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QUINONES OF HOMOAZULENE. THE FIRST QUINONES OF AN ALTERNANT HYDROCARBON WITH A NONALTERNANT HOMOCONJUGATIVE PERTURBATION

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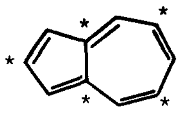
Abstract. The first three quinones of homoazulene (5, 6, and 15) have been prepared. Unlike quinones of ordinary alternant hydrocarbons, these new quinones have long-wavelength maxima in their UV-VIS absorption spectra which all fall at shorter wavelength than that of the parent hydrocarbon, homoazulene (2). In this respect, the quinones of homoazulene behave much like the corresponding quinones of the prototypical nonalternant hydrocarbon azulene (1).

The σ bond holding two atoms of like parity together in azulene (1) imposes a nonalternant character on the [10]annulene perimeter of this molecule, which, in the absence of that one transannular conjugative interaction, would be classified as a simple alternant hydrocarbon.[1] In homoazulene (2), the same [10]annulene perimeter also exhibits nonalternant character, despite the replacement of a transannular conjugative interaction by a much weaker homoconjugative interaction.[2] This ability of the homoazulene skeleton to confer nonalternant character on an otherwise alternant π system through homoconjugation opens the door to studies beyond those on the perturbed annulene and its substituted relatives. Our growing interest in all aspects of cyclic homoconjugation,[2,3] on the one hand, and in nonbenzenoid quinones,[4] on the other, has led us to synthesize several quinones of homoazulene. Herein we report on the synthesis and unusual properties of these unique compounds, the first quinones of an alternant hydrocarbon with a nonalternant homoconjugative perturbation.



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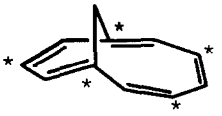

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Figure 1 shows two of the homoazulene quinones that constitute the subject of this paper (syntheses described below). The corresponding quinones of azulene, which have also been synthesized recently for the first time in our laboratory,[4c,d] are included for comparison.

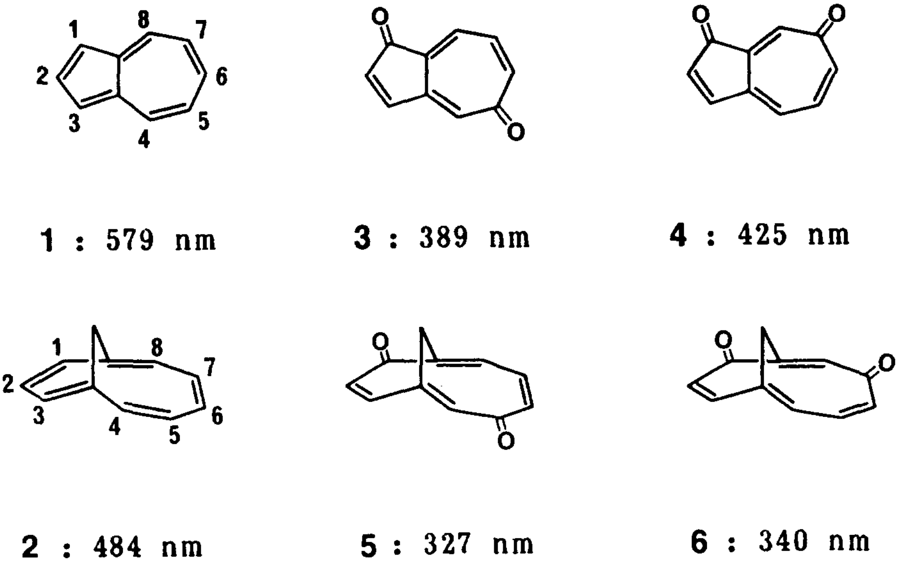
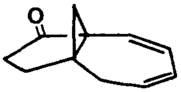


Figure 1. Long wavelength maxima in the UV-VIS absorption spectra of azulene, homoazulene, and some of their quinones.

Note that these quinones of azulene absorb light at shorter wavelengths than does azulene itself. Such behavior is precisely the reverse of that which is observed for alternant systems; the quinones of benzene and naphthalene, for example, are yellow, orange, and red, whereas the parent hydrocarbons are colorless.[5] This peculiarity of the azulenic compounds is well accounted for by theoretical calculations which take into consideration the nonalternant nature of the π-system and, in fact, was even predicted.[4a] In the homoazulenic series, this same peculiarity is preserved (Figure 1). Thus, quinones 5 and 6 behave more like the nonalternant quinones of azulene than like quinones of a purely alternant [10]annulene. Clearly, the nonalternant homoconjugative perturbation enforced by the homoazulene skeleton affects the electronic properties of these new quinones just as it affects the properties of the parent hydrocarbon.

Propellane 7, which is easily prepared from hydrocinnamic acid in four steps,[6] provided the starting point for syntheses of both 5 and 6.[7] Desaturation of 7 via the α-phenylselenide[8] gave 8, which was converted by photooxygenation into endoperoxide 9. Hünig's base efficiently isomerized 9 to a 3:2 mixture of the γ-hydroxyenones 10 and 11 (25% overall yield from 7). From the major isomer, it was anticipated that the 1,5-quinone (5) could be obtained by a Grob fragmentation reaction (12). This transformation was most conveniently accomplished in a single step by the action of trifluoroacetic anhydride on 10 in the presence of triethylamine (77% yield).



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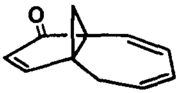

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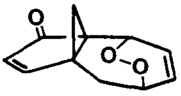

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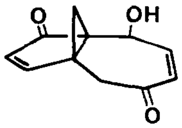

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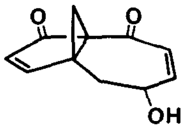

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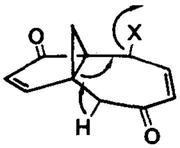

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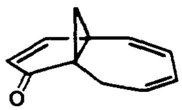
Transposition of the enone in 8 by the Wharton procedure[9] gave 13, our precursor to the 1,7-quinone (6). The remaining steps in this synthesis paralleled those for the conversion of 8 to 5.

Allylic bromination (NBS) of the previously known[2] trienedione 14, followed by treatment with triethylamine, gave a third quinone of homoazulene, 15. Though not isolable, this quinone could be purified chromatographically and characterized by NMR, IR, and UV spectroscopy, provided that solvent was never completely removed.



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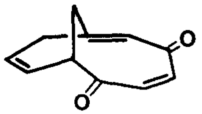

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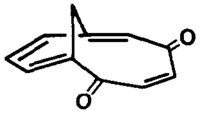

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The long-wavelength absorption maximum of 15 at 382 nm appears at considerably longer wavelength than the maxima of the first two homoazulene quinones (5 and 6); however, it still falls at shorter wavelength than that of the parent hydrocarbon. The UV spectral characteristics of the homoazulene 4,7-quinone (15) are in complete agreement with those expected for the corresponding azulene quinone; the 4,7-quinone of azulene, though presently unknown, is predicted likewise to absorb at longer wavelength than the 1,5- and 1,7-quinones (3 and 4) but at shorter wavelength than azulene.[4a]

The nonalternant character of quinones 5, 6, and 15 beautifully illustrates the fact that cyclic homoconjugation can have important consequences even in non-aromatic organic molecules.

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(7) All new compounds were characterized by the usual spectroscopic methods and, except for the very unstable 15, also by either high resolution mass spectroscopy or C,H analysis.

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