

immediate color change occurred, from red to pale yellow. The mixture was then stirred for 2 h at room temperature, at which point the solution became colorless. Excess LiAlH_4 was hydrolyzed with 10 mL of wet THF (10% H_2O). The solvent was removed in vacuo and the residue extracted with toluene. The toluene solution was dried again in vacuo and the resulting pale-yellow solid dissolved in heptane. After cooling to -10°C (ethylene glycol bath), large pale yellow crystals appeared. IR data $\nu(\text{Ir-H})$ 1950 cm^{-1} (in heptane); ^1H NMR triplet at $\tau = 21$ with $J_{\text{PH}} = 12$ Hz.

The title compound crystallizes in the triclinic space group $P\bar{1}$, $Z = 1$, with $a = 7.837$ (1) Å, $b = 10.700$ (1) Å, $c = 7.424$ (1) Å, $\alpha = 106.99$ (1)°, $\beta = 104.22$ (1)°, $\gamma = 72.55$ (1)°, at $T = 80$ K.⁸ A room temperature single-crystal X-ray analysis^{9a} was first performed on a small crystal of $\text{H}_3\text{Ir}[\text{P}(i\text{-Pr})_3]_2$ yielding the positions of the non-hydrogen atoms [$R(F) = 0.023$ for 2210 reflections]. Neutron diffraction data subsequently were collected at the Brookhaven High Flux Beam reactor on a crystal of dimensions $0.75 \times 1.36 \times 3.78$ mm at 80 K.^{9b} All the H atoms were located from a series of difference Fourier syntheses; full-matrix least-squares refinement of a structure model with anisotropic thermal parameters for all atoms (332 variable parameters) then led to an agreement factor of $R(F^2) = 0.071$ for all 4457 measured reflections [$(\sin \theta)/\lambda_{\text{max}} = 0.78 \text{ \AA}^{-1}$].

The $\text{H}_3\text{Ir}(\text{PC}_3)_2$ core of the molecule (a pentagonal bipyramid with five equatorial H atoms) is shown in Figure 1. Selected distances and angles are given in Table I. Since the iridium atom is situated at an inversion center, what is actually observed is a disordered superposition of two pentagons of H atoms (i.e., a decagon of half-hydrogens). The $\text{H}\cdots\text{H}$ separations are sufficiently large, however, to enable the individual half-hydrogens to be readily resolved; the H parameters refined without any difficulty. The result (Table I) is an average Ir-H distance of 1.603 (9) Å and an average nonbonding $\text{H}\cdots\text{H}$ distance of 1.87 (1) Å. As additional consequences of the crystallographic inversion center at the Ir atom, the P-Ir-P axis is required to be linear, and the six ipso-carbon atoms are staggered with respect to this axis.

The terminal Ir-H distance of 1.603 (9) Å compares well with the values of 1.59 Å found in $[\text{H}_4\text{IrPt}(\text{PEt}_3)_4]^+ 10a$ and 1.594 (3) Å in $\text{H}_2\text{Ir}(\text{SiEt}_3)_2(\text{C}_5\text{Me}_5)$,^{10b} the only other iridium hydride complexes (with terminal hydrides) analyzed to date by single-crystal neutron diffraction, and is slightly shorter, as expected, than the average Os-H distance of 1.659 (3) Å, which we measured several years ago in the complex $\text{H}_4\text{Os}(\text{PMe}_2\text{Ph})_3$.^{2b} The compound Sr_2IrD_5 , studied by powder neutron diffraction methods, showed an Ir-D distance of 1.714 (5) Å.¹¹ In $\text{H}_3\text{Ir}[\text{P}(i\text{-Pr})_3]_2$ the entire IrH_5 equatorial group is planar within ± 0.02 Å, thus showing no evidence for any "rippling" or "doming" effect.

It should be noted, incidentally, that all attempts to prepare the analogous $\text{H}_3\text{Rh}[\text{P}(i\text{-Pr})_3]_2$ failed... instead, the reduction of the corresponding starting material $\text{HRhCl}_2[\text{P}(i\text{-Pr})_3]_2$ yielded only $\text{H}_2\text{RhCl}[\text{P}(i\text{-Pr})_3]_2$.^{7,12}

(8) The above unit cell parameters are from the low-temperature neutron diffraction analysis. For the preliminary X-ray diffraction study carried out at room temperature, the corresponding values are $a = 7.956$ (1) Å, $b = 10.840$ (1) Å, $c = 7.515$ (1) Å, $\alpha = 107.9$ (1)°, $\beta = 104.4$ (2)°, $\gamma = 72.21$ (1)°.

(9) (a) For the X-ray analysis, data were collected on a Nicolet-Syntex P21 diffractometer with $\text{Mo K}\alpha$ radiation up to a 2θ value of 50° ($\theta/2\theta$ scan). The structure was solved by the standard heavy-atom method. (b) The details of the low-temperature neutron data collection are similar to those described in an earlier publication (ref 2b). Initial phases for the neutron data were calculated on the basis of the non-hydrogen atomic positions derived from the X-ray analysis.

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(11) The value quoted is for the disordered cubic phase at room temperature. At 4.2 K, the structure is tetragonal with equatorial and axial Ir-D distances of 1.693 (7) and 1.82 (3) Å, respectively: Zhuang, J.; Hastings, J. M.; Corliss, J. M.; Bau, R.; Wei, C. Y.; Moyer, R. O., Jr. J. Solid State Chem. 1981, 40, 352.

(12) Both $\text{HRhCl}_2[\text{P}(i\text{-Pr})_3]_2$ and $\text{H}_2\text{RhCl}[\text{P}(i\text{-Pr})_3]_2$ have been chemically isolated and structurally characterized by X-ray diffraction (Garlaschelli, L.; Khan, S. I.; Huang, S. H.; Bau, R., unpublished results).

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Supplementary Material Available: A listing of the final atomic parameters for $\text{H}_3\text{Ir}[\text{P}(i\text{-Pr})_3]_2$ (Table A) (1 page). Ordering information is given on any current masthead page.

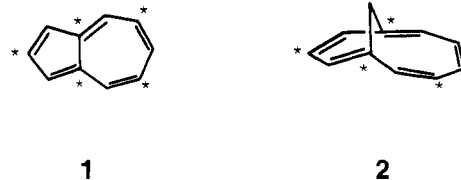
An Alternant Hydrocarbon π -System with Nonalternant Character. Evidence from UV-Vis Spectroscopy for Cyclic Homoconjugation in Homoazulene

Lawrence T. Scott,* Mitsunori Oda, and Ihsan Erden

Department of Chemistry and Center for Advanced Study, College of Arts and Science University of Nevada, Reno, Nevada 89557

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Azulene (1), when subjected to the Coulson "starring" proce-



dure, is found to contain two adjacent atoms of like parity (see asterisks in 1) and is therefore classified as a *nonalternant* hydrocarbon π -system.¹ Many of the peculiar properties of azulene can be traced to the presence of the lone transannular bond that makes this molecule nonalternant.² Herein we present the first experimental evidence that even *homoconjugation* between atoms of like parity can impart nonalternant character to a neutral hydrocarbon π -system. Homoazulene 2 and several derivatives thereof constitute the focus of these studies.^{3,4}

Among the special "nonalternant properties" of azulene, the response of the UV-vis absorption spectrum of the introduction of substituents on the chromophore is particularly striking. In general, benzenoid aromatics and other alternant hydrocarbons obey Woodward's familiar rules, i.e., ca. +5 nm shift in the long-wavelength absorption maximum for each alkyl substituent.⁵ Azulene, however, does not conform. A single alkyl substituent can shift the visible absorption maximum of azulene by as much as +29 nm toward longer wavelength or by as much as -14 nm toward shorter wavelength, depending on the site of attachment. This unusual behavior has required the development of a totally different set of empirical rules, now known as Plattner's rules, to correlate the spectral properties of azulene derivatives.⁶ Stronger donor substituents, such as OMe, cause proportionally larger shifts of the same sign.⁷

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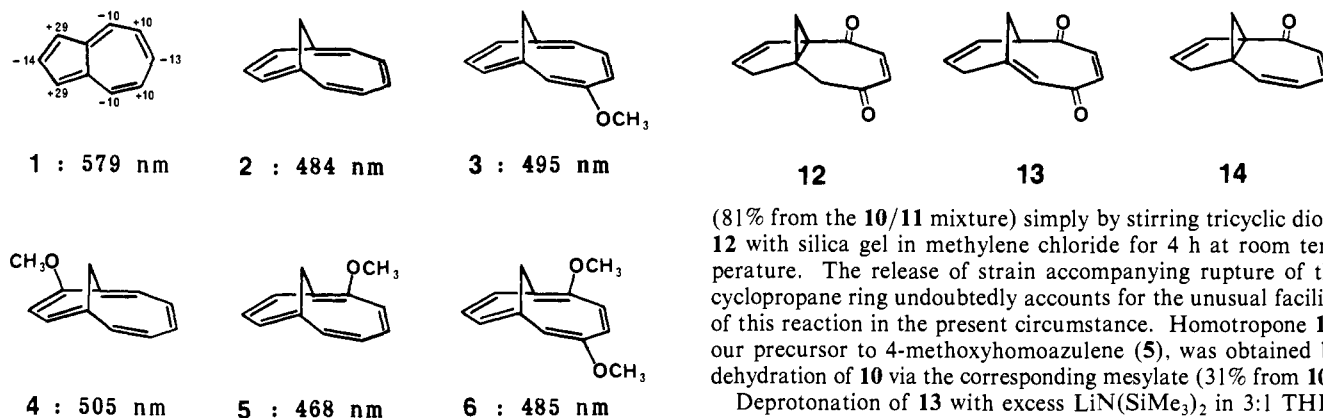
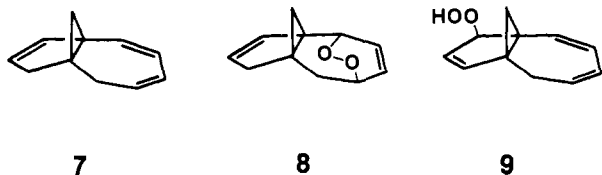


Figure 1. Visible absorption spectral maxima and Plattner's rules for the effects of alkyl substituents on the azulene absorption maximum.

Figure 1 summarizes Plattner's rules and gives the visible absorption maximum for each of five homoazulenes, two of which have been synthesized specifically for this project (see below). One can see immediately that homoazulene exhibits spectroscopic behavior toward substitution by a donor substituent which is decidedly atypical of an alternant hydrocarbon and in this regard appears far more similar to azulene than to an alternant hydrocarbon. For example, depending on the point of attachment of a single OMe group to homoazulene, the absorption maximum can be shifted either toward longer wavelength (3 and 4) or toward shorter wavelength (5) and by differing amounts. When two strong donor groups are judiciously counterpoised (6), the absorption maximum moves hardly at all! These data provide compelling evidence for the fact that even homoconjugation between atoms of like parity can impart nonalternant character to a neutral hydrocarbon π -system.⁸

Both 3-methoxyhomoazulene (3) and 1-methoxyhomoazulene (4) have been reported previously, the former from this laboratory^{4a,c} and the latter by Masamune et al.^{3a} The two new methoxyhomoazulenes (5 and 6) were synthesized⁹ from propellane 7, a key intermediate in our route to the parent homoazulene 2.^{4b,c}



Photooxygenation of 7 gave the endoperoxide 8 (61%)¹⁰ and a minor amount of the ene reaction product 9 (4%), which was easily separated by chromatography on silica gel.

Isomerization of 8 with triethylamine at room temperature produced a 2:1 mixture of the γ -hydroxy enones 10 and 11 (89%).



This mixture was oxidized with pyridinium chlorochromate to give a single dione (12). A retro-Michael reaction then served to remove the superfluous propellane bond. Thus, bicyclic dione 13, our precursor to 4,7-dimethoxyhomoazulene (6), was obtained

(81% from the 10/11 mixture) simply by stirring tricyclic dione 12 with silica gel in methylene chloride for 4 h at room temperature. The release of strain accompanying rupture of the cyclopropane ring undoubtedly accounts for the unusual facility of this reaction in the present circumstance. Homotropone 14, our precursor to 4-methoxyhomoazulene (5), was obtained by dehydration of 10 via the corresponding mesylate (31% from 10).

Deprotonation of 13 with excess $\text{LiN}(\text{SiMe}_3)_2$ in 3:1 THF/HMPA at 0 °C gave a cherry red solution of the bis enolate, which, on quenching at -78 °C with methyl fluorosulfonate ("Magic Methyl"), yielded 4,7-dimethoxyhomoazulene (6, 58%). The same procedure served to convert 14 into 4-methoxyhomoazulene (5, 61%). It should be noted that this latter transformation is initiated by deprotonation of a homocyclopentadiene ring.

These two new methoxyhomoazulenes (5 and 6) and the other compounds in Figure 1 vividly underscore the importance of cyclic homoconjugation in neutral organic molecules and provide the first clear-cut example of an alternant hydrocarbon π -system with nonalternant character.

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Application of Spin Trapping To Probe the Radical Pair Model in Magnetic-Field-Dependent Photoreduction of Naphthoquinone in SDS Micellar Solution

Masaharu Okazaki,[†] Shigeru Sakata,[‡] Ryusei Konaka,[‡] and Takeshi Shiga^{*†}

Department of Physiology, School of Medicine
Ehime University, Shigenobu, Onsen-gun
Ehime 791-02, Japan
Shionogi Research Laboratories, Shionogi & Co., Ltd.
Fukushima-ku, Osaka 553, Japan

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The effects of magnetic field on photochemical reactions¹ have been successfully interpreted in terms of the radical pair model,² in which the intersystem crossing rate between triplet and singlet radical pairs is influenced by an external magnetic field (reaction scheme, eq 1, 2). To investigate the relevance of the radical pair model further, it is very important to detect the intermediates,³⁻⁵ preferably both of the radicals.

In this paper, we show that the spin trapping method⁶ can be used to detect the unstable radical intermediates (as the function

[†] Ehime University.

[‡] Shionogi & Co., Ltd.

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(8) The proposal that homoazulene might obey Plattner's rules, at least qualitatively, was originally based on quite limited data.^{4c}

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