C7				3.985	3.966	3.952			
H1	0.900	0.901	0.930	0.948	0.921	0.946	0.938	0.873	0.867
H2	0.901	0.899	0.902	0.911	0.915	0.915	0.907	0.910	0.930
H3	0.908	0.937	0.928	0.919	0.942	0.939	0.913	0.926	0.890
H4	0.925	0.945	0.939	0.941	0.946	0.949	0.947	0.935	0.939
H5	0.903	0.911	0.940	0.964	0.951	0.947	0.990	0.940	0.939
O1	6.546	6.479	6.498						
O2	6.461	6.520	6.512						
N	3.893	3.910	3.869	4.934	4.919	4.939			
F							7.273	7.231	7.219

Table 6. Evaluation of substituent effects using MINDO – Forces calculations. (energies are in kcal/mole).

	OH	NH_2	CH_3	NO_2	CN	F
 $+CH_3CH_3 \rightarrow$  $+CH_3CH_2\times$	29.459	39.903	11.102	1.103	9.437	12.163
 $+CH_3CH_3 \rightarrow$  $+CH_3CH_2\times$	33.900	46.992	9.493	3.683	7.937	13.922
 $+CH_3CH_3 \rightarrow$  $+CH_2CH_2\times$	27.842	43.705	8.374	7.274	6.630	7.501

which the substituent is attached, apart from F substituent. This resembles our recent calculations on 2-substituted allyl cations and anions [13].

Stabilization by Substituents:

The stabilizing effect of a substituent is often assessed by using isodesmic reactions (conserved bond type) [13]. A positive heat of formation (Table 6) indicates stabilization of the reactant by the substituent. The results show that all the substituents are stabilizing. The stabilization is most prononced in the case of OH and NH_2 substituents and very weak in the case of NO_2 substituent.

Electron Densities:

It can be seen from Table 4 and 5 that the substituents OH, NH_2 and F decrease the electron densities on the carbon atom to which the substituent is attached and increase the electron densities on the adjacent carbon atoms, i.e. they act as electron releasing. CH_3 and CN substituents act as very weak by electron releasing.

In the case of the electron withdrawing substituent NO_2, the electron density increases on the carbon atom to which it is attached and decreases on the adjacent carbon atoms, opposite to the effect found for OH, NH_2 and F.

The electron density on H1 and H4 (α-protons) is greater than that on H2 and H3 (β-protons) for OH, NH_2, F, CH_3 and CN substituents, but not so for NO_2, which is in agreement with the experimental result [7] of dimethylfulvene.

Spin Densities:

The result of cation 1 in Table 7 shows that the unpaired electron resides largely at C1 and C4 and to a small degree at C2 and C3. The results eliminate the possibility of spin density at C5 and C6, which is in

Atom	Cat. 1	Cat. 2	Cat. 5	Cat. 8	Cat. 11	Cat. 14	Cat. 17
C1	0.3574	0.3702	0.3820	0.3537	0.3489	0.3551	0.3620
C2	0.1364	0.1154	0.0500	0.1110	0.1461	0.1201	0.1308
C3	0.1427	0.1359	0.2069	0.1856	0.1395	0.1543	0.1317
C4	0.3634	0.3769	0.3313	0.3671	0.3649	0.3671	0.3748
C5	0.0000	0.0008	0.0160	0.0015	0.0001	0.0001	0.0003
C6	0.0001	0.0005	0.0054	0.0032	0.0003	0.0019	0.0001

Table 7. Calculated spin densities of fulvene and 6-substituted fulvene radical cations. See Fig. 5 for numbering.

Atom	Cat. 3	Cat. 6	Cat. 9	Cat. 12	Cat. 15	Cat.18
C1	0.1736	0.1165	0.3350	0.4217	0.3311	0.2328
C2	0.2535	0.2946	0.1665	0.0779	0.1505	0.2139
C3	0.0766	0.0457	0.1070	0.1452	0.1021	0.1001
C4	0.3930	0.3509	0.3234	0.2193	0.2986	0.3786
C5	0.0033	0.0038	0.0003	0.0001	0.0001	0.0026
C6	0.0261	0.0332	0.0010	0.0007	0.0003	0.0124

Table 8. Calculated spin densities of 1-substituted fulvene radical cations. See Fig. 5 for numbering

Table 9. Calculated first ionization potentials (eV) of fulvene and 6-substituted fulvene radical cations. See Fig. 5 for numbering.

Cation	1	2	5	8	11	14	17
First Ionization potential (eV)	10.77	10.09	9.70	10.44	11.26	10.58	10.71

good agreement with CIDNP results [7]. Thus the substituent interacts strongly with the unpaired electron spin at C1 or C4 and weakly at C6. This is exactly what we found in the case of OH and NH_2 substituents at C1 (Table 8), which interact strongly with the electron spin while F substituent shows slight interaction. This kind of interaction is supported by the results shown in Table 6, where OH and NH_2 at C1 show strong stabilization in comparison to C6 and C2, while the rest of the substituents show very weak or no stabilization.

The substituents at C6 (Table 7) interact very weakly with the unpaired spin, in agreement CIDNP results [7].

The first ionization potentials of these fulvene radical cations (Table 9) are substituent dependent, an observation which precludes a HOMO without an appreciable coefficient at C6. These results suggest that charge density and not spin density exists at C6, in agreement with CIDNP results [7].

Conclusions

The results presented here support the existence of some degree of twisting in the fulvene radical cation and the residence of the unpaired electron in the endocyclic diene. The positive charge is delocalised throughout the entire molecule (at atoms C1, C4, C6). The substituents at the exocyclic double bond show weak interaction with the unpaired spin as compared with the substituents at the endocyclic diene.

Acknowledgements

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[1] P. Yates, Advanced in Alicyclic chemistry (Edited by H. Hart and G. J. Karabatsos), Vol. 2, p. 59 Academic Press, New York 1968.

[2] E. D. Bergmann, Chem Rev. **41,** 68 (1968).

[3] J. H. Day, Chem. Rev. **53,** 167 (1953).

[4] K. N. Houk, J. K. George, R. E. Duke, Jr., Tetrahedron, 30, 523 (1974); D. H. Lo and M. A. Whitehead, Tetrahedron **25,** 2615 (1969).

[5] P. A. Baron, R. D. Brown, F. R. Burden, P. J. Domaille, and J. E. Kent, J. Mol. Spectros. 43, 401 (1972).

[6] (a) A. Pines and M. Rabinowith, J. Chem. Soc. B **1971,** 385; (b) R. Hollenstein, W. v. Philipsborn, R. Vogeli, and M. Neuenschwander, Helv. Chim. Acta **56,** 847 (1973); (c) L. Knothe, H. Prinzbach, and H. Fritz, Leibigs Ann. Chem. **1977,** 687.

[7] C. J. Abelt and H. D. Roth, J. Amer. Chem. Soc. **107,** 6814 (1985).

[8] (a) S. M. Khalil and M. Shanshal, Theor. Chim. Acta **46,** 23 (1977), (b) S. M. Khalil and M. Shanshal, Z. Naturforsch. **33a,** 722 (1978), (c) S. M. Khalil, Z. Naturforsch. **40a,** 1278 (1985), (d) H. M. Jarjis and S. M. Khalil, J. Chem. Soc. Perkin Trans. **2,** 1701 (1986), (e) H. M. Jarjis and S. M. Khalil, Z. Naturforsch. **42a,** 174 (1987), (f) H. M. Jarjis and S. M. Khalil, Z. Naturforsch. **42a,** 297 (1987).

[9] R. C. Bingham, M. J. S. Dewar, and D. H. Lo, J. Amer. Chem. Soc. **97,** 1285 (1975).

[10] B. A. Murtagh and R. W. H. Sargent, Comput. J. **13,** 185 (1970).

[11] P. Pulay, Mol. Phys. **17,** 197 (1969).

[12] M. J. S. Dewar, E. G. Zoebisch, H. F. Healy, and J. J. P. Stewart, J. Amer. Chem Soc. **107,** 3902 (1985).

[13] S. M. Khalil and H. M. Jarjis, Z. Naturforsch. **42a,** 761 (1987).