A Theoretical Study of Fulvene Radical Anions

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MINDO-Forces calculations have been performed, with complete optimization of geometry on fulvene and X-fulvene radical anions, where X is OH, NH_2, CH_3, NO_2, CN, F, dimethyl and cyclopropyl. A twisted structure with angle 5° was found for fulvene anion. All substituents are stabilizing. The stabilization effect is more pronounced in the case of NO_2 and very weak in the case of CH_3. It was found that the substituents CH_3 and CN show amphielectronic behaviour. Geometrical parameters, heats of formation, dipole moments, electron and spin densities are reported.

Having studied the effect of substituents on fulvene radical cations [1], we now report the effect of substituents (OH, NH_2, CH_3, NO_2, CN, F, dimethyl and cyclopropyl) on fulvene radical anion.

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 given by Dewar et al. [2]. Taking an electron from the fulvene molecule, a twisted structure with an angle 5° was found, and the heat of formation changed to 248.125 kcal/mole for the fulvene radical cation [1].

There exist no advanced calculations on fulvene and monosubstituted fulvene radical anion. This paper reports the geometry, heat of formation, dipole moment, electron and spin densities of monosubstituted fulvene radical anions from calculations by the semiempirical MINDO-Forces MO method [3]. The molecular energy of the radical anion obtained from the semiempirical MINDO/3 method [4] was completely minimized according to the Murtagh-Sargent minimization technique [5]. The derivative of the energy was calculated according to Pulay's Force method [6]. A full description of the program and its application is given in reference [3a].

Results and Discussion

1. Fulvene Radical Anion

In order to find whether the fulvene radical anion is planar or twisted we have calculated the heat of formation as a 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 in Table 1. In these calculations the energy is minimized with respect to all geometrical parameters. It can be seen from Table 1 that the most stable anion corresponds to $\phi = 5°$. This anion was called anion 1 and represents the ground state of fulvene radical anion. All the substituents relate to this anion.

It can be seen from Fig. 1 that adding an electron to the fulvene molecule to form anion 1 causes an increase in the bond lengths of C1–C2, C3–C4, C5–C6, a decrease in C1–C5, C4–C5, C2–C3 and a twist of the CH_2 group out of the molecular plane by 5°. This shows that there is a decrease in the degree of cross conjugation in the fulvene radical anion. This result resembles our result on the fulvene radical cation [1] though it is less pronounced.

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 anion:

(a) an increase in the C1–C2 and C5–C6 bond lengths;

(b) a decrease in the C1–C5 bond length and almost no change in the C2–C3 bond length;

Table 1. Calculated heats of formation (ΔH_f in kcal/mole) for fulvene radical anions as function of the dihedral angle (ϕ) (degrees).

Angle (ϕ)	ΔH_f
0	64.021
5	63.594
10	63.811
40	69.266
60	71.897
80	77.164
90	73.200

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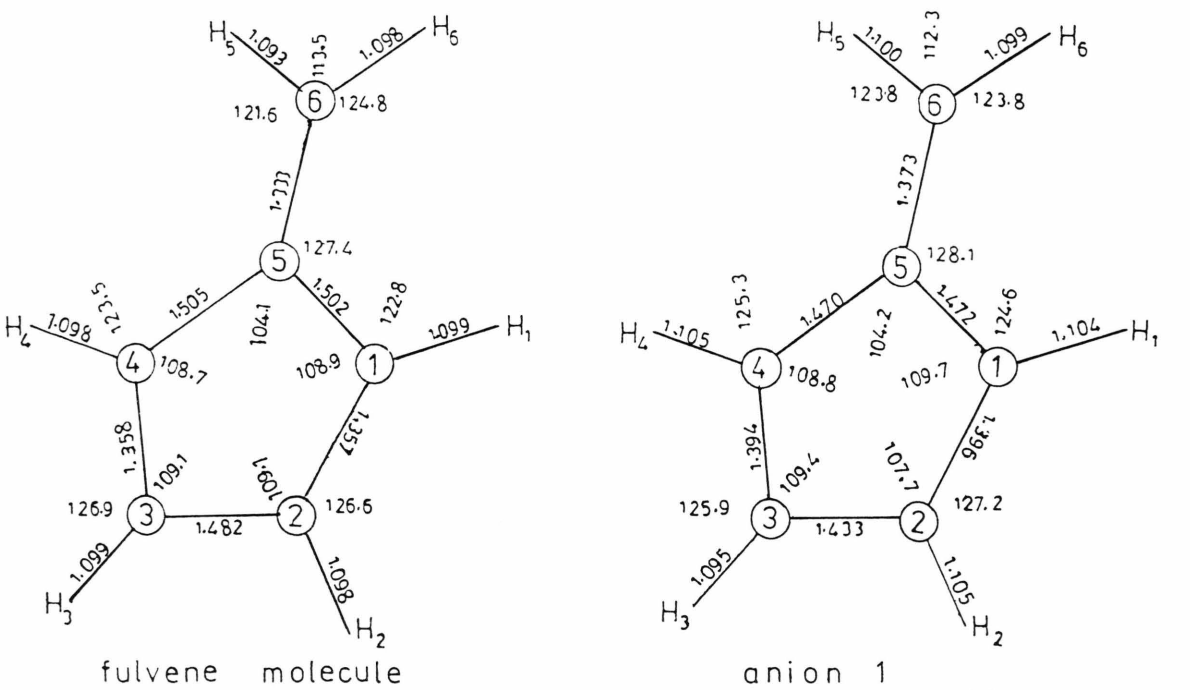


Fig. 1. Optimized geometry for fulvene molecule and radical anion 1 ($\phi = 5°$). Bond lengths are in Ångstroms and bond angles in degrees.

(c) a slight increase in C5C1C2 and C3C4C5 and almost no change in C1C2C3, C1C5C4 and C2C3C4. Figures 2 and 3 show the changes in the bond lengths and bond angles, respectively, of the fulvene radical anions as functions of the dihedral angle (ϕ).

The calculated electron densities of the carbon atoms in the fulvene radical anion with different ϕ values are plotted in Figure 4. On rotating the CH_2 group towards the perpendicular transition state, the electron density increases on C2 and C5, and decreases on C1 and C6.

2. *Effect of Substituents*

Structural Details

Introduction of a substituent into fulvene radical anion increases the adjacent bond lengths (Figure 5). This effect is in the order of $NO_2 > CN > CH_3 > NH_2 > OH$. F substituent is found to decrease the adjacent bond length except C5–C6. This is similar to our result on fulvene radical cations apart from the F substituent [1]. The dimethyl substituent is found to increase C5–C6 more than all substituents while cyclopropyl shows a slight increase in C5–C6 as compared with other substituents.

NO_2, CN, and CH_3 substituents are found to decrease the bond angle to which the substituent is attached in the order of $NO_2 < CN < CH_3$ in a similar

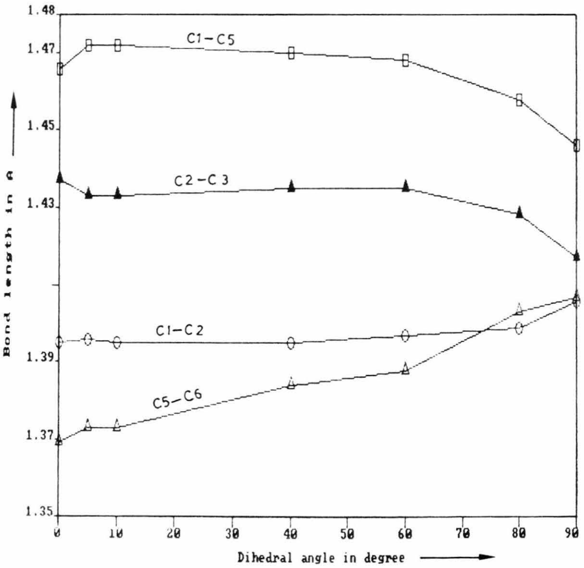


Fig. 2. C–C bond lengths vs. dihedral angle (ϕ) for fulvene radical anions.

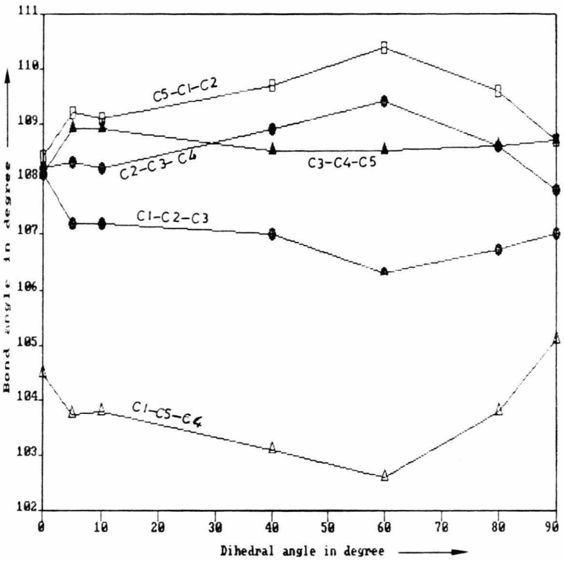


Fig. 3. Bond angles vs. dihedral angle (ϕ) for fulvene radical anions.

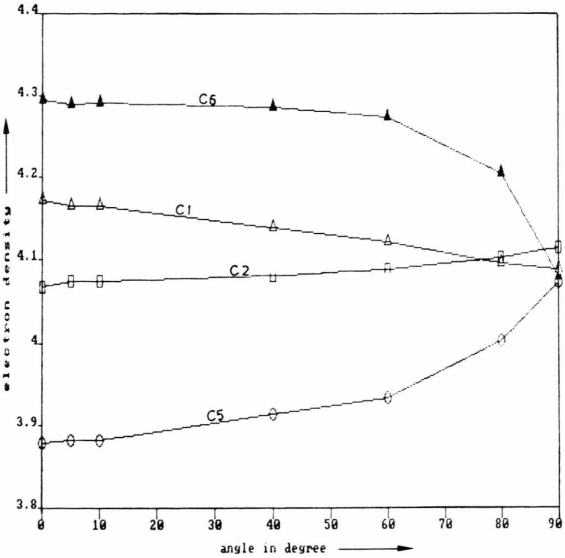
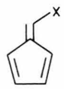
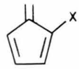
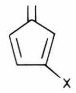


Fig. 4. Calculated electron densities as functions of the dihedral angle (ϕ) for fulvene radical anions.

Table 2. Evaluation of substituent effects using MINDO-Forces calculations (energies are in kcal/mole).

	OH	NH_2	CH_3	NO_2	CN	F	dimeth.	cycl.
 $+ CH_3CH_3 \rightarrow$  $+ CH_3CH_2X$	11.996	14.596	12.666	52.027	22.560	22.209	24.723	15.904
 $+ CH_3CH_3 \rightarrow$  $+CH_3CH_2X$	17.268	16.152	8.147	52.379	17.466	18.389		
 $+ CH_3CH_3 \rightarrow$  $+ CH_3CH_2X$	18.149	16.711	9.763	54.521	18.649	19.608		

fashion to that found in the case of fulvene radical cation [1]. But for OH, NH_2 and F substituents it was found that the substituent increases the bond angle when it is attached at carbon atoms C1 and C2 and decreases it at C6. This effect is more pronounced in the case of F substituent. Dimethyl and cyclopropyl substituents produce a decrease in the bond angle where the substituent is attached.

Stabilization by Substituents

The stabilizing effect of substituents is often assessed by using isodesmic reactions [7, 8, 9]. A positive heat of formation (Table 2) indicates stabilization of the reactant by the substituent. The results show that all the substituents are stabilizing. This is in agreement with our calculation on fulvene radical cation [1]. The stabilization is more pronounced in the case of NO_2 and very weak in the case of CH_3.

Electron Density

It can be seen from Tables 3 and 4 that the substituents OH, NH_2, F, dimethyl and cyclopropyl, decrease the electron densities on the carbon atom to which the substituent is attached and increase the

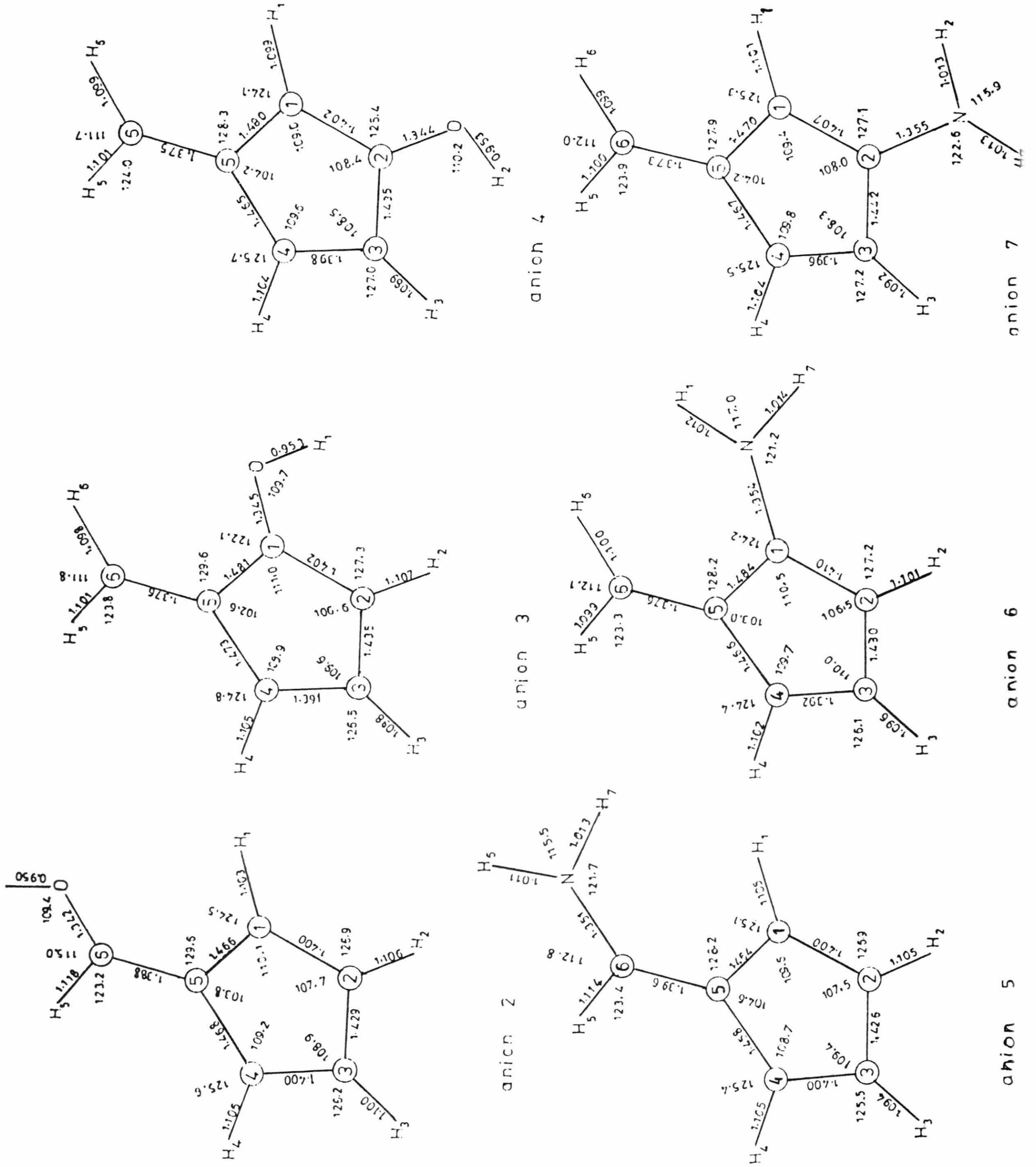
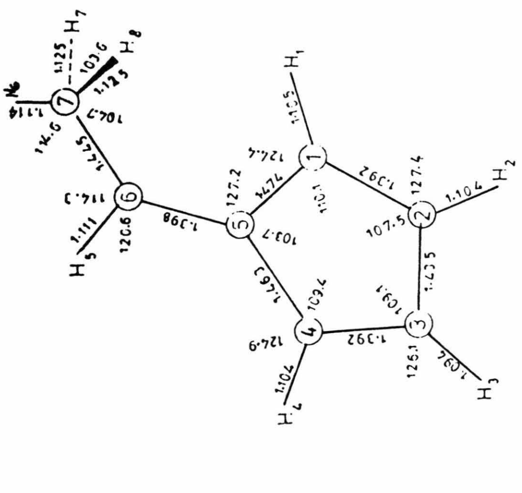
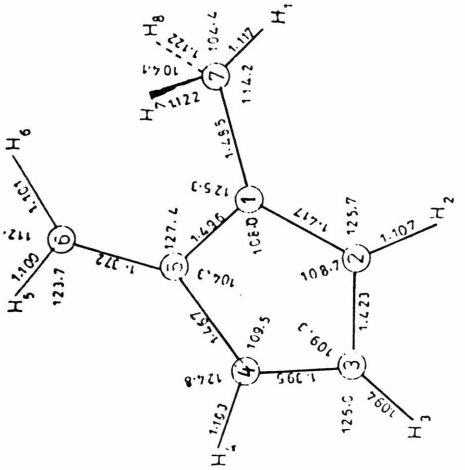


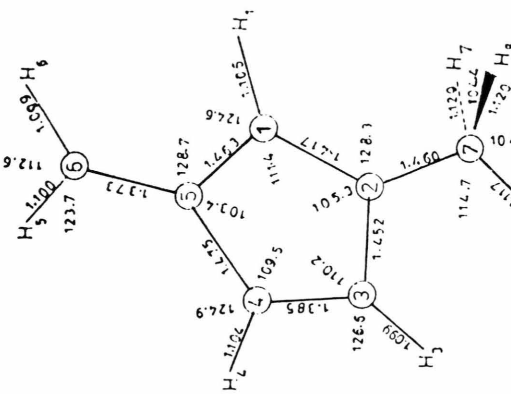
Fig. 5. Optimized geometries for monosubstituted fulvene radical anions. Bond lengths are in Ångstroms and bond angle in degrees.



anion 8



anion 9



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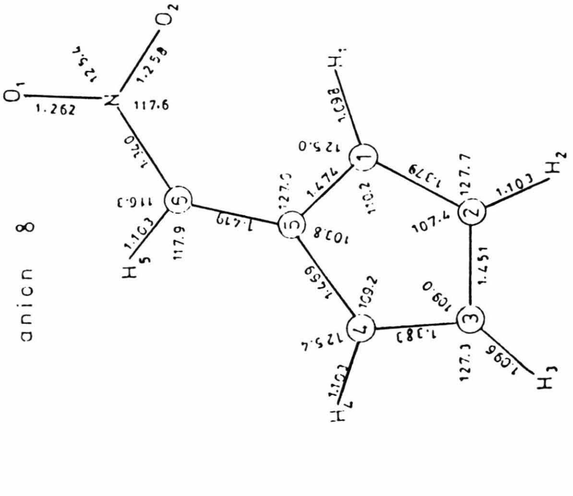
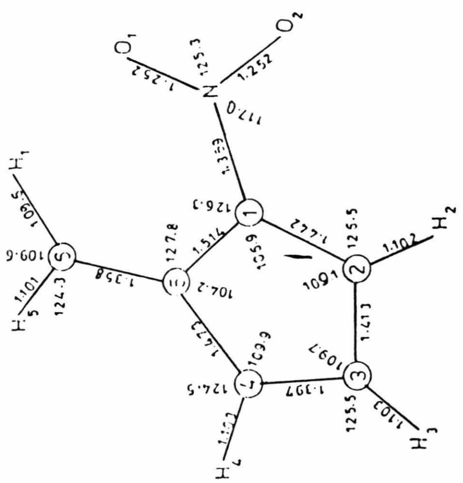


anion 11



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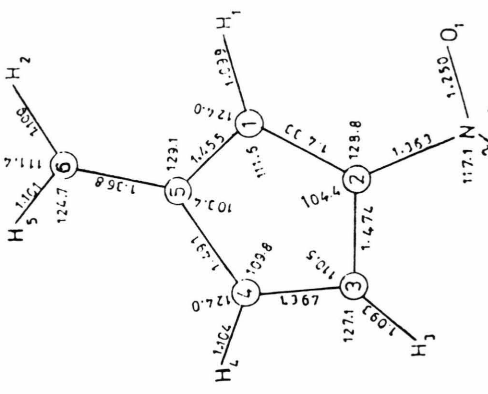

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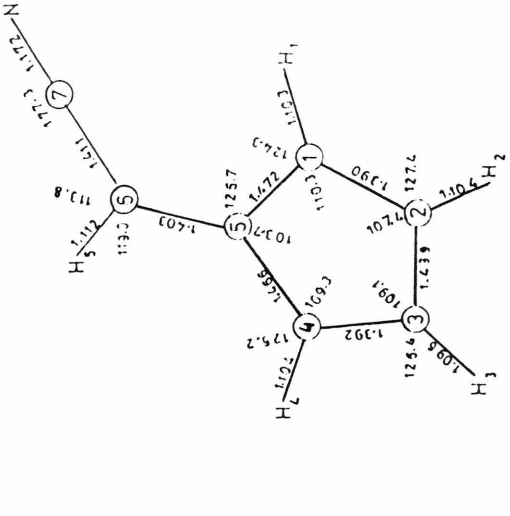
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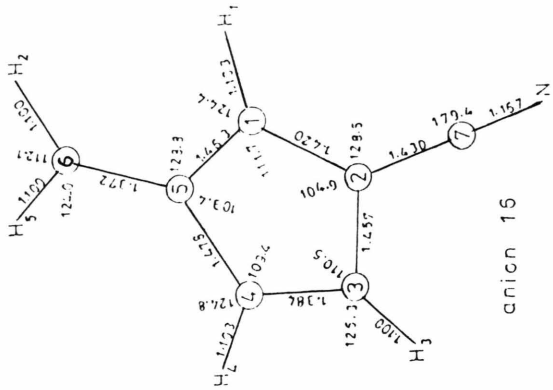
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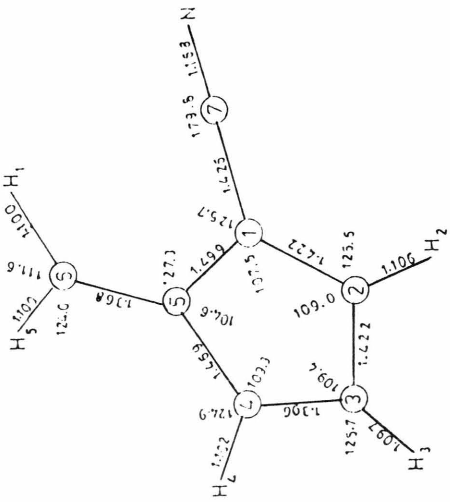
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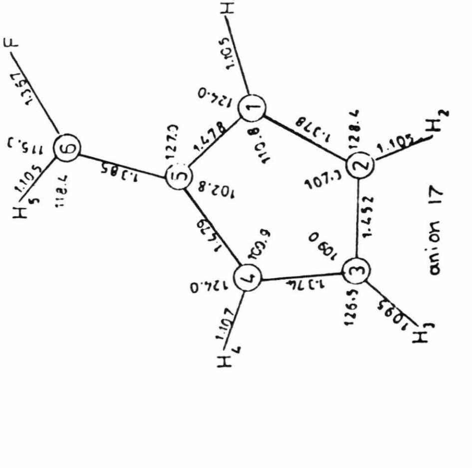
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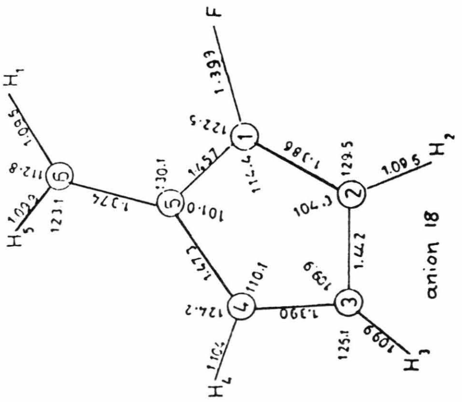
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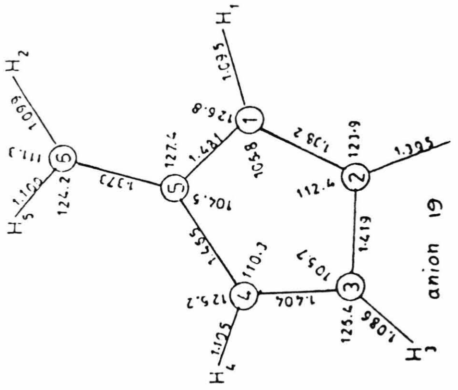
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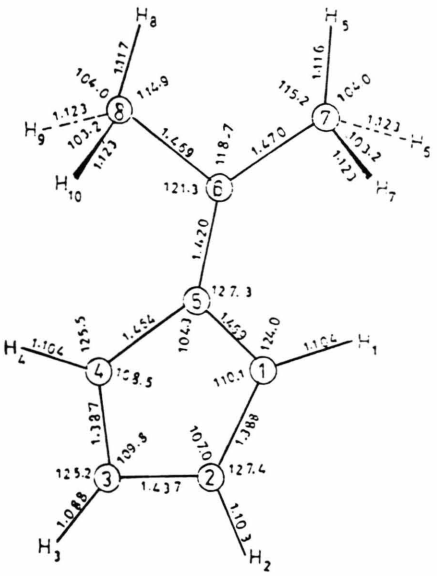

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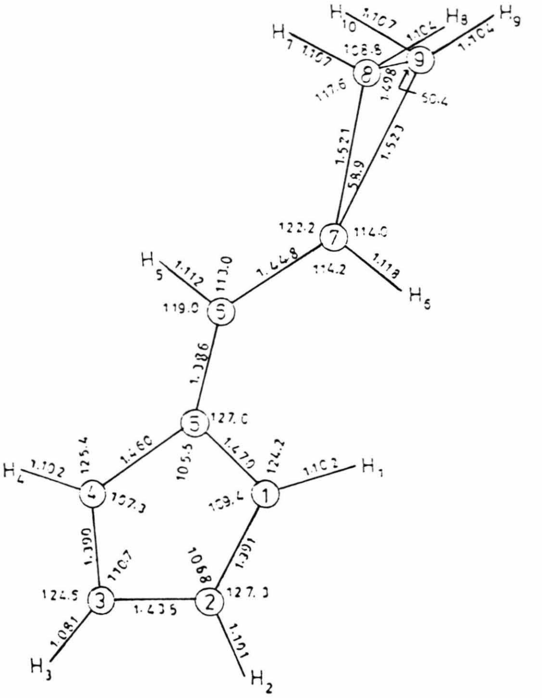

anion 21

Table 3. Calculated electron densities of monosubstituted (OH, NH_2, CH_3, dimethyl and cyclopropyl) fulvene radical anions. See Fig. 5 for numbering.

Atom	anion 1	anion 2	anion 3	anion 4	anion 5	anion 6	anion 7	anion 8	anion 9	anion 10	anion 20	anion 21
C1	4.165	4.135	3.802	4.291	4.152	3.969	4.284	4.135	4.180	4.153	4.119	4.136
C2	4.075	4.088	4.240	3.714	4.086	4.207	3.887	4.074	4.072	4.107	4.076	4.077
C3	4.067	4.074	4.032	4.198	4.081	4.023	4.144	4.070	4.049	4.042	4.065	4.064
C4	4.170	4.159	4.190	4.144	4.151	4.021	4.151	4.143	4.175	4.156	4.130	4.145
C5	3.883	3.986	3.943	3.862	3.978	3.921	3.854	3.918	3.877	3.886	3.940	3.930
C6	4.289	3.940	4.275	4.296	4.119	4.300	4.310	4.243	4.265	4.279	4.223	4.221
C7								3.785	3.804	3.821	3.843	3.851
C8												4.028
H1	1.061	1.057	0.800	1.028	1.070	0.959	1.042	1.052	1.102	1.057	1.051	1.052
H2	1.077	1.076	1.050	0.795	1.078	1.054	0.966	1.070	1.068	1.094	1.065	10.65
H3	1.080	1.080	1.081	1.058	1.082	1.084	1.064	1.073	1.076	1.075	1.071	1.074
H4	1.057	1.066	1.051	1.058	1.066	1.053	1.059	1.058	1.053	1.055	1.046	1.047
H5	1.038	1.101	1.037	1.036	1.051	1.034	1.038	1.042	1.036	1.035	1.103	1.040
H6	1.038	0.809	1.029	1.035	0.989	1.040	1.035	1.111	1.028	1.034	1.100	1.059
H7					0.956	0.974	0.970	1.113	1.108	1.103	1.101	1.038
H8								1.113	1.108	1.104		1.053
O		6.430	6.470	6.483								
N					5.139	5.182	5.196					

electron densities on the adjacent carbon atoms, i.e. they act as electron releasing. The effect is more pronounced in the case F, OH and NH_2. NO_2 substituent produces an increase in the electron density on the carbon atom to which it is attached and a decrease on the adjacent carbon atom, i.e. it acts as electron withdrawing. CH_3 and CN substituents act very weakly as electron withdrawing, which is different from our reults on fulvene radical cation [1]. Therefore CH_3 and CN show amphielectronic behaviour. They, thus

Table 4. Calculated electron densities of monosubstituted (NO_2, CN, F) fulvene radical anions. See Fig. 5 for numbering.

Atom	anion 11	anion 12	anion 13	anion 14	anion 15	anion 16	anion 17	anion 18	anion 19
C1	4.087	4.335	4.074	4.122	4.171	4.144	3.968	3.698	4.319
C2	4.068	4.000	4.277	4.074	4.065	4.108	4.108	4.227	3.597
C3	4.040	4.021	3.951	4.066	4.038	4.023	4.084	4.041	4.202
C4	4.117	4.152	4.122	4.133	4.179	4.150	4.044	4.176	4.148
C5	3.884	3.849	3.900	3.962	3.869	3.888	4.243	3.976	3.861
C6	4.342	4.169	4.121	4.211	4.248	4.266	3.577	4.257	4.284
C7				3.833	3.832	3.845			
H1	0.984	0.973	1.017	1.045	1.023	1.051	1.058	1.021	1.008
H2	1.046	1.027	1.021	1.064	1.073	1.031	1.060	1.023	1.031
H3	1.056	1.058	1.033	1.069	1.072	1.071	1.070	1.073	1.028
H4	1.038	1.036	1.037	1.054	1.046	1.049	1.070	1.048	1.052
H5	0.978	1.037	1.024	1.040	1.033	1.032	1.236	1.034	1.033
O1	6.735	6.718	6.708						
O2	6.712	6.725	6.716						
N	3.914	3.900	3.908	5.359	5.356	5.342			
F							7.521	7.425	7.438

Table 5. Calculated spin densities of monosubsituted fulvene radical anions. See Fig. 5 for numbering.

Atom	anion 1	anion 2	anion 3	anion 4	anion 5	anion 6	anion 7	anion 8	anion 9	anion 10	anion 11
C1	0.1591	0.1497	0.1868	0.0954	0.1339	0.1909	0.0914	0.1260	0.1638	0.1846	0.0763
C2	0.1203	0.0934	0.0658	0.1160	0.0839	0.0569	0.1247	0.1093	0.1390	0.1338	0.1172
C3	0.1198	0.0982	0.1364	0.1444	0.0834	0.1408	0.1434	0.1149	0.1015	0.0934	0.1390
C4	0.1542	0.1443	0.1042	0.2109	0.1318	0.0938	0.2045	0.1214	0.1668	0.1301	0.0668
C5	0.0733	0.0085	0.0898	0.0704	0.0301	0.0955	0.0708	0.1024	0.0555	0.0652	0.2410
C6	0.3729	0.4351	0.3956	0.3499	0.4357	0.3731	0.3354	0.3578	0.3455	0.3686	0.1750

Atom	anion 12	anion 13	anion 14	anion 15	anion 16	anion 17	anion 18	anion 19	anion 20	anion 21
C1	0.0923	0.3193	0.3335	0.1577	0.2086	0.0032	0.1801	0.1000	0.1072	0.1225
C2	0.2495	0.1005	0.1055	0.1582	0.1338	0.0016	0.0763	0.1119	0.1077	0.1038
C3	0.0404	0.0301	0.1153	0.0907	0.0779	0.0093	0.1308	0.1429	0.1106	0.1077
C4	0.2483	0.0481	0.1068	0.1952	0.1447	0.0473	0.1111	0.2272	0.1002	0.1135
C5	0.0114	0.0347	0.1267	0.0434	0.0579	0.0816	0.0822	0.0647	0.2261	0.0972
C6	0.2503	0.3380	0.3613	0.3262	0.3633	0.4893	0.4067	0.3553	0.3421	0.3509

Table 6. Calculated heats of formation (ΔH_f in kcal/mole) and dipole moments (μ in Debyes) for monosubstituted fulvene anions. See Fig. 5 for numbering.

Anion	ΔH_f	μ
1	63.594	13.659
2	10.298	13.306
3	5.026	15.060
4	4.145	14.995
5	56.998	12.475
6	55.442	13.081
7	54.383	14.361
8	47.228	15.278
9	51.747	14.445
10	50.131	13.184
11	13.249	23.143
12	12.897	19.922
13	10.755	12.489
14	66.980	18.811
15	72.090	17.227
16	70.907	12.290
17	−2.915	18.513
18	0.905	14.935
19	−0.314	12.933
20	40.499	15.626
21	69.622	16.016

act as electron releasing and withdrawing depending on the electron demand [9–14].

Spin Densities

The result on anion 1 (Table 5) shows that the unpaired electron resides largely at C6, to a small degree at C1 and C4 and even less at C2 and C3. The spin density at C5 is very low. This result is different from that on fulvene radical cation [1] which showed that the spin resides largely on the endocyclic diene.

Thus adding on electron to the fulvene molecule results in an exocyclic rather than endocyclic diene, and also removing an electron from the exocyclic double bond of the fulvene molecule.

The interaction of the substituent (either releasing or withdrawing) is more pronouced at C6, followed by substitution at C1 and then at C2.

Dipole Moment

The electron releasing substituents OH and NH_2 decrease the dipole moment at the exocyclic double bond and increase the dipole moment (Table 6) at the endocyclic diene. This is due to the high electron and spin densities at the exocyclic double bond of the fulvene anion. This result is different from that on fulvene radical cation [1]. F substituent shows a different effect due to it is peculiarity [15].

However, the introduction of CH_3, NO_2 and CN substituents increases the dipole moment at the exocyclic double bond more than that at the endocyclic diene. This is because they are electron withdrawing according to the present result. Dimethyl and cyclopropyl increase the dipole moment because they act as weakly electron releasing.

Conclusions

The results presented here support the existence of some degree of twisting in fulvene radical anion and the residence of the unpaired electron in the exocyclic double bond. The negative charge is delocalized throughout the entire molecule (C1, C4, C6). The substituents at the exocyclic double bond show strong interaction with the unpaired spin as compared with the substituent at the endocyclic diene. Electron releasing substituents are found to decrease the dipole moment at the exocyclic double bond, while the electron withdrawing substituents increase the dipole moment at the exocyclic double bond.

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