Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 75 (2007) 669–674
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Ab initio SCF-MO study of quinones of azulene

Issa Yavari [a,b,*], Nader Zabarjad-Shiraz [c]

[a] *Department of Chemistry, Tarbiat Modarres University, PO Box 14115-175, Tehran, Iran*
[b] *Chemistry Department, Science and Research Campus, Islamic Azad University, Ponak, Tehran, Iran*
[c] *Department of Chemistry, Islamic Azad University, Central Tehran Branch, Tehran, Iran*

Received 19 June 2006; accepted 22 June 2006
Available online 15 September 2006

Abstract

Ab initio calculations at HF/6-31G** and B3LYP/6-31G** levels of theory for geometry optimization, and MP2/6-31G**//HF/6-31G** and MP2/6-31G**//B3LYP/6-31G** for single point total energy calculations are reported for azulene and 16 quinones of azulene. Among azuloquinones, the 1,5-isomer is calculated to be having the most stable geometry; the 1,7- and 1,6-isomers are 2.78 and 27.36 kJ mol^{-1} less stable, respectively.

Keywords: Ab initio calculations; Molecular modeling; Azuloquinones

1. Introduction

Quinones constitute an important class of naturally occurring compounds that are involved in many biological processes. Quinones have important synthetic and industrial applications such as dyes as well as antibiotics, antifungal, and antitumor medicines. However, almost all of them belong to benzenoid compounds [1,2]. Among the non-benzenoid aromatics, azulene has attracted considerable attraction for many years [3]. Azulene is a non-alternant compound with 10 π-electrons and has either a C_s or C_{2v} symmetry depending on the different carbon bonding. Quinones of azulene are important class of non-benzenoid quinones in which some of them have stable tropone and unstable cyclopentadienone rings. The presence of these two annulenones in many azulene quinones provides a basis for preliminary predictions about properties of these novel compounds [1]. For ease of reference, abbreviated names rather than arbitrary numbers will be used for the azuloquinones. Thus, for example, 1,2-azuloquinone will be referred to simply as 1,2-AQ (Fig. 1). Formally 11 classical azuloquinones, and five *meta*-azuloquinones are possible (see Figs. 1 and 2).

1,2-AQ was synthesized as the first unsubstituted quinone of azulene [4]. Subsequently 1,5- and 1,7-AQs were synthesized as stable compounds [4,5]. Highly reactive 1,4- and 1,6-AQs were generated and trapped as Diels–Alder adducts [5]. 2,5-AQ isomers are highly reactive, and dimerise to stable compounds [6]. Other azuloquinones have not been yet synthesized or isolated as stable compounds [7].

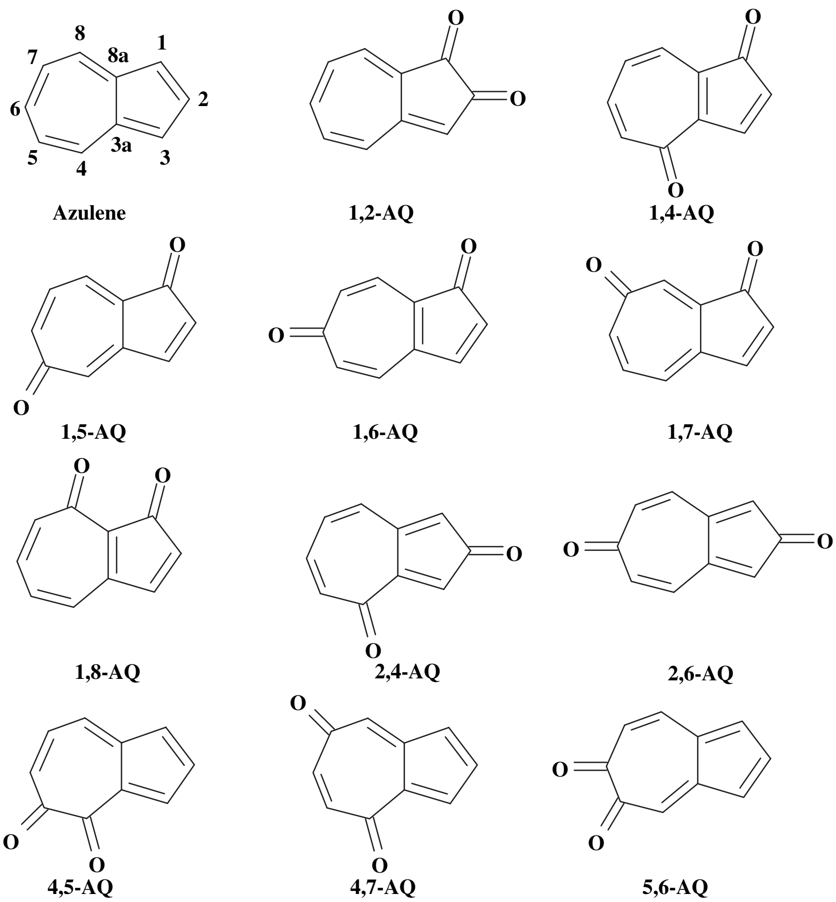
Even though some of the AQs are not presently available for more studies, it is possible to carry out *ab initio* calculations at the Hartree–Fock and DFT levels, from which many properties can be obtained with an accuracy that is competitive with experiment [8–12]. Since the theoretical results are free from intermolecular interactions, they remain a valuable tool for a systematic study of structural effects in simple organic molecules. This study was undertaken to investigate the structural optimizations of azuloquinones shown in Figs. 1 and 2. Although some theoretical studies have been reported for azuloquinones [1], in order to compare experimental and theoretical results, we studied classical and non-classical azuloquinones by *ab initio* methods.

---

[*] Corresponding author. Department of Chemistry, Tarbiat Modarres University, PO Box 14115-175, Tehran, Iran. Tel.: +98 21 88006631; fax: +98 21 88006544.

E-mail address: yavarisa@modares.ac.ir (I. Yavari).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.06.034

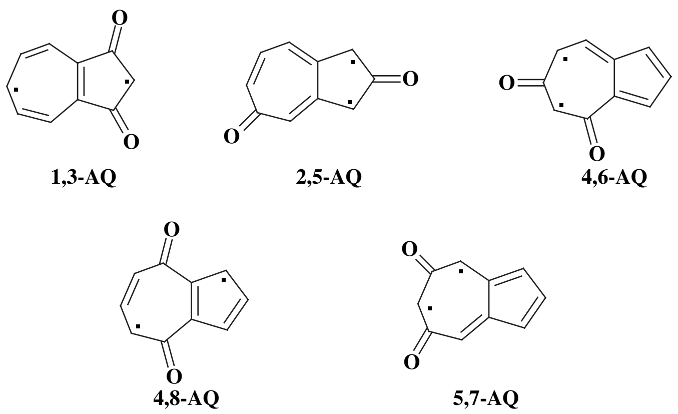


Azulene 1,2-AQ 1,4-AQ 1,5-AQ 1,6-AQ 1,7-AQ 1,8-AQ 2,4-AQ 2,6-AQ 4,5-AQ 4,7-AQ 5,6-AQ

Fig. 1. Azulene and 11 possible Kekule quinones of azulene.

2. Calculations

Semiemprical calculations were carried out using AM1 and MINDO 3 methods with MOPAC 7.0 program package [13,14]. Energy minimum geometries were located by minimizing energy, with respect to all geometrical coordinates, and without imposing any symmetry constrains. The AM1 results were used as input for the *ab initio* calculations, which were carried out using Gaussian 98 [15] at the HF/6-31G** and B3LYP/6-31G** levels of theory for geometry optimization and MP2/6-31G**//HF/6-31G** and MP2/6-31G**//B3LYP/6-31G** for a single point total energy



1,3-AQ 2,5-AQ 4,6-AQ 4,8-AQ 5,7-AQ

Fig. 2. Five possible azulene quinones related to *meta*-benzoquinones (non-Kekule quinones).

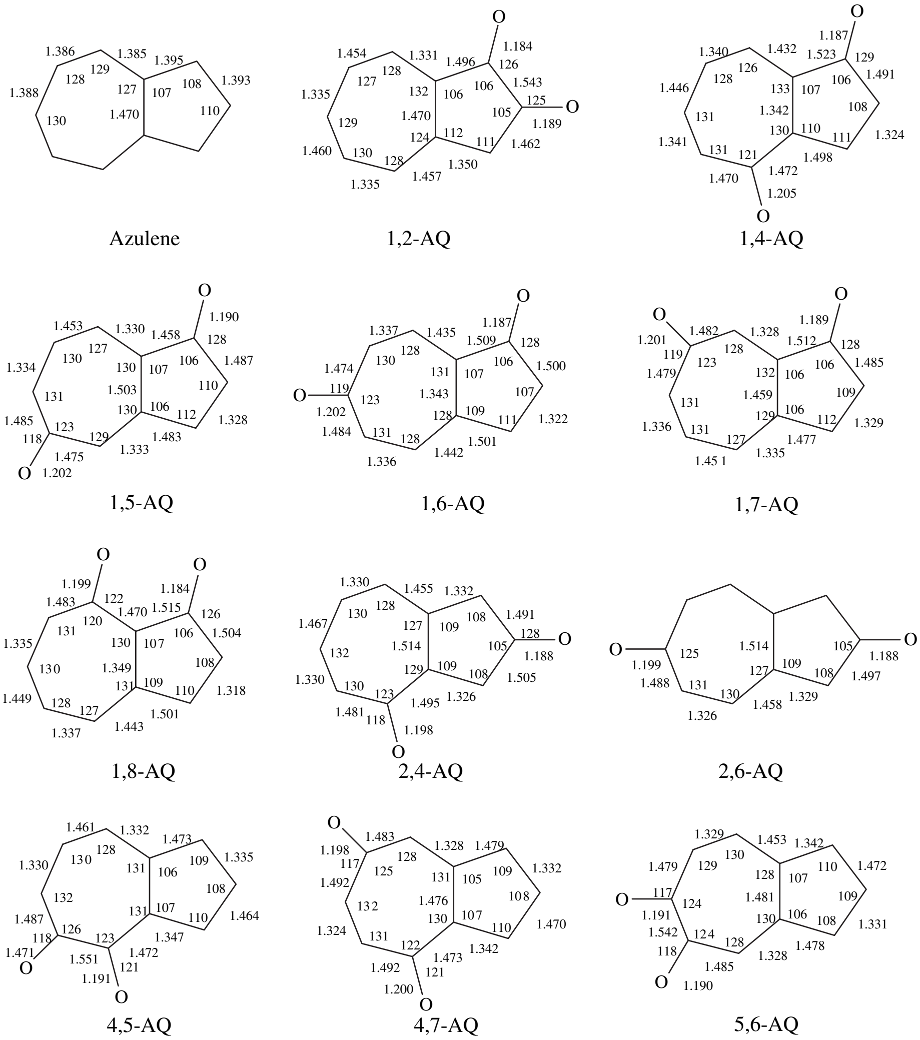


Fig. 3. HF/6-31G**//HF/6-31G** calculated bond lengths (in angstrom) and bond angles (in degree) for azulene and azulene quinones related to Kekule quinones. All structures are planar.

calculation. Vibrational frequencies were calculated at 6-31G** level for all geometries, which were confirmed to have zero imaginary frequency. The frequencies were scaled by a factor of 0.9135 for HF and 0.9804 for B3LYP method and used for computation of the zero-point vibrational energies [16–19].

3. Results and discussion

The results of *ab initio* calculations for azulene and azuloquinones (AQs) are shown in Figs. 3 and 4 and Tables 1 and 2. According to these calculations, the 1,5-AQ is the most stable isomer by all methods. The 1,7-AQ is 2.78 kJ mol^{-1} less stable than 1,5-isomer. 1,6-AQ, which is 27.36 kJ mol^{-1} less stable than 1,5-AQ, is predicted to be the third stable isomer.

Azuloquinones which contain a tropone ring and have no cyclopentadienone system, namely, 1,5- and 1,7-AQs are the most stable isomers. AQs which possess both tropone and cyclopentadienone rings, for example 1,4-, 1,6-, and 1,8-AQs, are less stable than the 1,5-, and 1,7-isomers. Azuloquinones containing cyclopentadienone but not tropone rings, namely, 2,4- and 2,6-AQs, are the least stable isomers among classical AQs (see Table 1). A part of the low stability of 1,2-AQ is due to the dipole-repulsion of planar electron pairs (Fig. 5).

Comparison of the results of geometry optimization by AM1 and MINDO/3 methods with those of *ab initio* calculations indicated that MINDO/3 method is better than AM1 in predicting the relative energies of azuloquinones (Tables 1 and 2).

As shown in Tables 1 and 2, the non-classical *meta*-azuloquinones are less stable than the classical isomers. Both HF and DFT methods predict the triplet (T) electronic configurations of the non-classical benzoquinones and pyridoquinones

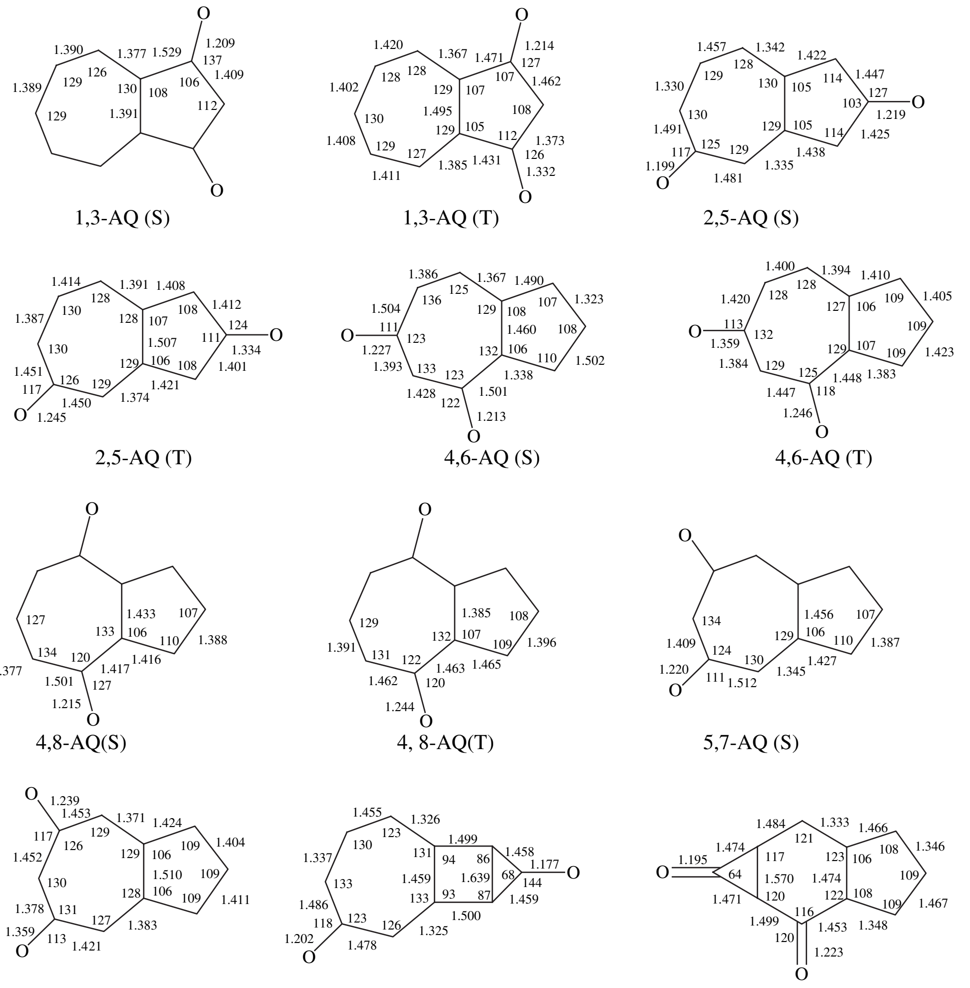


Fig. 4. HF/6-31G**//HF/6-31G** calculated bond lengths (in angstrom) and bond angles (in degree) for azulene quinones related to non-Kekule quinones. All structures except 2,5-AQ (B) and 4,6-AQ (B) are planar.

to be more stable than the singlet (S) configurations, due to higher multiplicity; however, predictions made by the MP2 methods for the triplet and singlet configurations are reversed.

Energy minimization without any symmetry constrains of non-classical AQs indicated that 2,5-AQ (S) and 4,6-AQ (S) are not energy minimum, but collapse to highly strained cyclopropanone derivatives by C–C bond formation. These tricyclic cyclopropanones, namely, 2,5-AQ (B) and 4,6-AQ (B) are less stable than 2,5-AQ (T) and 4,6-AQ (T), respectively (Fig. 4 and Table 2).

Selected geometrical data for azulene and azuloquinones are given in Figs. 3 and 4. Although many of AQs are planar, some of them are nonplanar. A major reason for nonplanarity is the relief of eclipsing that can occur with vicinal carbonyl groups. Thus, dipole-repulsion of electron pairs makes tropone ring of 2,4-, 4,5-, and 5,6-AQs to be significantly nonplanar. The slight nonplanarity of the tropone ring in 1,8-AQ relieves *peri* interactions between oxygens (Fig. 5).

The C=O bond lengths in the *meta*-isomer of AQs are longer than those calculated for the classical isomers. Carbon–carbon double bonds in classical AQs are shorter than the corresponding bonds in the non-classical *meta*-quinones. These results indicate that some other resonance structures may become important for *meta*-quinones as hybrid structures for 1,3-AQ, as an example (Fig. 6).

In summary, *ab initio* calculations provide a picture of geometries of azuloquinones from both structural and energetic points of view. 1,5-AQ is the most stable isomer. 1,7-AQ and 1,6-AQ are calculated to be 2.78 and 27.36 kJ mol^{-1} less stable than 1,5-isomer. The singlet configurations of non-classical *meta*-azuloquinones are 37–230 kJ mol^{-1} less stable than the corresponding triplet configurations. It would be interesting, of course, to have direct structural data on all of the azuloquinones for comparison with the results of the *ab initio* calculations.

Table 1
Calculated heats of formation (kJ mol^{-1}), total and zero-point vibrational energies (Hartree) and relative energies (including zero-point energy, kJ mol^{-1}, in parentheses) for azulene and 11 azulene quinones (AQs) related to Kekule quinines

Feature	Azulene	1,2-AQ	1,4-AQ	1,5-AQ	1,6-AQ	1,7-AQ	1,8-AQ	2,4-AQ	2,6-AQ	4,5-AQ	4,7-AQ	5,6-AQ
AM1	352.49	59.66 (2.42)	83.43 (26.19)	57.24 (0.00)	83.01 (25.77)	59.92 (2.68)	98.21 (40.97)	115.22 (57.99)	122.55 (55.31)	128.03 (70.79)	116.36 (59.12)	132.34 (75.10)
MINDO 3	357.58	−17.05 (10.69)	−4.37 (23.37)	−27.74 (0.00)	−3.22 (24.52)	−22.91 (4.83)	−4.33 (23.41)	14.08 (41.82)	18.98 (46.72)	27.82 (55.56)	24.11 (51.85)	37.77 (65.51)
HF/6-31G**	−383.2970	−531.8556 (38.74)	−531.8609 (24.37)	−531.87 (0.00)	−531.8579 (31.61)	−531.8683 (5.43)	−531.8496 (52.99)	−531.8438 (68.59)	−531.8490 (45.95)	−531.8391 (80.68)	−531.8523 (46.57)	−531.8405 (76.96)
ZPE	0.1408	0.1424	0.1422	0.1424	0.1420	0.1424	0.1418	0.1420	0.1420	0.1419	0.1420	0.1418
MP2/6-31G**// HF/6-31G*	−384.6188	−533.4806 (32.44)	−533.4882 (12.50)	−533.4930 (0.00)	−533.4849 (21.18)	−533.4920 (2.68)	−533.4762 (44.12)	−533.4658 (71.36)	−533.4699 (60.74)	−533.4672 (67.86)	−533.4753 (46.40)	−533.4669 (68.54)
B3LYP/6-31G**	−385.8508	−535.0708 (27.90)	−535.0747 (18.21)	−535.0819 (0.00)	−535.0710 (27.36)	−535.0808 (2.78)	−535.0623 (49.52)	−535.0542 (71.20)	−535.0587 (59.23)	−535.0541 (71.43)	−535.0622 (49.45)	−535.0536 (71.06)
ZPE	0.1434	0.1320	0.1318	0.1320	0.1315	0.1320	0.1313	0.1314	0.1314	0.1314	0.1316	0.1312
MP2/6-31G**// B3LYP/6-31G**	−384.6202	−533.4890 (31.11)	−533.4968 (10.73)	−533.5009 (0.00)	−533.4923 (22.40)	−533.5001 (1.92)	−533.4844 (43.13)	−533.4652 (93.54)	−533.4781 (59.81)	−533.4756 (66.24)	−533.4833 (46.18)	−533.4751 (67.57)

Zero-point vibrational energy is scaled by a factor of 0.9135 for HF and 0.9804 for B3LYP methods to eliminate known errors in calculations.

Table 2
Calculated heats of formation (kJ mol^{-1}), total and zero-point vibrational energies (Hartree) and relative energies (including zero-point energy, kJ mol^{-1}, in parentheses) for five azulene quinones (AQs) related to non-Kekule quinines

Feature	1,3-AQ		2,5-AQ			4,6-AQ			4,8-AQ		5,7-AQ	
	(S)	(T)	(S)	(T)	(B)	(S)	(T)	(B)	(S)	(T)	(S)	(T)
AM1	181.51 (124.27)	120.96 (63.72)	318.18 (260.94)	176.23 (112.99)	296.79 (212.55)	345.22 (287.98)	178.04 (120.80)	180.54 (123.30)	358.59 (301.35)	231.31 (174.07)	323.67 (266.43)	148.06 (90.82)
HF/6-31G**	−531.8284 (107.02)	−531.8396 (63.00)	−531.7709 (254.44)	−531.8360 (70.32)	−531.7747 (249.43)	−531.7447 (320.42)	−531.8286 (88.65)	−531.8117 (153.55)	−531.7545 (293.01)	−531.8282 (90.13)	−531.7671 (263.52)	−531.8337 (75.25)
ZPE	0.14108	0.1351	0.1396	0.1341	0.1405	0.1384	0.1336	0.1423	0.1378	0.1338	0.1393	0.1337
MP2/6-31G**// HF/6-31G*	−533.4697 (61.17)	−533.3343 (416.72)	−533.4219 (186.56)	−533.3645 (337.46)	−533.4108 (215.86)	−533.3738 (312.85)	−533.2756 (570.82)	−533.4490 (115.52)	−533.4007 (242.34)	−533.3016 (502.47)	−533.3989 (247.16)	−533.3132 (472.20)
B3LYP/6-31G**	−535.0612 (53.23)	−535.0120 (173.66)	−535.0154 (168.92)	−535.0326 (121.01)	−534.9966 (218.03)	−534.9886 (232.87)	−535.0182 (153.87)	−535.0300 (131.70)	−535.0031 (196.45)	−535.0266 (134.67)	−535.0020 (199.13)	−534.9923 (223.63)
ZPE	0.1316	0.1282	0.1299	0.12873	0.1297	0.1277	0.1272	0.1302	0.1284	0.1283	0.1279	0.1276
MP2/6-31G**// B3LYP/6-31G**	−533.4749 (68.17)	−533.3782 (322.17)	−533.4316 (181.97)	−533.3668 (351.90)	−533.4185 (216.31)	−533.4006 (263.23)	−533.2842 (568.75)	−533.4560 (117.95)	−533.418 (215.50)	−533.3924 (284.93)	−533.4069 (244.71)	−533.3509 (393.75)

Zero-point vibrational energy is scaled by a factor of 0.9135 for HF and 0.9804 for B3LYP methods to eliminate known errors in calculations.

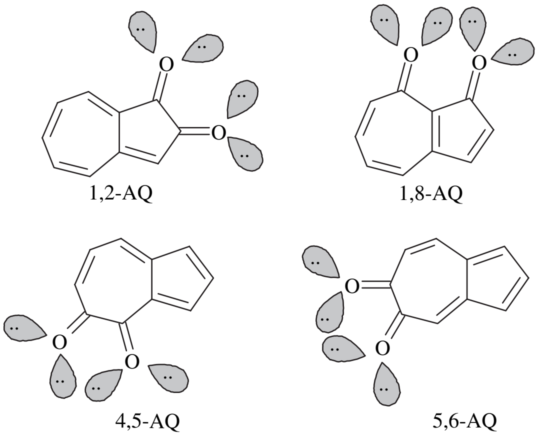

1,2-AQ 1,8-AQ 4,5-AQ 5,6-AQ

Fig. 5. Repulsive interactions of adjacent electron pairs in 1,2-, 1,8-, 4,5- and 5,6-AQs.

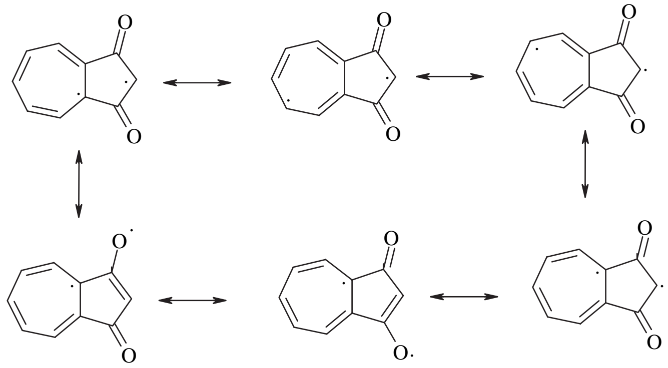


Fig. 6. Resonance structures of 1,3-AQ.

References

[1] Patai S, Rappaport Z. The chemistry of the quinoid compounds, vol. 2. New York: Wiley; 1998.

[2] Thomson RH. Naturally occurring quinones: recent advances. 3rd ed. London: Chapman and Hall; 1987.

[3] Heilbronner E. In: Ginsberg D, editor. Nonbenzenoid aromatic hydrocarbons. New York: Wiley-Interscience; 1959 [chapter 5].

[4] Morita T, Karasawa M, Takase K. The synthesis and some properties of 1,2-azulenequinone (1,2-azulenedione) and its derivatives. Chem Lett 1980;197.

[5] Scott LT, Rozeboom MD, Houk KN, Fukunaga T, Hafner K. The quinones of azulene. A theoretical prognosis. J Am Chem Soc 1980;102:5169.

[6] Kosuge S, Morita T, Takase K. The synthesis of 6-methylen-2(6*H*)-azulenone (2,6-azulenoquinone 6-methide) derivatives. Chem Lett 1975;733.

[7] Kawakami H, Yan YZ, Kato N, Mori A, Takeshita H, Nozoe T. Photodimerizations of 1,5- and 1,7-azulenequinones: solvent, substituent, and concentration effects on the product distribution. Bull Chem Soc Jpn 1998;71:711–6.

[8] Freeman F, Phornvoranunt A, Hehre WJ. *Ab initio* molecular orbital study of the conformational energies ($-\Delta G^0$ or A values) of 4-alkyltetrahydro-2*H*-thiopyrans (tetrahydrothiopyrans, thiacyclohexanes, thianes). J Phys Org Chem 1998;11:831.

[9] Gilbert TM. *Ab initio* prediction of ring strain enthalpies of cyclic amine-boranes. Tetrahedron Lett 1998;39:9147.

[10] Remko M, Lyne PD, Richards WG. Molecular structure, gas-phase acidity and basicity of *n*-hydroxyurea. Phys Chem Chem Phys 1999;1:5353.

[11] Bally T, Chai S, Neuenshwander M, Zhu Z. Pentalene: formation, electronic, and vibrational structure. J Am Chem Soc 1997;119:1869.

[12] Arnason I, Thorarinson GK, Matern E. Conformations of silicon-containing rings: part 1. A conformational study on 1,3,5-trisilacyclohexane. Comparison of *ab initio*, semiempirical, and molecular mechanics calculations. Conformational energy surface of 1,3,5-trisilacyclohexane. J Mol Struct (Theochem) 1998;454:91.

[13] Stewart JJP. QCPE 581. Department of Chemistry, Indiana University, Bloomington, IN.

[14] Stewart JJP. J Comput Aided Mol Des 1990;4:1.

[15] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 98, Revision A.6. Pittsburgh, PA: Gaussian Inc. 1998.

[16] Grev RS, Janssen CL, Schaefer HF. Chem Phys 1991;95:5128.

[17] Jensen F. Introduction to computational chemistry. New York: Wiley; 1999.

[18] Hehre W, Radom L, Schleyer PvR, Pople JA. *Ab initio* molecular orbital theory. New York: Wiley; 1986.

[19] Seminario JM, Politzer P, editors. Modern density functional theory. A tool for chemistry. Amsterdam: Elsevier; 1995.