A Theoretical Study of Monosubstituted Fulvenes

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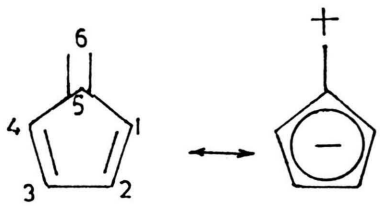
MINDO-forces calculations have been done after complete optimization of geometry on X-monosubstituted fulvenes, where X is OH, NH_2, CH_3, NO_2, CN, F, dimethyl and cyclopropyl. It was found that all the substituents are stabilizing. The electron releasing substituents increase the dipole moment at the exocyclic double bond while the electron withdrawing ones increase the dipole moment at the endocyclic diene. Geometrical parameters, heats of formation, orbital energies and electron densities are reported.

Fulvenes have long been of interest as cross-conjugated molecules with some unique properties [1, 2]. Their structure and electron distribution have been investigated theoretically [3–11] and experimentally [12–14].

Recently [15], we have studied the parent fulvene and the effect of substituents on the fulvene radical cations. The calculated heat of formation and the dipole moment of the parent molecule after complete optimization of geometry were found to be 67.797 kcal/mole and 0.412 D respectively. The dipole moment can be understood as resulting from intramolecular charge transfer from exocyclic double bond to five membered ring [2, 16],



thereby acquiring pseudoaromatic cyclopentadienide character.

Substituents can affect the degree of zwitterionic character, and such perturbations manifest themselves as shielding effect in NMR spectra [17, 18]. Furthermore, substituents which reinforce the zwitterionic structure, i.e. electron releasing groups at C6 and/or electron accepting groups on the ring, stabilize the fulvene and reduce its tendency for dimerization, polymerization and oxygenation [2].

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A detailed NMR study of fulvenes substituted at the 6-position has been published [12] which demonstrates the importance of the charge separated form, which is stabilized by electron releasing groups at C6. It has been assumed that the cyclopentadienylidene ring interacts strongly with donor groups [5], thereby approaching a cyclopentadienide ion. Pertinent examples are 6-aminofulvene [11] and 6,6-diaminofulvene [20, 21]. The charge delocalization and the development of the electronic structure of the cyclopentadienide ion are evidenced by large dipole moments [20, 22]. The dipolar character of the exocyclic double bond in fulvenes [2] gives them reactivities similar to carbonyl compounds. A proton α to the exocyclic double bond is fairly acidic, pK = 22.7 (DMSO) [23], i.e. comparable to a proton α to the carbonyl group in an aldehyde or a ketone. Fulvenes are also prone to undergro cycloadditions, in which they act either as diene or dienophile [24–28]. It was shown that 6,6-dimethylfulvene readily differentiate typical electrophilic from nucleophilic carbenes on the basis of their regiochemical selectivity [29], i.e. acts as indicator.

This paper reports the geometry, heat of formation, dipole moment, electron density, orbital energy, (HOMO, LUMO) and the stability of substituted fulvene molecules using the MINDO-forces MO method [30].

Dipole Moments

The dipole moment character of fulvene resulting from the shift of a π electron from the exocyclic carbon toward the cyclopentadienyl ring is well known [2].

The electron releasing substituents OH, NH_2, CH_3, dimethyl, and cyclopropyl increase the dipole moment (Table 1), and it is found to be more pro-

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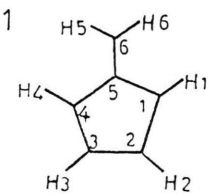
Table 1. Calculated heats of formation (ΔH_f in kcal/mole) and dipole moments (μ in Debye) for monosubstituted fulvenes. See Table 2 for numbering.

Molecule	ΔH_f	μ	Molecule	ΔH_f	μ
1	67.797	0.412	11	53.499	5.149
2	9.167	3.306	12	46.320	5.296
3	6.968	0.903	13	45.566	5.801
4	7.840	2.284	14	84.143	2.250
5	54.125	3.480	15	85.576	2.673
6	54.189	2.048	16	84.704	3.103
7	54.732	1.575	17	10.605	1.322
8	56.434	0.549	18	11.196	1.664
9	59.172	0.414	19	11.408	2.236
10	57.834	0.429	20	56.339	0.643
			21	80.029	1.176

nounced at C6, which is in agreement with the experimental results [16]. The electron releasing groups OH and NH_2 increase the dipolar contribution and give greater molecular stability, which agrees with theoretical calculations [3]. Introduction of the electronegative substituents NO_2, CN and F has the opposite effect, which is again in agreement with the experimental results [16], i.e. the electron releasing substituent at the exocyclic double bond as well as the electron withdrawing substituent at the endocyclic diene increase the zwitterionic character.

Table 2. Calculated geometrical parameters (bond lengths are in Ångstrom and bond angles in degrees) of monosubstituted fulvenes.

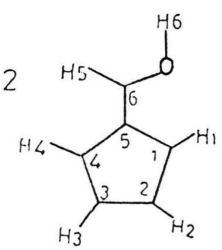
1



C1C2, 1.357; C2C3, 1.482; C3C4, 1.358; C4C5, 1.505; C5C1, 1.502; C5C6, 1.333; C3H3, 1.099; C4H4, 1.101; C6H5, 1.093.

C1C5C4, 104.1; C5C4C3, 108.7; C4C3C2, 109.1; C3C2C1, 109.1; C2C1C5, 108.9; C5C1H1, 122.8; C5C4H4, 123.4; C1C2H2, 126.0; C4C3H3, 126.9; C6C5C1, 127.4; C5C6H5, 121.6; H5C6H6, 113.5.

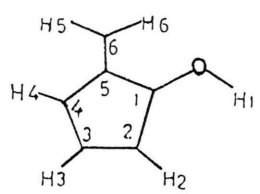
2



C1C2, 1.363; C2C3, 1.470; C3C4, 1.364; C4C5, 1.500; C5C1, 1.498; C5C6, 1.357; C3H3, 1.100; C4H4, 1.101; C6H5, 1.120; C6O, 1.311; OH6, 0.951.

C1C5C4, 102,9; C5C4C3, 109.6; C4C3C2, 108.9; C3C2C1, 108.5; C2C1C5, 109.9; C5C1H1, 123.0; C5C4H4, 123.6; C1C2H2, 127.6; C4C3H3, 127.7; C6C5C1, 129.8; C5C6H5, 122.5; H5C6O, 114.6; C6OH6, 112.9.

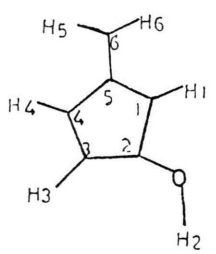
3



C1C2, 1.371; C2C3, 1.471; C3C4, 1.359; C4C5, 1.506; C5C1, 1.521; C5C6, 1.336; C3H3, 1.098; C4H4, 1.099; C6H5, 1.100; C1O, 1.317; OH1, 0.953.

C1C5C4, 101.6; C5C4C3, 109.8; C4C3C2, 110.5; C3C2C1, 106.9; C2C1C5, 111.0; C5C1O, 118.3; C5C4H4, 122.4; C1C2H2, 128.6; C4C3H3, 127.6; C6C5C1, 130.9; C5C6H5, 123.9; H5C6H6, 109.2; C1OH1, 111.7.

4



C1C2, 1.371; C2C3, 1.487; C3C4, 1.335; C4C5, 1.506; C5C1, 1.504; C5C6, 1.338; C3H3, 1.091; C4H4, 1.100; C6H5, 1.101; C2O, 1.319; OH2, 0.952.

C1C5C4, 103.8; C5C4C3, 109.6; C4C3C2, 108.7; C3C2C1, 109.0; C2C1C5, 108.7; C5C1H1, 122.6; C5C4H4, 123.8; C1C2O, 125.7; C4C3H3, 128.6; C6C5C1, 128.9; C5C6H5, 125.1; H5C6H6, 109.9; C2OH2, 112.6.

Table 2 (continued)

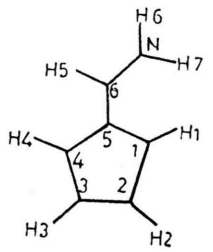
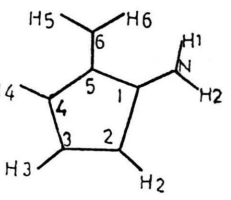
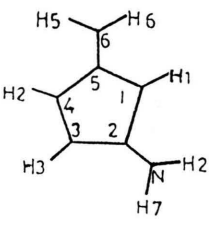
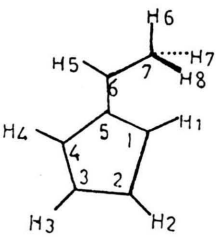
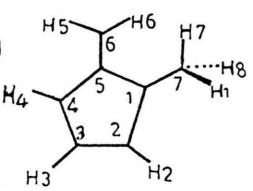
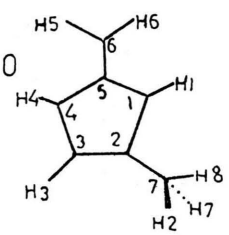
5		C1C2, 1.364; C2C3, 1.466; C3C4, 1.365; C4C5, 1.489; C5C1, 1.494; C5C6, 1.368; C3H3, 1.094; C4H4, 1.100; C6H5, 1.118; C6N, 1.332; NH6, 1.010; NH7, 1.013. C1C5C4, 103.5; C5C4C3, 109.0; C4C3C2, 109.4; C3C2C1, 108.1; C2C1C5, 109.7; C5C1H1, 123.5; C5C4H4, 123.5; C1C2H2, 127.5; C4C3H3, 127.1; C6H5C1, 128.2; C5C6H5, 121.8; H5C6N, 112.4; C6NH6, 124.8; H6NH7, 112.6.
6		C1C2, 1.385; C2C3, 1.471; C3C4, 1.360; C4C5, 1.506; C5C1, 1.532; C5C6, 1.334; C3H3, 1.107; C4H4, 1.098; C5H5, 1.101; C1N, 1.346; NH1, 1.015. C1C5C4, 103.1; C5C4C3, 109.8; C4C3C2, 109.6; C3C2C1, 108.9; C2C1C5, 108.3; C5C1N, 123.4; C5C4H4, 122.4; C1C2H2, 127.6; C4C3H3, 126.6; C6C5C1, 129.1; C5C6H5, 124.7; H5C6H6, 109.3; C1NH1, 124.2; H1NH7, 108.9.
7		C1C2, 1.385; C2C3, 1.504; C3C4, 1.359; C4C5, 1.505; C5C1, 1.506; C5C6, 1.343; C3H3, 1.098; C4H4, 1.103; C6H5, 1.104; C2N, 1.359; NH2, 1.019. C1C5C4, 101.6; C5C4C3, 110.1; C4C3C2, 110.7; C3C2C1, 104.5; C2C1C5, 112.8; C2C1H1, 120.9; C5C4H4, 123.0; C1C2N, 129.9; C4C3H3, 126.3; C6C5C1, 130.3; C5C6H5, 125.1; H5C6H6, 110.2; C2NH2, 124.5; H2NH7, 105.3.
8		C1C2, 1.356; C2C3, 1.477; C3C4, 1.358; C4C5, 1.530; C5C1, 1.509; C5C6, 1.353; C3H3, 1.095; C4H4, 1.099; C6H5, 1.112; C6C7, 1.472; C7H6, 1.108; C7H7, 1.112. C1C5C4, 102.9; C5C4C3, 109.2; C4C3C2, 109.5; C3C2C1, 108.2; C2C1C5, 110.0; C5C1H1, 122.5; C5C4H4, 123.3; C1C2H2, 127.8; C4C3H3, 127.6; C6C5C1, 126.7; C5C6H5, 118.5; H5C6C7, 113.0; C6C7H6, 114.9; H6C7H7, 105.3.
9		C1C2, 1.373; C2C3, 1.471; C3C4, 1.356; C4C5, 1.503; C5C1, 1.531; C5C6, 1.338; C3H3, 1.094; C4H4, 1.099; C6H5, 1.100; C1C7, 1.476; C7H1, 1.100; C7H7, 1.112. C1C5C4, 104.0; C5C4C3, 109.5; C4C3C2, 108.9; C3C2C1, 110.4; C2C1C5, 107.0; C5C1C7, 124.6; C5C4H4, 123.1; C1C2H2, 126.7; C4C3H3, 128.1; C6C5C1, 127.8; C5C6H5, 125.2; H5C6H6, 109.8; C1C7H1, 112.7; H1C7H7, 106.1.
10		C1C2, 1.377; C2C3, 1.498; C3C4, 1.355; C4C5, 1.504; C5C1, 1.492; C5C6, 1.338; C3H3, 1.100; C4H4, 1.097; C6H5, 1.101; C2C7, 1.477; C7H2, 1.111. C1C5C4, 102.0; C5C4C3, 109.9; C4C3C2, 110.2; C3C2C1, 105.2; C2C1C5, 112.4; C5C1H1, 122.8; C5C4H4, 123.2; C1C2C7, 129.6; C4C3H3, 127.6; C6C5C1, 129.2; C5C6H5, 124.3; H5C6H6, 110.9; C2C7H2, 114.6; H2C7H7, 105.5.

Table 2 (continued)

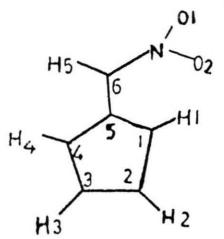
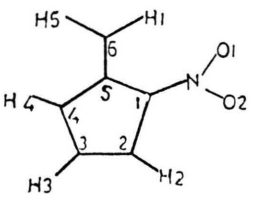
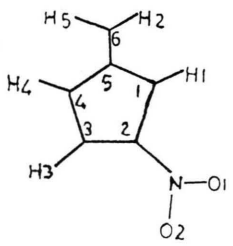
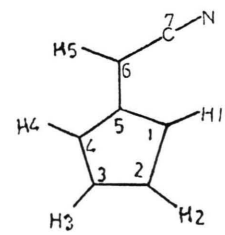
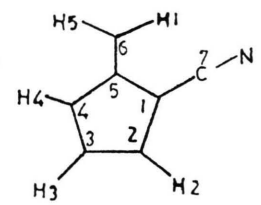
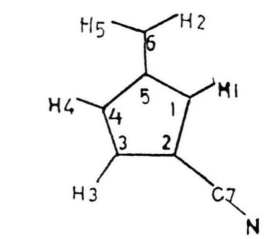
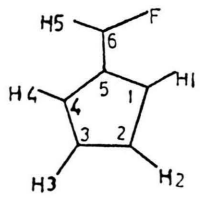
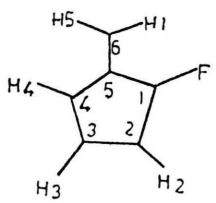
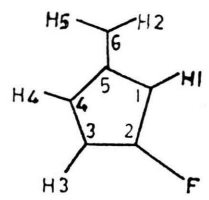
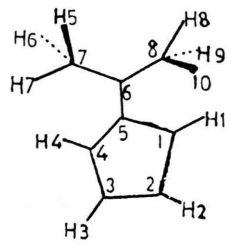
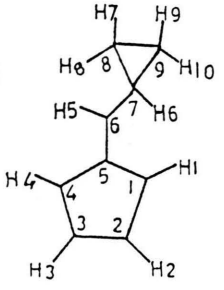
11		C1C2, 1.353; C2C3, 1.483; C3C4, 1.356; C4C5, 1.512; C5C1, 1.514; C5C6, 1.360; C3H3, 1.096; C4H4, 1.098; C6H5, 1.115; C6N, 1.423; NO1, 1.226. C1C5C4, 102.8; C5C4C3, 109.2; C4C3C2, 109.4; C3C2C1, 108.5; C2C1C5, 109.9; C5C1H1, 124.2; C5C4H4, 123.7; C1C2H2, 127.5; C4C3H3, 128.2; C6C5C1, 127.4; C5C6H5, 119.5; H5C6N, 114.3; C6NO1, 115.3; O1NO2, 129.7.
12		C1C2, 1.385; C2C3, 1.465; C3C4, 1.361; C4C5, 1.500; C5C1, 1.529; C5C6, 1.340; C3H3, 1.097; C4H4, 1.101; C6H5, 1.100; C1N, 1.411; NO1, 1.230. C1C5C4, 103.1; C5C4C3, 110.6; C4C3C2, 108.5; C3C2C1, 110.0; C2C1C5, 107.6; C5C1N, 125.2; C5C4H4, 122.9; C1C2H2, 128.0; C4C3H3, 127.9; C6C5C1, 129.1; C5C6H5, 124.3; H5C6H6, 108.9; C1NO1, 115.4; O1NO2, 129.6
13		C1C2, 1.380; C2C3, 1.499; C3C4, 1.354; C4C5, 1.502; C5C1, 1.504; C5C6, 1.342; C3H3, 1.091; C4H4, 1.097; C6H5, 1.103; C2N, 1.419; NO1, 1.229. C1C5C4, 101.8; C5C4C3, 110.6; C4C3C2, 109.8; C3C2C1, 105.6; C2C1C5, 112.0; C5C1H1, 122.1; C5C4H4, 122.9; C1C2N, 129.1; C4C3H3, 128.1; C6C5C1, 129.3; C5C6H5, 124.0; H5C6H6, 111.5; C2NO1, 112.6; O1NO2, 131.7.
14		C1C2, 1.357; C2C3, 1.478; C3C4, 1.358; C4C5, 1.503; C5C1, 1.512; C5C6, 1.355; C3H3, 1.095; C4H4, 1.097; C6H5, 1.113; C6C7, 1.441; C7N, 1.161. C1C5C4, 102.3; C5C4C3, 109.8; C4C3C2, 109.4; C3C2C1, 107.9; C2C1C5, 110.5; C5C1H1, 122.5; C5C4H4, 122.9; C1C2H2, 128.3; C4C3H3, 127.3; C6C5C1, 127.7; C5C6H5, 120.8; H5C6C7, 112.5; C6C7N, 177.6.
15		C1C2, 1.375; C2C3, 1.472; C3C4, 1.357; C4C5, 1.503; C6C1, 1.530; C5C6, 1.338; C3H3, 1.095; C4H4, 1.099; C6H5, 1.100; C1C7, 1.442; C7N, 1.162. C1C5C4, 104.0; C5C4C3, 109.6; C4C3C2, 108.8; C3C2C1, 110.3; C2C1C5, 107.0; C5C1C7, 124.8; C5C4H4, 123.1; C1C2H2, 126.7; C4C3H3, 127.6; C6C5C1, 128.0; C5C6H5, 125.1; H5C6H6, 109.7; C1C7N, 179.9.
16		C1C2, 1.374; C2C3, 1.494; C3C4, 1.355; C4C5, 1.504; C5C1, 1.504; C5C6, 1.339; C3H3, 1.097; C4H4, 1.097; C6H5, 1.102; C2C7, 1.444; C7N, 1.160. C1C5C4, 101.8; C5C4C3, 110.2; C4C3C2, 110.0; C3C2C1, 105.8; C2C1C5, 112.0; C5C1H1, 123.6; C5C4H4, 123.1; C1C2C7, 128.8; C4C3H3, 127.8; C6C5C1, 129.5; C5C6H5, 124.2; H5C6H6, 111.3; C2C7N, 178.7

Table 2 (continued)

17		C1C2, 1.360; C2C3, 1.474; C3C4, 1.360; C4C5, 1.504; C5C1, 1.499; C5C6, 1.332; C3H3, 1.096; C4H4, 1.099; C6H5, 1.099; C6F, 1.360. C1C5C4, 103.6; C5C4C3, 108.9; C4C3C2, 109.3; C3C2C1, 123.5; C2C1C5, 109.4; C5C1H1, 122.3; C5C4H4, 123.1; C1C2H2, 127.7; C4C3H3, 126.9; C6C5C1, 130.2; C5C6H5, 130.2; H5C6F, 106.0.
18		C1C2, 1.353; C2C3, 1.479; C3C4, 1.360; C4C5, 1.504; C5C1, 1.497; C5C6, 1.336; C3H3, 1.094; C4H4, 1.098; C6H5, 1.101; C1F, 1.365. C1C5C4, 99.7; C5C4C3, 109.7; C4C3C2, 111.5; C3C2C1, 103.4; C2C1C5, 115.5; C5C1F, 118.7; C5C4H4, 122.4; C1C2H2, 128.9; C4C3H3, 125.6; C6C5C1, 130.4; C5C6H5, 124.1; H5C6H6, 110.2.
19		C1C2, 1.353; C3C3, 1.467; C3C4, 1.358; C4C5, 1.506; C5C1, 1.507; C5C6, 1.338; C3H3, 1.086; C4H4, 1.100; C6H5, 1.101; C2F, 1.370. C1C5C4, 103.1; C5C4C3, 110.4; C4C3C2, 107.0; C3C2C1, 111.4; C2C1C5, 107.8; C5C1H1, 123.8; C5C4H4, 123.2; C1C2F, 126.9; C4C3H3, 128.1; C6H5C1, 128.4; C5C6H5, 124.6; H5C6H6, 110.5.
20		C1C2, 1.355; C2C3, 1.476; C3C4, 1.355; C4C5, 1.500; C5C1, 1.504; C5C6, 1.367; C6C7, 1.488; C3H3, 1.087; C4H4, 1.100; C7H5, 1.109; C7H6, 1.111. C1C5C4, 103.9; C5C4C3, 108.3; C4C3C2, 110.1; C3C2C1, 108.2; C2C1C5, 109.4; C5C1H1, 122.3; C5C4H4, 123.5; C1C2H2, 127.5; C4C3H3, 126.6; C6C5C1, 127.0; C5C6C7, 121.8; C7C6C8, 117.3; C6C7H5, 113.1; H5C7H6, 106.7.
21		C1C2, 1.355; C2C3, 1.475; C3C4, 1.356; C4C5, 1.493; C5C1, 1.504; C5C6, 1.346; C6C7, 1.469; C7C8, 1.510; C8C9, 1.483; C3H3, 1.086; C4H4, 1.099; C6H5, 1.113; C8H7, 1.101; C8H8, 1.106. C1C5C4, 104.4; C5C4C3, 107.8; C4C3C2, 110.4; C3C2C1, 108.0; C2C1C5, 109.0; C5C1H1, 122.9; C5C4H4, 123.4; C1C2H2, 127.6; C4C3H3, 126.6; C6C5C1, 126.5; C5C6H5, 119.7; H5C6C7, 111.9; C6C7C8, 120.2; C6C7H6, 113.0; H7C8H8, 112.2; C7C8C9, 60.5; C8C7C9, 58.8.

Structural Details

For the OH substituent we have assumed that the OH is in the plane of the molecule according to our previous calculation on fulvene radical cation [15].

Introduction of a substituent into the fulvene molecule increases the adjacent bond length (Table 2). This effect is more pronounced for NH_2 and NO_2, which is in agreement with the high dipole moment calculated (Table 1). All substituents are found to produce a small decrease in the bond angle to which the substituent is attached, with the exception of the F substituent.

This resembles our recent calculations on fulvene radical cations [15].

Table 3. Calculated electron densities of monosubstituted (OH, NH_2, CH_3, dimethyl and cyclopropyl) fulvenes. See Table 2 for numbering.

Atom	1	2	3	4	5	6	7	8	9	10	20	21
C1	4.038	3.989	3.631	4.222	4.010	3.824	4.206	4.035	4.023	4.040	4.036	4.032
C2	3.996	4.028	4.237	3.617	4.023	4.196	3.804	4.000	4.006	3.987	4.000	4.005
C3	3.995	4.010	3.923	4.109	4.023	3.921	4.045	3.995	3.998	4.006	3.992	3.996
C4	4.037	4.010	4.098	3.989	4.006	4.106	4.008	4.035	4.033	4.033	4.042	4.037
C5	3.956	4.131	4.006	3.929	4.130	3.974	3.919	3.977	3.967	3.958	3.989	3.995
C6	4.004	3.581	3.969	4.021	3.780	4.006	4.036	3.967	3.996	3.997	3.969	3.950
C7								3.916	3.902	3.908	3.925	3.972
C8												3.981
H1	0.994	1.003	0.750	0.959	1.023	0.926	0.988	1.000	1.029	1.002	0.999	1.000
H2	1.000	0.999	0.967	0.752	1.004	0.980	0.922	0.997	1.001	1.029	0.999	0.999
H3	1.000	1.002	1.008	0.987	1.006	1.010	1.001	1.001	0.997	1.000	1.004	1.006
H4	0.993	1.011	0.987	0.998	1.014	0.990	0.999	0.996	0.995	0.996	0.994	0.994
H5	0.996	1.078	0.998	0.996	1.023	0.991	0.996	1.017	0.995	0.995	1.026	1.023
H6	0.990	0.744	0.989	0.990	0.915	1.005	0.992	1.022	0.996	0.994	1.019	1.015
H7					0.908	0.922	0.925	1.021	1.031	1.028	1.019	1.006
H8								1.021	1.031	1.028		1.001
O		6.414	6.438	6.431								
N					5.135	4.196	5.159					

Table 4. Calculated electron densities of monosubstituted (NO_2, CN, F) fulvenes. See Table 2 for numbering.

Atom	11	12	13	14	15	16	17	18	19
C1	4.062	4.263	3.879	4.036	4.020	4.015	3.985	3.556	4.948
C2	3.983	3.842	4.219	3.997	3.980	3.985	4.018	4.190	4.462
C3	3.959	4.055	3.958	3.988	4.008	4.001	3.997	3.949	4.097
C4	4.073	3.965	4.040	4.043	4.023	4.003	4.013	4.068	3.994
C5	3.810	3.952	3.993	3.950	3.968	3.965	4.129	4.043	3.938
C6	4.252	3.962	3.951	3.973	3.988	3.987	3.511	3.945	4.003
C7				3.904	3.896	3.899			
H1	0.940	0.949	0.985	0.993	0.991	0.999	0.988	0.980	0.948
H2	0.981	0.981	0.987	0.992	0.997	0.992	0.992	0.948	0.986
H3	0.988	0.973	0.968	0.998	0.992	0.994	0.996	0.995	0.959
H4	0.974	0.990	0.981	0.993	0.992	0.993	1.001	0.987	0.992
H5	0.930	0.993	0.982	1.001	0.993	0.991	1.039	0.995	0.991
O1	6.578	6.607	6.594						
O2	6.598	6.598	6.585						
N	3.873	3.871	3.876	5.131	5.150	5.144			
F							7.330	7.344	7.334

Table 5. Evaluation of substituted effects using MINDO-forces calculations (energies are in kcal/mole).

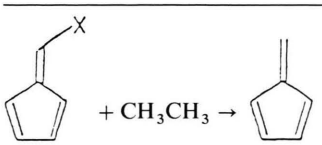
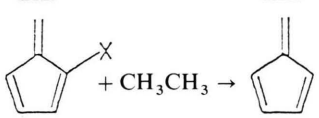
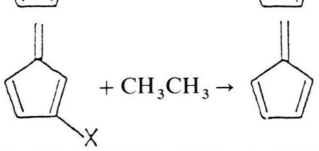
	OH	NH_2	CH_3	NO_2	CN	F	dimeth.	cyclo.
	17.330	21.672	7.663	15.980	9.616	12.892	13.086	9.700
	19.529	21.608	4.925	23.159	8.183	12.301		
	18.657	21.065	6.263	23.913	9.055	12.089		

Table 6. Calculated orbital energies (HOMO, LUMO in eV) of monosubstituted fulvenes. See Table 2 for numbering.

Molecule	HOMO	LUMO	Molecule	HOMO	LUMO
1	−8.6860	0.3660	11	−9.4648	−1.0836
2	−8.3145	0.6141	12	−9.5603	−0.8774
3	−8.0287	0.4603	13	−9.4801	−0.8566
4	−8.2452	0.3729	14	−8.8165	−0.1307
5	−7.8298	0.6980	15	−8.6021	−0.0153
6	−7.4165	0.5658	16	−8.7110	−0.0146
7	−7.6128	0.5157	17	−8.7648	0.2294
8	−8.6358	0.2069	18	−8.5483	0.0892
9	−8.4738	0.2573	19	−8.7958	0.0221
10	−8.5704	0.2534	20	−8.6227	0.1020
			21	−8.5155	0.3027

Electron Densities

It can be seen from Tables 3 and 4 that the OH, NH_2, F and cyclopropyl substituents decrease the electron densities on the carbon atom to which the substituent is attached and increase the electron density on the adjacent carbon atoms, i.e. they act as electron releasing. CH_3, CN and dimethyl substituents are very weakly electron releasing. The NO_2 substituent shows an opposite effect to that found for OH, NH_2, F, CH_3 and CN, i.e. acts as electron withdrawing. These results are in agreement with our recent calculations on fulvene radical cations [15].

Stabilization by Substituents

The stabilizing effect of a substituent is often assessed by using isodesmic reactions (conserved bond type) [31]. A positive heat of formation (Table 5) indicates stabilization of the reactant by the substituent. The results show that all the substituents are stabilizing. It was found that NO_2 stabilizes the fulvene molecule more than other substituents because of the high dipole moment (Table 1) which suggests an increase in the degree of zwitterionic character. The CH_3 substituent shows slight stabilization, which may be due to the low dipole moment.

Orbital Energies

According to Koopmans' theorem (the negative HOMO is equal to the ionization potential), it was found that the energy of HOMO for fulvene (−8.686 eV, Table 6) is in good agreement with the ionization potential (8.55 eV) obtained from photon electron spectroscopy [32]. Also the HOMO of dimethyl fulvene (−8.622 eV, Table 6) is in good agreement with the experimental value (8.75 eV) [33].

The electron releasing NH_2, OH, CH_3, dimethyl and cyclopropyl substituents are found to increase the energy of HOMO (Table 6) to a great extend. This effect is more pronounced in the case of NH_2, which also increases the energies of the LUMO. The high energy of LUMO suggests a high stability.

Thus amino group substitution produces aromatic like behaviour in fulvenes [16].

The inertness of amino fulvenes toward cycloaddition may be attributed to the high energy of the LUMO [4].

In case of electron withdrawing substituents, such as CN and F, the HOMO and LUMO decrease to a certain degree; the low energy of LUMO suggests a high reactivity. This is in agreement with the 6-C1 fulvene which has a high reactivity toward nucleophilic attack [34].

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