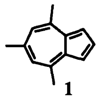
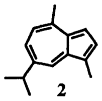
Stability and Resonance Energy of Azulenequinones and the Rule for Topological Charge Stabilization[1)]

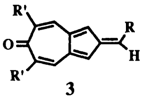
Teruo Kurihara,* Sumio Ishikawa,
and Tetsuo Nozoe†
Department of Chemistry, Faculty of Science, Josai University, Sakado, Saitama 350-02
†Tokyo Research Laboratories, Kao Corporation, 1-3 Bunka, Sumida-ku, Tokyo 131
(Received October 9, 1991)

Synopsis. An examination was made of the stability and formation pathways of azulenequinones produced by oxygenation in terms of Aihara's graph theory of aromaticity and Gimarc's TCS rule. In view of the TCS rule, the oxygen molecule in autoxidation first attacks C-1 of the azulenes, followed by the another oxygen molecule attacking at position *n* in 1-carbonylated azulenes to give azulenequinones.

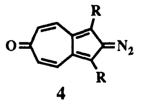
For the past several years, one of the authors (T. N.) and co-workers[2)] have studied the autoxidation[2a)] and peracetic acid oxidation[2b)] of 4,6,8-trimethylazulene (**1**), guaiazulene (**2**), and other azulenes. They obtained a wide variety of products possessing interesting structures of azulenequinone, naphthoquinone, 1*H*-inden-1-one, and dimeric compounds. Meanwhile, Scheuer et al.[3a)] isolated many kinds of interesting azulenes, including guaiazulenequinone,[3b)] from blue polyps of deep-sea gorgonian. In an early study of nonfused azulenequinones (AQs), Hafner et al.[4)] synthesized 2-methylene-6(2*H*)-azulenone derivatives (**3**), whereas Nozoe et al.[5)] reported several 2-diazo-6(2*H*)-azulenones (**4**). Later, Morita et al.[6)] reported the synthesis of 2,6-AQ derivatives (**5**) as a dimer, 1,2-AQ (**6**), as well as 1,5- (**8**:R=COOEt) and 1,7-AQ carboxylates (**10**: R=COOEt). More recently, Scott and co-workers[7)] synthesized 1,5- (**8**:R=H) and 1,7-AQ (**10**:R=H) as stable crystals; they also isolated unstable 1,4- (**7**) and 1,6-AQ (**9**) as Diels-Alder adducts. In this present study, an examination was made of the stability and formation pathways of AQs by oxygenation in terms of Aihara's graph theory of aromaticity[8)] as well as Gimarc's TCS rule.[9)] Standard HMO calculations, using the Hess and Schaad parameters for oxygen, were employed.[10)]


1

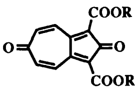

2



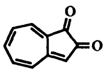
3



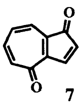
4



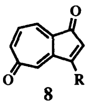
5



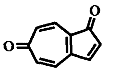
6



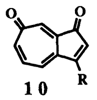
7



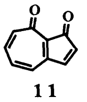
8



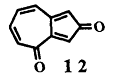
9



10



11



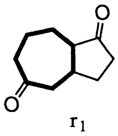
12

Results and Discussion

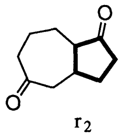
Table 1. Resonance Energies and Circuit Resonance Energies of Azulenequinones

Compd	RE[a)]	CRE[b)]			ΔH$_f$[c)]
		r_1	r_2	r_3	
6	0.0331	0.0509	−0.0190	0.0059	−0.4
7	0.0028	0.0458	−0.0511	0.0099	−0.8
8	0.0425	0.0482	−0.0168	0.0093	−6.4
9	0.0031	0.0463	−0.0521	0.0102	−0.6
10	0.0423	0.0482	−0.0168	0.0091	−5.3
11	0.0036	0.0451	−0.0502	0.0106	−0.6
5	−0.0355	0.0079	−0.0057	0.0132	4.7
12	−0.0353	0.0070	−0.0495	0.0137	4.7

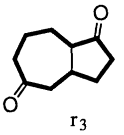
a) Resonance energy (in β unit). b) Circuit resonance energy (in β unit).



r₁



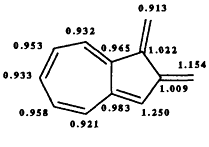
r₂



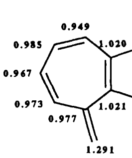
r₃

c) Heats of formation (kcal mol^{-1}) by means of MINDO/3 method (cf. Ref. 7).

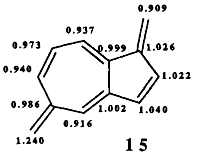
Scott et al.[7)] reported that the AQs which contain a tropone ring (**8** and **10**) are more stable than those which contain a cyclopentadienone ring (**5** and **12**); those which contain both types of annulenone ring (**7**, **9**, and **11**) fall in between. The calculated resonance energies and circuit resonance energies for **5**—**12** are given in Table 1. From the calculated circuit resonance energies, the tropone ring (r_1) is predicted to be aromatic, with a positive resonance energy; however, the cyclopentadienone ring (r_2) is predicted to be antiaromatic, with a negative resonance energy.[11)]



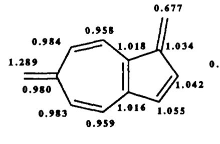
13



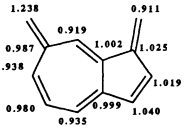
14



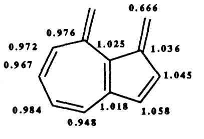
15



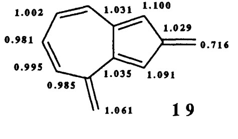
16



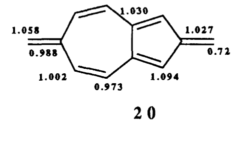
17



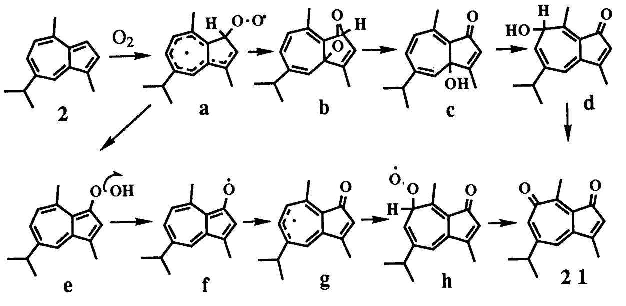
18



19



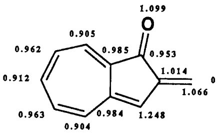
20



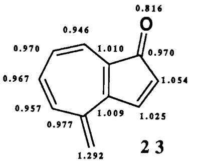
Scheme 1.

We consider the stability of *m*,*n*-AQs. The 1,*n*-and 2,*n*-dihydrodimethyleneazulenes are uniform reference frames (URFs) for 1,*n*-AQs (**6**—**11**) and 2,*n*-AQs (**5** and **12**); these charge densities are shown in **13**—**20**. All *exo*-carbons at the position *n* in the URFs (**13**—**18**) show the largest values of the charge densities, compared with their ring carbons. In each case, the oxygen atom is located at the *exo*-carbon of the maximum charge density in the URFs, **13**—**18**. According to the original TCS rule,[9] it is not necessary to place heteroatoms at all of the sites of high charge density in URF in order to stabilize the molecules. However, the charge densities of *exo*-carbons at position 1 are not high in the corresponding URFs. Thus, this position of the ketone oxygen does not conform to the TCS rule. Therefore, the AQs can not be designed by replacing the two *exo*-carbons by two oxygen atoms, in view of the TCS rule.

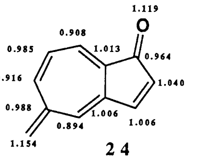
Although electrophilic substitution reactions of the azulenes are well known to take place most easily at the 1 position,[12] no detailed study on radical reactions of azulenes has been made thus far, except for a few, brief descriptions concerning radical methylation,[13] benzylation,[14] and bezoyloxylation,[15] all of which yield the corresponding substitution products preferentially at C-1. The possible pathways proposed for the formation of guaiazulenequinone (**21**) by oxygenation are shown in Scheme 1.[2] We now consider the stability of the *n*-methylene-1(*nH*)azulenones (**22**—**27**). In all cases, the oxygen atoms are situated at the sites of large charge density in the corresponding URFs, **22**—**27**. Thus, the 1,*n*-AQs can be designed by replacing the *exo*-carbon by an oxygen atom. On the contrary, when we consider the stability of the 1-methylene-*n*(1*H*)-azulenones (**30**—**35**), the charge densities of the *exo*-carbons at position 1 are, in all cases, not high in the corresponding URF's. Although the 1,*n*-AQs can not be formed by oxidation of the corresponding dihydrodimethyleneazulenes, the oxygen molecule first attacks position 1, followed by another oxygen molecule attacking position *n* in 1(*nH*)-azulenones to give azulenequinones in terms of the TCS rule.



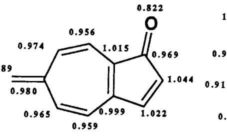
22



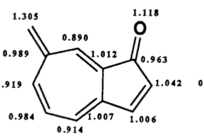
23



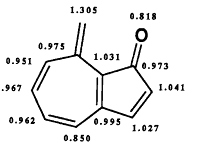
24



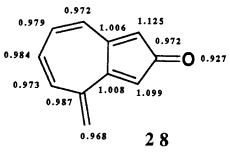
25



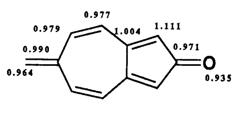
26



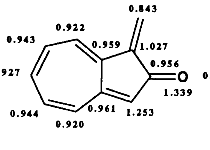
27



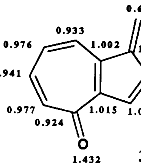
28



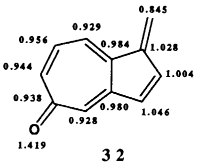
29



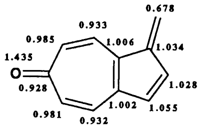
30



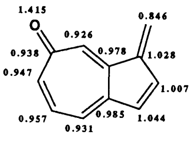
31



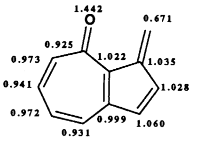
32



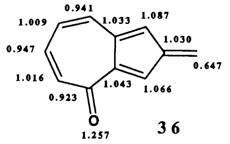
33



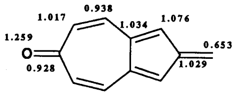
34



35



36



37

We wish to thank Professor Jun-ichi Aihara (Shizuoka Univ.) for helpful discussions concerning the resonance energy. We are grateful to Professor Hiroshi Yamamoto (Okayama Univ.) for his helpful advice.

References

1) A part of the results have been preliminarily presented: T. Kurihara, S. Ishikawa, and T. Nozoe, 52th National Meeting of the Chemical Society of Japan, Kyoto, 1986, Abstr., No. 2V26.

2) a) Y. Matsubara, S. Takekuma, K. Yokoi, H. Yamamoto, and T. Nozoe, *Bull. Chem. Soc. Jpn.*, **60**, 1415 (1987), and references cited therein. b) Y. Matsubara, A. Matsui, S. Takekuma, H. Yamamoto, and T. Nozoe, *Nippon Kagaku Kaishi*, **1988**, 1704.

3) a) M. K. W. Li and P. J. Scheuer, *Tetrahedron Lett.*, **25**, 587, 4707 (1984). b) P. J. Scheuer, Private communication to T. Nozoe.

4) K. Hafner, K. H. Vöpel, G. Ploss, and C. König, *Ann. Chem.*, **661**, 52 (1963).

5) T. Nozoe, S. Asao, H. Susumago, and M. Ando, *Bull. Chem. Soc. Jpn.*, **47**, 1471 (1974).

6) T. Morita, M. Karasawa, and K. Takase, *Chem. Lett.*, **1980**, 197; T. Morita, F. Ise, and K. Takase, *ibid.*, **1982**, 1303.

7) L. T. Scott, M. D. Rozenboom, K. N. Houk, T. Fukunaga, H. J. Lindner, and K. Hafner, *J. Am. Chem. Soc.*, **102**, 5169 (1980); L. T. Scott, *Pure Appl. Chem.*, **1983**, 363; L. T. Scott, P. Grutter, and R. Chamberlain, III, *J. Am. Chem. Soc.*, **106**, 4852 (1984); L. T. Scott and C. M. Adams, *ibid.*, **106**, 4857 (1984).

8) J. Aihara, *J. Am. Chem. Soc.*, **98**, 2750 (1976); J.

Aihara, *Bull. Chem. Soc. Jpn.,* **51**, 3540 (1978); J. Aihara, *J. Am. Chem. Soc.,* **101**, 5913 (1979); J. Aihara and T. Horikawa, *Bull. Chem. Soc. Jpn.,* **56**, 1853 (1983).

9) B. M. Gimarc, *J. Am. Chem. Soc.,* **105**, 1979 (1983); B. M. Gimarc and J. J. Ott, *ibid.,* **108**, 4298 (1986); J. J. Ott and B. M. Gimarc, *ibid.,* **108**, 4303 (1986).

10) B. A. Hess, Jr. and L. J. Schaad, *J. Am. Chem. Soc.,* **95**, 3907 (1973).

11) J. Aihara, *Bull. Chem. Soc. Jpn.,* **48**, 1501 (1975).

12) For reviews and monographs, see e.g., T. Nozoe and Asao, in "Comprehensive Organic Chemistry," ed by M. Kotake, Asakura, Tokyo (1960), Vol. 13, pp. 439—534; D. Lloyd, "Non-Benzenoid Conjugated Carbocyclic Compounds," Elsevier, Amsterdam (1984), pp. 351—357.

13) R. W. Adler and G. Whittacker, *J. Chem. Soc., Perkin Trans. 2,* **1975**, 1464.

14) J. F. Tilney-Bassett and W. A. Waters, *J. Chem. Soc.,* **1959**, 3123.

15) A. Anderson, Jr. and G. M. C. Chang, *J. Org. Chem.,* **23**, 1512 (1958).