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PM3 Study of the Electronic Structure of Coumarins

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The coumarins are a family of molecules that have been studied extensively because of their application as laser dyes and their substantial state-dependent variation in static dipole moment. In view of this, Parametric Method 3 (PM3) semi-empirical molecular orbital calculations are performed on the substituted coumarins for their geometry and electronic properties. It can be seen that our calculated results are in good agreement with available experimental and theoretical estimates.

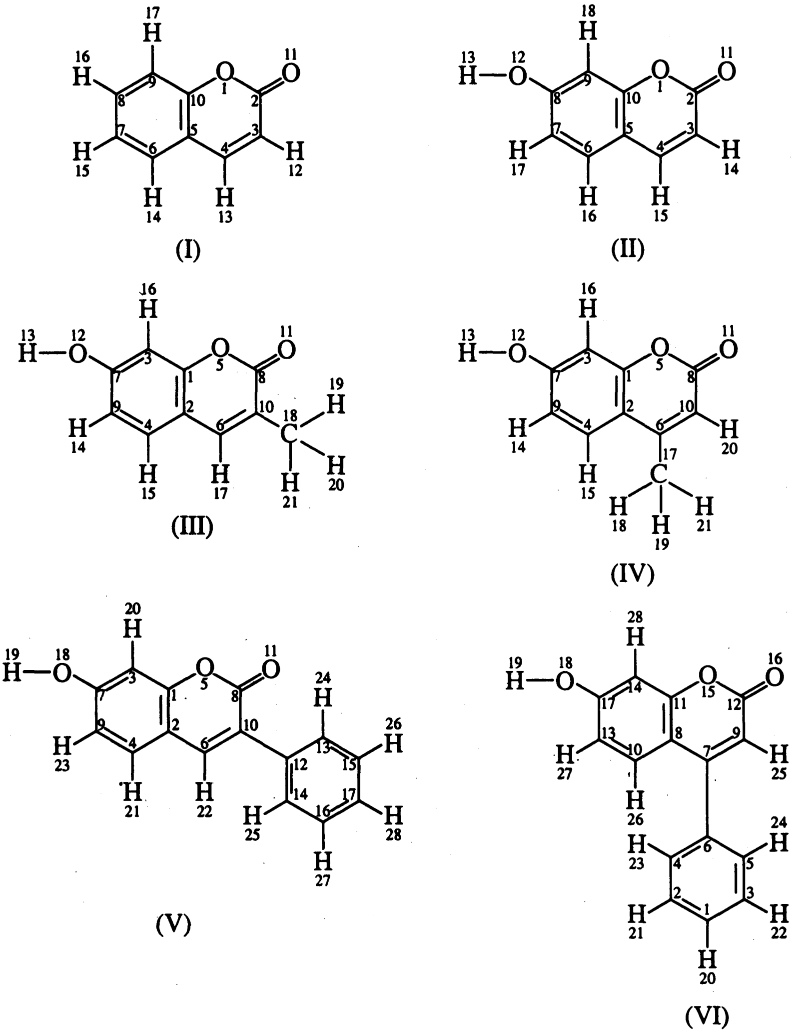
INTRODUCTION

Coumarins (benzo derivatives of α-pyrone) constitute an important class of naturally occurring oxygen heterocycles. Experimental study of various physical and chemical properties of these systems has drawn the attention of many workers. The electronic spectra of α-pyrone and their benzo derivatives (coumarins) have been investigated experimentally by a series of workers[1–16]. Photoreactivity of excited coumarins has drawn considerable attention. Musajo and his co-workers[17–19] have studied the photocycloaddition of coumarin to pyrimidine bases of DNA. Similar studies have also been made by Krahch *et al.*[20] and Kramer and Pathak[21]. Hammond *et al.*[22] have studied the photodimerization of coumarin, while Hanifin and Cohen[23] have studied the addition of 1,1-diethoxyethylene to the 3–4 bond of coumarin. Song *et al.*[24–26] have also studied the photoreactivity of coumarin with biological systems. Coumarin compounds are efficient fluorescers and several of them have been tested for their laser properties[27–31]. In view of all these facts, many attempts have been made earlier to study the electronic structures of coumarins. However, most of the earlier theoretical studies have been carried out either using simple Huckel Molecular Orbital (HMO) theory[32–36] or Pariser-Parr-Pople (PPP) method-3.[37–41]

Here, we have used the recently developed Parametric Method Third (PM3)[42] for studying the electronic structures of coumarins.

RESULTS AND DISCUSSION

Calculated equilibrium geometries of coumarin and substituted-hydroxy coumarins are listed in Tables 1–6. The predicted bond lengths and bond angles are in good agreement with experiment except O_{11}—C_2—O_1 and O_1—C_2—C_3 angles in the pyrone moiety of coumarins. The calculated O_{11}—C_2—O_1 angles in these systems are consistently smaller (108.4–108.8) than the experimental value (116.3–118.0). The predicted O_1—C_2—C_3 angles (120.0–121.4) are found to be larger than the experimental value (117.0–117.7).



(I) (II) (III) (IV) (V) (VI)

Fig. 1

TABLE-1

CALCULATED AND EXPERIMENTAL GEOMETRY OF COUMARIN[a]

Parameters[a]	PM3	Experimental[b]
Bond lengths (Å)		
O_1—C_2	1.380	1.367
C_2—C_3	1.468	1.448
C_3—C_4	1.344	1.344
C_4—C_5	1.447	1.431
C_5—C_6	1.402	1.390

Parameters[a]	PM3	Experimental[b]
C_6—C_7	1.384	1.369
C_7—C_8	1.399	1.368
C_8—C_9	1.385	1.391
C_9—C_{10}	1.404	1.383
C_2—C_{11}	1.212	1.204
C—H	1.095–1.096	0.850–0.890
Bond Angles (deg.)		
O_1—C_2—C_3	121.4	117.2
C_2—C_3—C_4	119.5	121.9
C_3—C_4—C_5	119.6	120.0
C_4—C_5—C_6	122.2	124.3
C_5—C_6—C_7	120.1	120.9
C_6—C_7—C_8	120.5	119.8
C_7—C_8—C_9	120.7	121.8
C_8—C_9—C_{10}	118.8	117.4
O_{11}—C_2—O_1	108.6	117.2
C—C—H	117.4–122.1	117.9–125.9

a. See Fig. 1 (I) b. Taken from Reference 43.

TABLE-2

CALCULATED GEOMETRY OF 7-HYDROXYCOUMARIN[a]

Atom No. (I)	Symbol	Bond length (Å) NA : I	Bond angle (deg.) NB : NA : I	NA	NB
1.	O				
2.	C	1.383		1	
3.	C	1.467	121.2	2	1
4.	C	1.345	119.5	3	2
5.	C	1.445	119.7	4	3
6.	C	1.404	122.1	5	4
7.	C	1.381	120.6	6	5
8.	C	1.411	119.4	7	6
9.	C	1.396	121.5	8	7
10.	C	1.401	117.9	9	8
11.	O	1.212	130.4	2	3
12.	O	1.363	115.7	8	7
13.	H	0.950	108.4	12	8
14.	H	1.095	117.3	3	2
15.	H	1.096	121.9	4	3
16.	H	1.096	119.2	6	5
17.	H	1.096	120.6	7	6
18.	H	1.097	121.9	9	8

a. See Fig. 1 (II)

TABLE-3
CALCULATED GEOMETRY OF 3-METHYL-7-OH COUMARIN[a]

Atom No. (I)	Symbol	Bond length (Å) NA : I	Bond angle (deg.) NB : NA : I	NA	NB
1.	C				
2.	C	1.407		1	
3.	C (–0.182)	1.400	121.7	1	2
4.	C (0.004)	1.402	118.9	2	1
5.	O	1.374	122.1	1	2
6.	C (0.0035)	1.443	119.2	2	1
7.	C	1.396	117.7	3	1
8.	C	1.381	118.4	5	1
9.	C	1.381	120.5	4	2
10.	C	1.349	119.0	6	2
11.	O (–0.330)	1.211	107.8	8	5
12.	O (–0.219)	1.363	115.9	7	3
13.	H	0.949	108.2	12	7
14.	H	1.096	119.9	9	4
15.	H	1.096	119.3	4	2
16.	H	1.097	121.0	3	1
17.	H	1.096	118.5	6	2
18.	C	1.482	122.3	10	6
19.	H	1.098	112.3	18	10
20.	H	1.098	110.8	18	10
21.	H	1.098	110.8	18	10

a. See Fig. 1 (III)

TABLE-4
CALCULATED GEOMETRY OF 4-METHYL-7-OH COUMARIN[a]

Atom No. (I)	Symbol	Bond length (Å) NA : I	Bond angle (deg.) NA : NB : I	NA	NB
1.	C				
2.	C	1.409		1	
3.	C (–0.184)[b]	1.401	122.0	1	2
4.	C (–0.001)	1.402	118.1	2	1
5.	O	1.374	122.8	1	2
6.	C	1.454	118.8	2	1
7.	C	1.395	117.9	3	1
8.	C	1.380	118.1	5	1
9.	C (–0.227)	1.381	121.1	4	2
10.	C (–0.236)	1.351	118.8	6	2

Atom No. (I)	Symbol	Bond length (Å) NA : I	Bond angle (deg.) NA : NB : I	NA	NB
11.	O (–0.333)	1.212	108.5	8	5
12.	O (–0.218)	1.363	116.2	7	3
13.	H	0.949	108.1	12	7
14.	H	1.096	119.8	9	4
15.	H	1.096	119.5	4	2
16.	H	1.097	120.8	3	1
17.	C	1.484	120.2	6	2
18.	H	1.098	112.1	17	6
19.	H	1.098	110.8	17	6
20.	H	1.096	122.7	10	6
21.	H	1.098	110.9	17	6

a. See Fig. 1 (IV) b. Net atomic charges

TABLE-5

CALCULATED GEOMETRY OF 3-PHENYL-7-HYDROXY COUMARIN[a]

Atom No. (I)	Symbol	Bond length (Å) NA : I	Bond angle (deg.) NB : NA : I	NA	NB
1.	C				
2.	C	1.408		1	
3.	C	1.400	121.8	1	2
4.	C	1.402	118.8	2	1
5.	O	1.373	122.1	1	2
6.	C	1.440	119.1	2	1
7.	C	1.396	117.7	3	1
8.	C	1.379	118.6	5	1
9.	C	1.381	120.5	4	2
10.	C	1.356	120.4	6	2
11.	O	1.215	107.4	8	5
12.	C	1.464	122.1	10	6
13.	C	1.399	120.7	12	10
14.	C	1.388	120.1	12	10
15.	C	1.388	120.2	13	12
16.	C	1.388	120.3	14	12
17.	C	1.391	120.2	15	13
18.	O	1.363	116.0	7	3
19.	H	0.949	108.2	18	7
20.	H	1.097	121.0	3	1
21.	H	1.100	120.0	2	1

Atom No. (I)	Symbol	Bond length (Å) NA : I	Bond angle (deg.) NB : NA : I	NA	NB
22.	H	1.100	120.0	3	1
23.	H	1.100	120.1	4	2
24.	H	1.100	120.1	5	3
25.	H	1.100	122.8	9	7
26.	H	1.102	119.0	10	8
27.	H	1.099	120.4	13	10
28.	H	1.098	120.7	14	11

a. See Fig. 1 (V)

TABLE-6
CALCULATED GEOMETRY OF 4-PHENYL-7-HYDROXY COUMARIN

Atom No. (I)	Symbol	Bond distance (Å) NA : I	Bond angle (deg.) B : NA : I	NA	NB
1.	C				
2.	C	1.395		1	
3.	C	1.395	119.9	1	2
4.	C	1.394	120.1	2	1
5.	C	1.394	120.2	3	1
6.	C	1.401	120.1	4	2
7.	C	1.465	119.7	6	4
8.	C	1.448	120.6	7	6
9.	C	1.357	120.4	7	6
10.	C	1.406	123.4	8	7
11.	C	1.413	118.4	8	7
12.	C	1.452	121.2	9	7
13.	C	1.384	121.1	10	8
14.	C	1.404	121.9	11	8
15.	O	1.377	122.8	11	8
16.	O	1.229	129.3	12	9
17.	C	1.410	119.5	13	10
18.	O	1.372	122.3	17	13
19.	H	0.969	108.1	18	17
20.	H	1.100	120.1	1	2
21.	H	1.096	119.2	4	2
22.	H	1.102	119.2	6	2
23.	H	1.096	119.9	9	4
24.	H	1.090	118.2	13	12
25.	H	1.100	119.3	14	12
26.	H	1.095	119.6	15	13
27.	H	1.095	119.8	16	14
28.	H	1.095	120.1	17	15

a. See Fig. 1 (VI)

Dipole moments of short-lived species are of considerable interest because, just as for stable molecules, they provide important information on the electronic and geometrical structures of these transients. A prior knowledge of the dipole moments of ground and electronically excited species is often useful in the design of non-linear optical materials and in the elucidation of the nature of the excited states and any photochemical transformation. The calculated dipole moments for the sub-α-pyrone derivatives are shown in Table-7, and the results are in reasonable agreement with available experimental values. The effect of substituents in the hydroxy-coumarin molecule has been observed experimentally. Table-7 exhibits the effect of methyl and phenyl group on the dipole moments of 7-hydroxy coumarin. The heats of formation, ionization potential and net atomic charges on the carbonyl oxygen are also reported here. It can be seen that there is increase in the dipole moment values on substitution. Further there is change in the net atomic charges on the carbonyl oxygen. This increase in μ-value, in ground state of these species in agreement with the experimental observation. The results have been compared with other theoretical estimates. In 7-OH coumarin, the 4th position is more reactive than 3rd position. It can be seen from Table-7 that methyl group at 4th position in 7-OH coumarin has larger dipole moment in comparison to the CH_3 group at third position.

TABLE-7

CALCULATED HEATS OF FORMATION (kcal), DIPOLE MOMENT (debye), IONIZATION POTENTIAL (ev) AND NET ATOMIC CHARGES ON CARBONYL OXYGEN OF SOME SUBSTITUTED 7-HYDROXY COUMARIN[a]

System	Δ_H	μ	I.P. (ev)	Net charge C=O
Coumarin		4.42 (4.40)	9.49	–0.330
3-CH_3-	–92.1	5.40	9.09	–0.330
4-CH_3-	–92.1 (–90.6)	5.98 (5.32)	9.21	–0.333
3,4-$(CH_3)_2$-	–99.5	5.73	9.05	–0.335
3-Phenyl-	–56.4	5.20	8.80	–0.337
4-Phenyl-	–46.9	6.59	9.18	–0.331

a. See Fig. 1.

b. The values in parentheses are taken from references 44 and 45 respectively.

Conclusion

It appears from the present study that simple PM3 method can be used quite successfully to discuss the equilibrium geometries, energetics and electronic structures of a number of related α-pyrone derivatives.

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