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Density functional theory study of 9,10-anthraquinone and its structural isomers

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Abstract

Ab initio molecular orbital calculations at B3LYP/6-31 + G^* and B3LYP/6-311 + G^{**} levels of theory are reported for 9,10-anthraquinone (9,10-AQ) and its structural isomers (1,4-AQ, 1,5-AQ, 1,7-AQ, 1,10-AQ, 2,3-AQ, 2,6-AQ, and 2,9-AQ). Relative energies, dipole moments, HOMO−LUMO energies, λ_{max} values, and charge densities for all structures are reported.

Keywords: *Ab initio* calculation; Anthraquinones; Molecular modeling; Structural isomers

1. Introduction

9,10-Anthraquinone (9,10-AQ) is the parent compound for a large palette of anthraquinone dyes and so it is the most important starting material in their production. Furthermore, anthraquinones are gaining importance as photoactive chemosensors [1]. A number of 1,4-AQ and 9,10-AQ derivatives have been studied as potential anticancer agents [2–4]. 1,10-AQs (*ana*-anthraquinones) are a novel class of quinonoides that have been the subject of several studies [5]. There are only a few examples of naturally occurring 1,2-AQs such as hallachrome and sinapiquinone [6,7].

Even though some of the structural isomers of 9,10-AQ are not presently available for more studies, it is possible to carry out *ab initio* calculations from which many properties and structural features can be obtained with an accuracy that is comparable with the experiment. Since the theoretical results are free from intermolecular interactions, they are a valuable tool for the systematic study of structural effects in simple organic molecules. This study was undertaken to investigate the structural optimization of 9,10-AQ and its neutral structural isomers. The results from B3LYP/6-311 + G^{**}//B3LYP/6-311 + G^{**} calculations are used in the energy discussions later.

2. Calculations

The *ab initio* molecular orbital calculations were carried out using the GAUSSIAN 98 program [8]. Geometries for all the structures were fully optimized by means of analytical energy gradients by Berny optimizer with no geometrical constraints [9]. Initial geometry optimizations were carried out at the B3LYP/6-31G^* and B3LYP/6-311 + G^{**} levels, and zero-point energies, obtained at this level, were scaled by a factor of 0.9135. In light of the fact that correction for electron correlation is often important in conformational studies, we have made use of several methods for calculating this correction. One approach involved the density functional theory at B3LYP/6-311 + G^{**} level. This makes use of a three-parameter functional that is a hybrid of exact (Hartree−Fock) exchange terms, similar to those first suggested by Becke in

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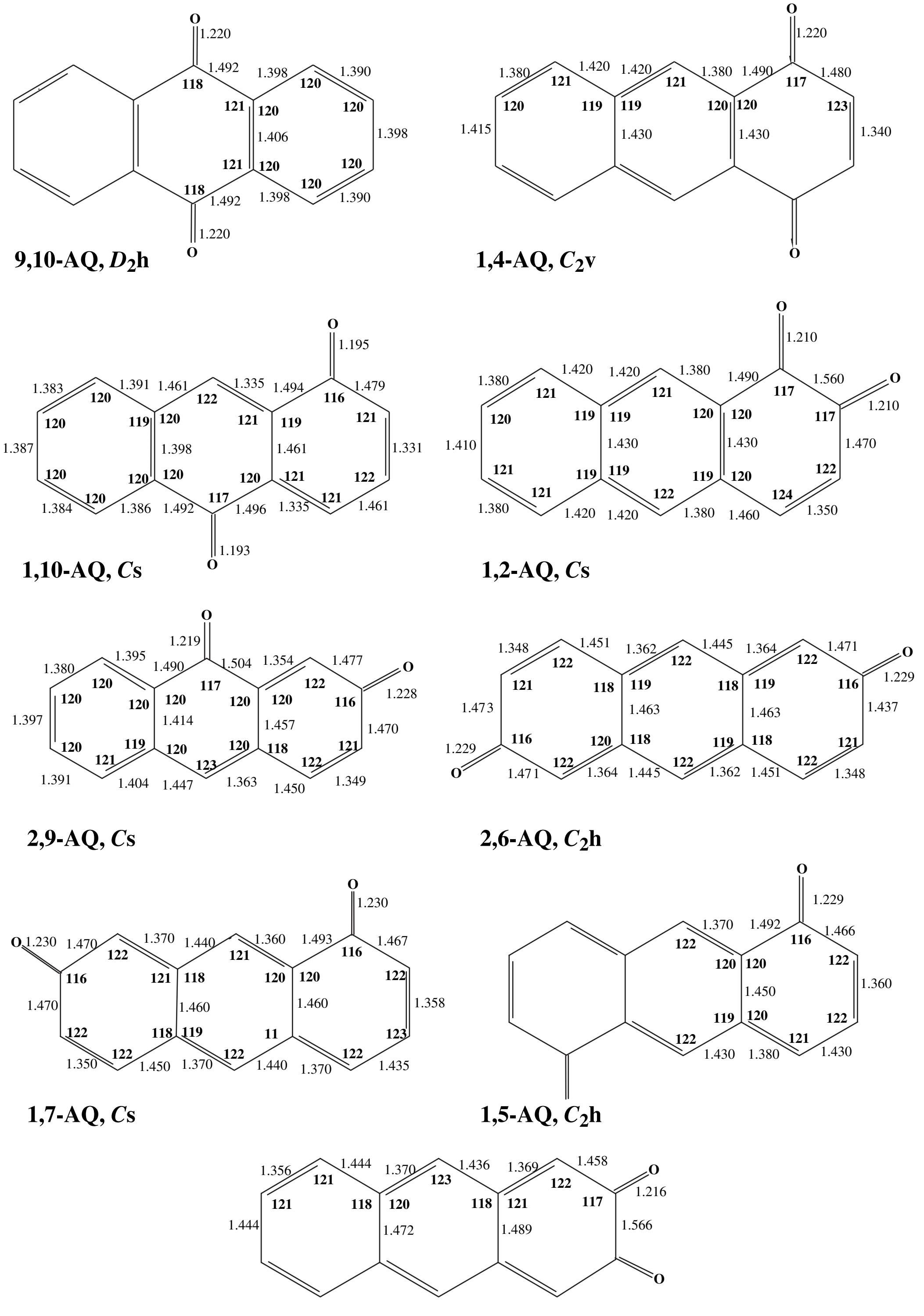

9,10-AQ, D_2h

1,4-AQ, C_2v

1,10-AQ, Cs

1,2-AQ, Cs

2,9-AQ, Cs

2,6-AQ, C_2h

1,7-AQ, Cs

1,5-AQ, C_2h

2,3-AQ, C_2v

Fig. 1. B3LYP/6-311 + G^{**}//B3LYP/6-311 + G^{**} calculated bond lengths (in Å) and bond angles (in °) for 9,10-AQ and its structural isomers.

Koch and Holthausen [10]. Geometry optimizations were also carried out using B3LYP/6-31G^* and B3LYP/6-311 + G^{**}.

HOMO–LUMO energies are obtained for fully optimized geometries, therefore, $\lambda_{\max}$ values are obtained by the equation: $\lambda = hc/\Delta E = 6.63 \times 10^{-34}$ (J s) $\times 3\times 10^8$ (m/s)/$\Delta E \times 4.36 \times 10^{-18}$ (J) then, λ (nm) = 45.62/ΔE.

3. Results and discussion

The results of *ab initio* calculations for 9,10-AQ and its structural isomers are shown in Table 1 and Figs. 1 and 2. According to these calculations, 9,10-AQ with D_{2h} symmetry is the most stable isomer. The C_{2v} symmetric 1,4-AQ is

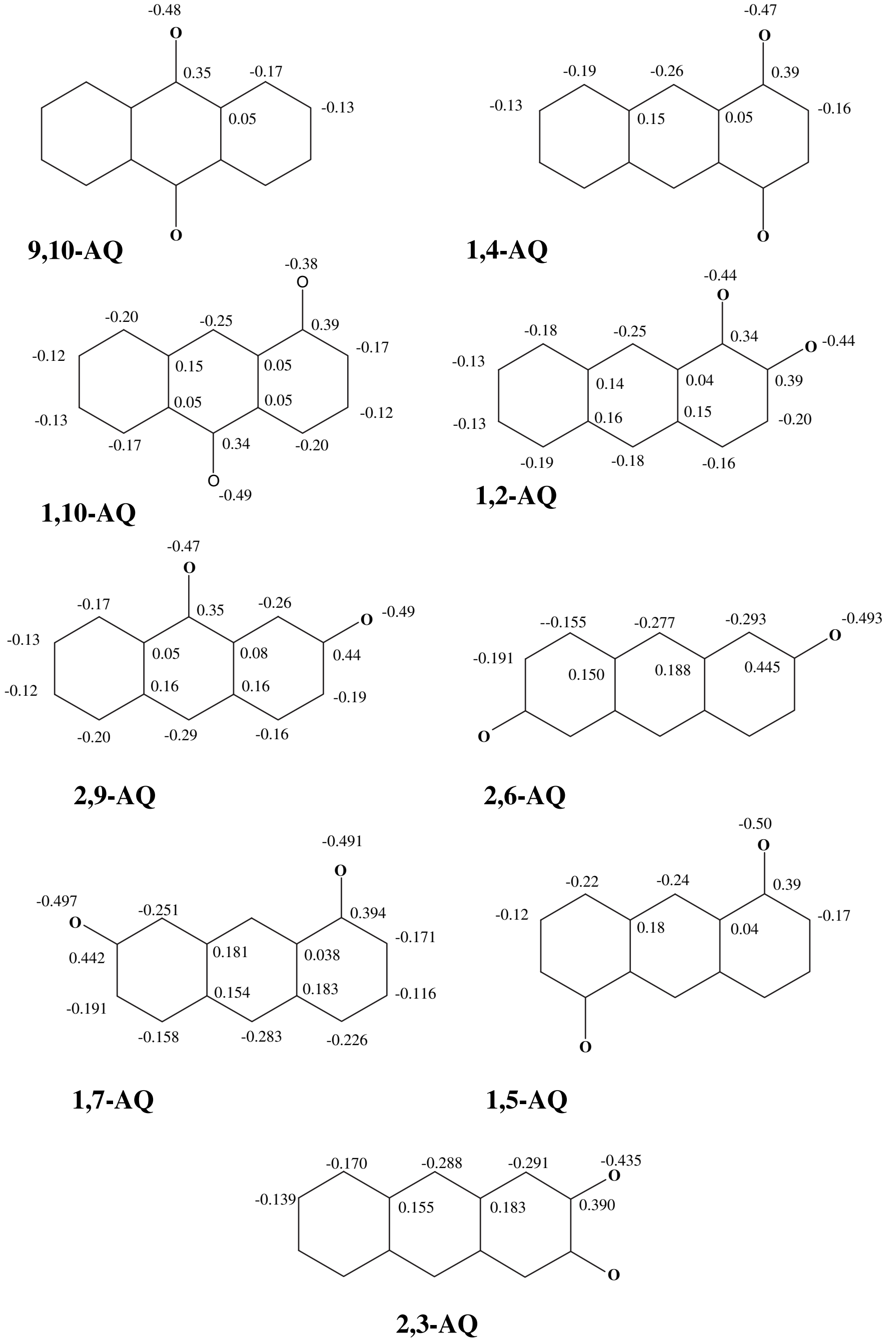

Fig. 2. B3LYP/6-311 + G^{**}//B3LYP/6-311 + G^{**} calculated net charges on atoms for 9,10-AQ and its structural isomers.

9.9 kcal mol^{-1} less stable than the 9,10-isomer. The plane symmetrical 1,10-AQ, 1,2-AQ, and 2,9-AQ isomers are 12.5–19.7 kcal mol^{-1} above 9,10-AQ. The remaining isomers, namely, 2,6-AQ, 1,5-AQ, 1,7-AQ, and 2,3-AQ having 31–48 kcal mol^{-1} more energy, are the least stable geometries. Highly symmetrical isomers, such as 9,10-AQ (D_{2h}), 2,6-AQ (C_{2h}), and 1,5-AQ (C_{2h}) have no permanent dipole moments. The dipole moments of 1,10-AQ and 1,4-AQ are about 2.0 and 2.7 debye, respectively, while other isomers are strongly polar with calculated dipole moments of 6.8–8.3 debye.

The HOMO–LUMO energies calculated from B3LYP/6-311 + G^{**} method were employed to obtain the λ_{max} values for 9,10-AQ and its structural isomers (see Table 1). All calculated λ_{max} values are in the UV–vis region of the electromagnetic spectrum. The calculated λ_{max} value for the most stable isomer, 9,10-AQ, is 296 nm, which is in good agreement with the experimentally observed value of 251 nm (in EtOH). 1,2-AQ or 1,4-AQ has a λ_{max} of about 370 nm. The λ_{max} for 1,10-AQ, 2,9-AQ, and 2,6-AQ have intermediate values in the range of 426–456 nm. The high-energy isomers, 1,5-AQ, 1,7-AQ, and 2,3-AQ possess the longest calculated λ_{max} values.

9,10-AQ and its structural isomers are planar. The bond lengths and bond angles for these compounds are shown in

Fig. 1. The carbonyl groups exhibit fairly compressed bond angles of about 116–118°, while the other bond lengths are about 121–123° (for C–CH–C) and 117–120° (for C–C–C). 1,2-AQ and 2,3-AQ possess vicinal dicarbonyl groups. The OC–CO bonds are fairly long (1.560–1.566 Å); in fact longer than the Csp^3–Csp^3 single bonds (l.530 Å). These unusual bond lengths are attributed to the repulsion of the lone pairs on the vicinal oxygen atoms. The single bonds of the carbonyl carbon atoms in 9,10-AQ and its structural isomers are also fairly long (1.437–1.550 Å). The other C–C bonds are almost normal.

The charge densities of all carbon and oxygen atoms in 9,10-AQ and its structural isomers are shown in Fig. 2. According to these calculations, 2,6-AQ and 1,7-AQ possess the most electron-deficient carbonyl groups.

In summary, *ab initio* calculations provide a picture of 9,10-AQ and its isomers from both structural and energetic points of view. The most stable structural isomer of anthraquinone is 9,10-AQ and the least stable structure is 2,3-AQ. The calculated λ_{max} value for isomers 2,3-AQ and 1,5-AQ are 845 and 634 nm, respectively.

Table 1
Calculated total and zero-point vibrational energies (Hartree; zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculations), relative energy including zero-point energy (kcal mol^{-1}), dipole moment (in debye), HOMO–LUMO energies (Hartree), and λ_{max} value (in nm) for 9,10-AQ and its structural isomers

Compound	9,10-AQ D_{2h}	1,4-AQ C_{2v}	1,10-AQ C_s	1,2-AQ C_s	2,9-AQ C_s	2,6-AQ C_{2h}	1,5-AQ C_{2h}	1,7-AQ C_s	2,3-AQ C_{2v}
B3LYP/6-31G*//B3LYP/6-31G*	−688.7791	−688.7611	−688.7462	−688.7503	−688.7449	−688.7195	−688.7227	−688.7202	−688.6974
ZPE	113.4613	112.9935	112.925	112.8135	112.8428	112.3724	112.5452	112.4513	111.8471
E_{rel}[a]	0.0	10.89	20.16	17.48	20.94	34.56	34.57	36.09	49.84
B3LYP/6-311 + G**//B3LYP/6-311 + G**	−688.9538	−688.9373	−688.9216	−688.9268	−688.9215	−688.8985	−688.8994	−688.8979	−688.8744
ZPE	112.6316	112.0902	112.0207	111.9559	111.9500	111.3553	111.5912	111.4783	110.9510
E_{rel}[b]	0.0	9.90	12.46	16.37	19.66	31.28	33.22	34.04	48.33
Dipole moment	0.0	2.71	1.99	7.49	7.44	0.0	0.0	6.80	8.28
E_{HOMO}	−0.271	−0.248	−0.240	−0.245	−0.246	−0.251	−0.226	−0.236	−0.216
E_{LUMO}	−0.117	−0.124	−0.140	−0.125	−0.139	−0.153	−0.154	−0.154	−0.162
$\Delta E_{HOMO-LUMO}$	0.154	0.124	0.100	0.123	0.107	0.098	0.072	0.082	0.054
λ_{max}	296	368	456	371	426	456	634	556	845

[a] Relative energy with respect to 9,10-AQ from B3LYP/6-31G*//B3LYP/6-31G*.

[b] Relative energy with respect to 9,10-AQ from B3LYP/6-311 + G**//B3LYP/6-311 + G**.

References

[1] Kumar S, Kaur P, Kaur S. Tetrahedron Lett 2002;43:1097–9.
[2] Cardia MC, Belgala M, Delogu A, Maccioni E. II Farmaco 2001;56:549–54.
[3] (a) Jin G-Z, You Y-J, Kim Y, Nam N-H, Ahn B-Z. Eur J Med Chem 2001;36:361–6;
(b) Wei B-L, Wu S-H, Chung M-I, Won S-J, Lin C-N. Eur J Med Chem 2000;35:1089–98.
[4] Apostolova E, Krumova S, Tuparev N, Molina MT, Filipova TS, Petkanchin I, et al. Colloids Surf B Biointerfaces 2003;29:1–12.
[5] Gritsan NP, Klimenko LS, Leonenko ZV, Mainagashev IY, Mamatyuk VI, Vetchinov VP. Tetrahedron 1995;51:3061–76.
[6] Cameron DW, Coller DR, McDonald CA. Aust J Chem 1999;52:833–6.
[7] Gill M, Milanovic NM. Aust J Chem 1999;52:1035–9.
[8] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, et al. Gaussian 98, revision A.6. Pittsburg, PA: Gaussian Inc; 1998.
[9] Jensen F. Introduction to computational chemistry. New York: Wiley; 1999.
[10] Koch W, Holthausen MC. A chemist's guide to density functional theory. Weinheim: Wiley-VCH; 2000.