Bond Alternation in Azulenes

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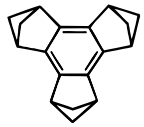
Abstract: 5,6-Azulyne, the first azulyne to be prepared, has been trapped with furan to give an adduct whose crystal structure reveals marked bond alternation in the azulene π system. The double bond in the furan moiety is responsible in part for the bond localization, as hydrogenation of that bond attenuates the effect. The regiochemistry of electrophilic attack on the adduct has been examined briefly, with results contrary to the prediction of frontier orbital theory. Quantum mechanical calculations have shed light on these phenomena.

Introduction

There has been much interest recently in discovering the requirements for introducing bond alternation (or localization) into aromatic systems (other than by direct π-conjugation, e.g. benzo fusion), and benzene has been the principal focus of attention. Siegel has succeeded in creating a bond length difference of 9.1 pm by the fusion of three highly strained bicyclobutane rings to the benzene skeleton, making tris(bicyclo[2.1.1]hexeno)benzene (**1**).[1] Kohnke[2] found ∼7 pm alternation in *anti*-tris(7-oxabicyclo[2.2.1]heptadieno)benzene (**2**), while De Lucchi and Balci observed a ∼5 pm difference in bond lengths in *syn*-**3**.[3] *syn*-Tris(bicyclo[2.2.1]hepteno)benzene (**4**) displayed ∼4 pm alternation,[4] and the less strained heptiptycene (**5**)[5] and tris(bicyclo[2.2.2]octeno)benzene (**6**)[6] revealed 2.2 and 1.5 pm bond alternation, respectively. Interestingly, ring strain alone does not suffice, as the bonds of the central ring of tris(cyclobuteno)benzene (**7**) differ in length by only 2 pm.[7]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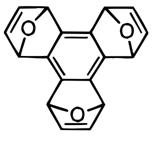
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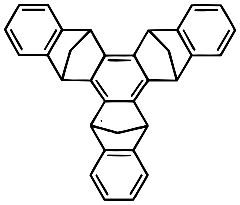
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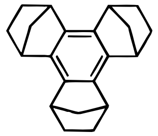
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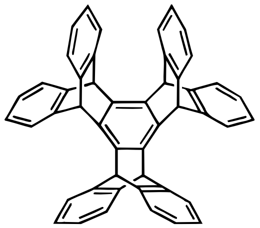
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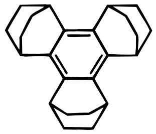
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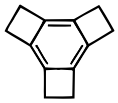
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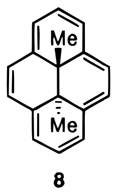
Introduction of bond localization by bicycloannellation has been explored experimentally in one other aromatic system, dimethyldihydropyrene (**8**), in which the peripheral bonds are all essentially the same length. Furan derivatives **9** and **10** have been synthesized and studied by Mitchell and Siegel.[8] In **9** the fusion of a single furan ring onto the 14π-electron framework suffices to induce bond alternation to the extent of 5.2 pm (average value). In this system ring current changes are easily probed through the chemical shifts of the vinyl and especially the methyl protons, and the ring current in **9** was found to be reduced 16−17% from that of the parent hydrocarbon **8.** A reduction of 35−40% was found in **10a**, whereas there was almost none in **10b** where the two furan rings oppose instead of reinforcing each other's influence.



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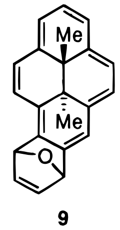

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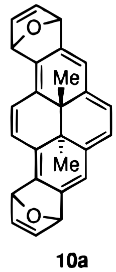

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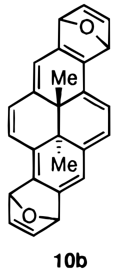

10b

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(1) Frank, N. L.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 2102. Bürgi, H.-B.; Baldridge, K. K.; Hardcastle, K.; Frank, N. L.; Gantzel, P.; Siegel, J. S.; Ziller, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1454. See also: Rouhi, A. M. *Chem. Eng. News* **1996**, *April 1*, 27.

(2) Cardullo, F.; Giuffrida, D.; Kohnke, F. H.; Raymo, F. M.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 339.

(3) Cossu, S.; De Lucchi, O.; Lucchini, V.; Valle, G.; Balci, M.; Dastan, A.; Demirci, B. *Tetrahedron Lett.* **1997**, *38*, 5319. The De Lucchi group has also synthesized tris(bicyclo[2.2.1]heptadieno)benzene, but the crystal structure is not available. Durr, R.; De Lucchi, O.; Cossu, S.; Lucchini, V. *J. Chem. Soc., Chem. Commun.* **1996**, 2447. Durr, R.; Cossu, S.; Lucchini, V.; De Lucchi, O. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2805.

(4) Frank, N. L.; Baldridge, K. K.; Gantzel, P.; Siegel, J. S. *Tetrahedron Lett.* **1995**, *36*, 4389.

(5) Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427. Venugopalan, P.; Bürgi, H.-B.; Frank, N. L.; Baldridge, K. K.; Siegel, J. S. *Tetrahedron Lett.* **1995**, *36*, 2419.

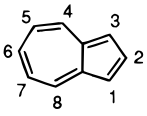
(6) Komatsu, K.; Jinbu, Y.; Gillette, G. R.; West, R. *Chem. Lett.* **1988**, 2029. Komatsu, K.; Aonuma, S.; Jinbu, Y.; Tsuji, R.; Hirosawa, C.; Takeuchi, K. *J. Org. Chem.* **1991**, *56*, 195.

(7) Boese, R.; Bläser, D.; Billups, W. E.; Haley, M. M.; Maulitz, A. H.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 313.

(8) Mitchell, R. H.; Chen, Y.; Iyer, V. S.; Lau, D. Y. K.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2907.

10.1021/ja984113i CCC: $19.00

Azulene (**11**, $C_{10}H_8$) is a theoretically interesting compound with many unusual properties.[9,10] This polar ($\mu = 1$ D), deep blue, nonbenzenoid aromatic hydrocarbon enjoys more than 30 kcal/mol of resonance energy. Azulene has nearly equal bond lengths (138.7−140.4 pm) around its 10π-electron periphery and C_{2v} symmetry[11] but, surprisingly, ab initio quantum mechanical calculations even at the HF/6-31G* and HF/6-311G** levels predict C_s geometry with strongly alternating double bonds. Haddon has shown that inclusion of dynamic electron correlation is required to predict the structure of azulene correctly.[12]



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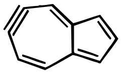
These observations suggest that only modest perturbation may be required to induce bond alternation in azulene. A test of that surmise is described here. Since bicycloannellation to induce bond alternation had been carried out only on a 6π and a 14π system and only on six-membered rings, we wished to explore its effect on a 10π molecule with five- and seven-membered rings. Our plan included annellation at each ring, but began with the 5- and 6-positions in the seven-membered ring where ring fusion could not introduce steric hindrance.

Results and Discussion

To create the desired ring fusion, it was necessary to generate and trap 5,6-azulyne (**12**). Surprisingly, no azulyne had been prepared at the outset of this work.[13] Our initial approach was based on the known 5,6-dichloroazulene (**13**),[14] but attempts to form the azulyne from this compound directly with organolithiums and magnesium were unavailing. 5-Chloro-6-iodoazulene (**14**) should be a superior precursor for **12**, and the very large LUMO coefficient at the 6-position of azulene boded well for preparing **14** by attack of iodide ion on the dichloride **13**.[15] Even at 160 °C, though, tetrabutylammonium iodide failed to bring about the desired nucleophilic substitution. Fortunately, attack by ammonia was effective at that temperature, yielding red crystals of 6-amino-5-chloroazulene (**15**). The hypsochromic shift of the visible spectrum from that of the blue starting material was to be expected, as conjugation with the amino group raises the LUMO energy level but does not influence the HOMO with a node at the 6-position. While the nucleophilic constant for iodide ion is greater than those of ammonia derivatives,[16] these values are based on S_N2 reactions and the reactivity order for nucleophilic aromatic substitution is reversed.[17] Sandmeyer reaction on **15** was expected to give the chloroiodo compound **14**, but attempts to diazotize the amino compound went awry. Apparently electrophilic attack occurred at the electron-rich 1- and/or 3-positions of the azulene.



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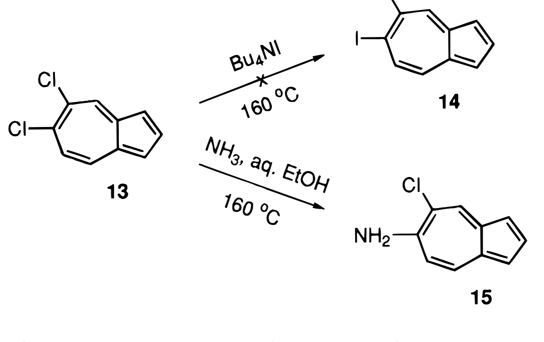
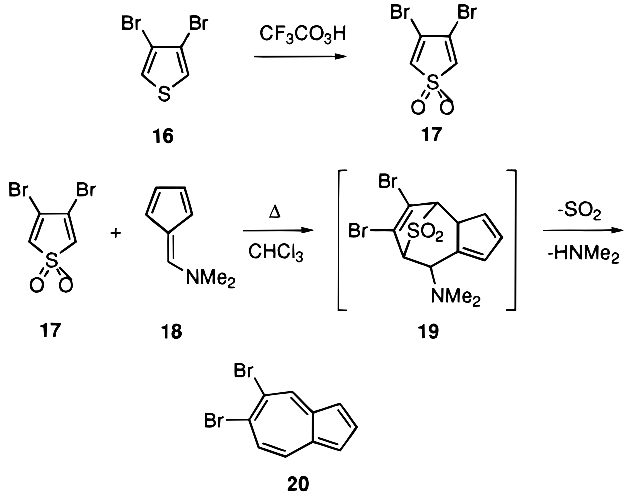


Scheme 1



In the wake of these results, a decision was made to synthesize 5,6-dibromoazulene as the 5,6-azulyne progenitor. The synthesis is presented in Scheme 1. 3,4-Dibromothiophene (**16**)[18] was prepared by reduction of the tetrabromide[19] according to Gronowitz, and oxidized to the sulfone (**17**) with peroxytrifluoroacetic acid.[20] Dimethylformamide dimethyl acetal transformed cyclopentadiene into 6-dimethylaminofulvene (**18**).[21,22] Finally, [6 + 4] cycloaddition of the fulvene to the thiophene dioxide to give **19** followed by extrusion of sulfur dioxide and dimethylamine yielded blue crystals of 5,6-dibromoazulene (**20**). Condensation of thiophene dioxides with aminofulvenes is a general method for the synthesis of azulenes.[14]

Treatment of dibromide **20** with phenyllithium generated azulyne **12**,[23] which in the presence of excess furan gave the

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(9) Zeller, K.-P. *Azulene*. In *Houben-Weyl; Methoden der Organischen Chemie*; 4th ed; Georg Thieme: Stuttgart, 1985; Vol. V, Part 2C, pp 127−418.

(10) Lemal, D. M.; Goldman, G. D. *J. Chem. Educ.* **1988**, *65*, 923.

(11) Hansen, A. W. *Acta Crystallogr.* **1965**, *19*, 19.

(12) Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* **1982**, *104*, 3516. Haddon, R. C.; Raghavachari, K. *J. Chem. Phys.* **1983**, *79*, 1093.

(13) An attempt to prepare a 1,2-azulyne has been reported. Nakazawa, T.; Kodama, M.; Kinoshita, S.; Murata, I. *Tetrahedron Lett.* **1985**, *26*, 335.

(14) Copland, D.; Leaver, D.; Menzies, W. B. *Tetrahedron Lett.* **1977**, 639. Reiter, S. E.; Dunn, L. C.; Houk, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 4199.

(15) Bolton, R.; Hamilton, D. G.; Sandall, J. P. B. *J. Chem. Soc., Perkin Trans. 2*, **1991**, 431. Bolton, R.; Hamilton, D. G.; Sandall, J. P. B. *J. Chem. Soc., Chem. Commun.* **1990**, 917.

(16) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 3rd ed.; Plenum: New York, 1990; Part A, p 286.

(17) Bunnett, J. F.; Zahler, R. E. *Chem. Rev.* **1951**, *49*, 339.

(18) Gronowitz, S. *Acta Chem. Scand.* **1959**, *13*, 1045.

(19) Gronowitz, S.; Moses, P.; Hakansson, R. *Ark. Kemi* **1960**, *16*, 267.

(20) Rozen, S.; Bareket, Y. *J. Org. Chem.* **1997**, *62*, 1457. These authors prepared the sulfone using $HOF{\cdot}CH_3CN$.

(21) Meerwein, H.; Florian, W.; Schön, N.; Stopp, G. *Liebig's Ann. Chem.* **1961**, *641*, 1.

(22) Hafner, K.; Vöpel, K. H.; Ploss, G.; König, C. *Organic Syntheses*; Wiley: New York, 1973; Collect Vol. V, p 431.

(23) Gilchrist, T. L. In *The Chemistry of Functional Groups, Supplement C*; Patai, S., Ed.; Wiley: New York, 1983; Part 1, pp 383−419. Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, 1967.

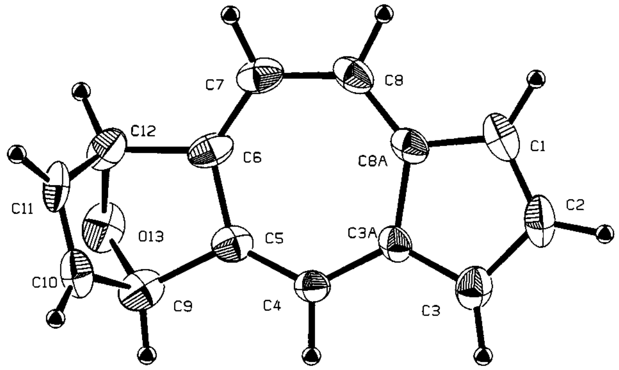
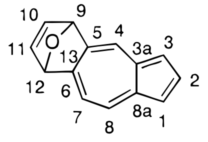


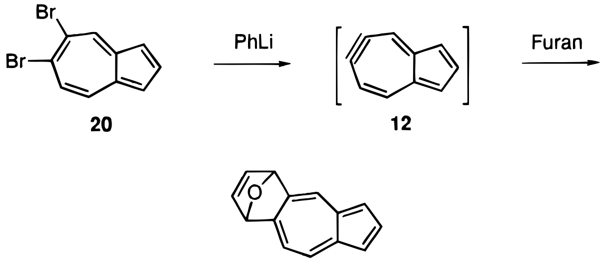
Figure 1. ORTEP drawing of **21** (30% probability ellipsoids).

Table 1. C−C and C−O Bond Lengths in Furan Derivative **21**



bond	length (pm)	bond	length (pm)
1, 2	137	3a, 8a	148
2, 3	143	5, 9	153
3, 3a	137	6, 12	156
3a, 4	142	9, 10	154
4, 5	136	9, 13	145
5, 6	142	10, 11	132
6, 7	135	11, 12	153
7, 8	143	12, 13	144
8, 8a	136		
8a, 1	141		

desired adduct **21** as a bluish-purple, microcrystalline powder after chromatography and sublimation. Evaporation of a methylene chloride solution of **21** yielded nearly black chunk crystals suitable for X-ray structure determination.



An ORTEP[24] drawing of the molecule appears in Figure 1, and bond distances are presented in Table 1. The data in the first two columns of the table reveal that fusion of a single furan ring onto the azulene skeleton does indeed induce bond alternation: the average difference in length of adjacent peripheral bonds is 6.0 pm (136.2 pm for the short bonds, 142.2 pm for the long ones). As expected, the bond bridging the 10π system is considerably longer than the peripheral bonds, 148 pm (cf. azulene itself, 149.8 pm).

After our work, a computational study was reported that addressed the question of how much energy is required to induce strong bond alternation in azulene. The level of theory employed was shown to reproduce well the experimental geometries of cyclic polyenes.[25] Geometry calculated at the RHF/6-31G* level was chosen for the localized structure, and the degree of bond alternation, average $|\Delta r| = 6.6$ pm, happens to be almost identical with that found in **21**. The single-point B3LYP/6-311+G** energy calculated for this geometry was compared with that for the geometry optimized at the same level, and found to lie just 2.6 kcal/mol above it. Thus, it is not surprising that fusion of a single furan ring onto the azulene skeleton is capable of causing marked bond alternation.

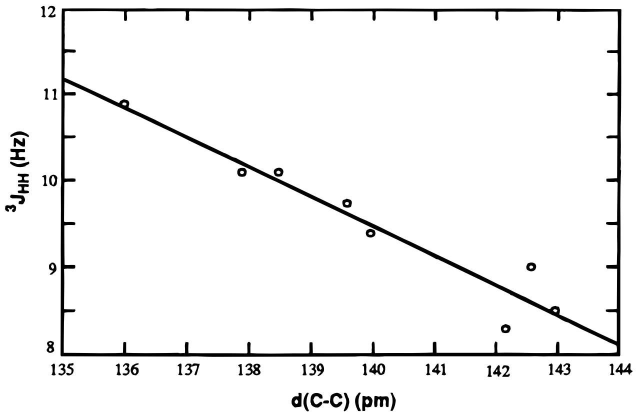
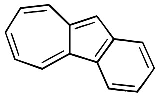


Figure 2. Vicinal proton coupling constants vs C−C bond lengths in the seven-membered ring of azulenes. The slope of the least squares line is −0.341 ± 0.039 and the intercept is 57.2 ± 5.5, with a standard deviation of 0.257.

In an NMR study by Bertelli and Crews,[26] vicinal proton coupling constants revealed bond alternation in benz[*a*]azulene (**22**). $^3J_{HH}$ values in the 7-ring alternated in magnitude: 10.9 Hz for the long bonds, 8.2 and 8.5 Hz for the short ones. Recently, Hansen et al.[27] have extended this work to 4-phenylbenz[*a*]azulene (**23**), for which they were also able to obtain an X-ray crystal structure. Their findings together with structural and NMR data for **21** and azulene make possible the correlation shown in Figure 2 between $^3J_{HH}$ and the C−C bond distance in the 7-ring of azulenes. While the correlation is rough, it will allow one to estimate the degree of bond alternation in an azulene for which X-ray data are unavailable.



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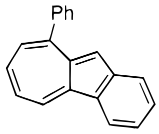

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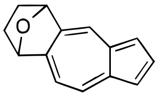
To gain a better understanding of the reasons underlying bond alternation induced by fusion of a furan ring to the azulene skeleton, the double bond at C_{10} was hydrogenated over palladium-on-charcoal, giving **24**. Crystals of the dihydro compound suitable for X-ray analysis were not obtained, but the ^1H NMR spectrum indicates a considerably smaller degree of bond alternation than in **21**: $^3J_{7,8} = 9.0$ Hz in **24**, as compared



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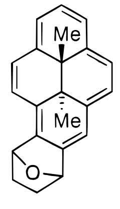
[24] Johnson, C. K., 1965, ORTEP Report ORNL-3794, Oak Ridge National Laboratory, TN.

[25] Nendel, M.; Houk, K. N.; Tolbert, L. M.; Vogel, E.; Jiao, H.; Schleyer, P.v. R. *J. Phys. Chem.* **1998**, *102*, 7191.

[26] Bertelli, D. J.; Crews, P. *Tetrahedron* **1970**, *26*, 4717.

[27] Bühl, M.; Kozminski, W.; Linden, A.; Nanz, D.; Sperandio, D.; Hansen, H.-J. *Helv. Chim. Acta* **1996**, *79*, 837.

with 8.5 Hz in **21** and 9.5 Hz in azulene (**11**). A small increase in the ring current is also apparent in **24** relative to **21**, as expected for a more delocalized π system. Averaged over all six protons in the azulene moiety, the difference is 0.12 ppm. These findings are consistent with the observation by Mitchell and Siegel[8] that the striking chemical shift perturbations found in **9** and **10a** are absent in **25** and **26**. Their calculations on the benzene derivative **27** also predict substantially less bond localization than that in **2**.



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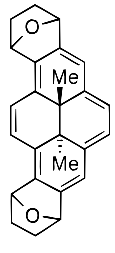

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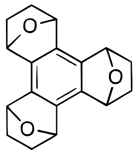

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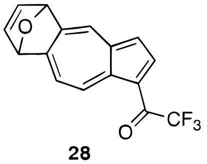
How does the $C_{10}-C_{11}$ double bond contribute to bond alternation in **21**? From the crystal structure and the tables of Mulliken,[28] the p−p overlap integral $(2p_\sigma,2p_\sigma + 2p_\pi,2p_\pi)$ between the ethylene and azulene π systems is calculated to be 0.131. Filled-orbital repulsion must be substantial, but should change very little with small changes in the 5,6-bond distance. Thus, the effect of the 10,11-π bond must be sought in differential stabilizing interactions. A simple model was adopted to pursue this query. Geometry-optimized at the semiempirical AM1 level of theory, azulene has strongly alternating bonds.[29] In particular, the 4,5- (and 6,7-) bonds measure 142 pm, while the 5,6- (and 7,8-) bonds measure 136 pm (almost identical with the corresponding long and short bonds in the crystal structure of **21**). In separate calculations, ethylene was allowed to interact with azulene at the 4,5-positions and at the 5,6-positions. In each case, second-order perturbation theory was employed to examine both the interactions between the π-orbital of ethylene and all five π^* orbitals of azulene and those between the π^* orbital of ethylene and all five of the π orbitals of azulene.[30] The energy change calculated in this way for **21** is −4.94 kcal/mol and that for its hypothetical bond-shift isomer is −1.70 kcal/mol, a difference of 3.24 kcal/mol. As expected, the frontier orbital interactions are major contributors to the stabilization of **21**, but the largest contribution comes from the ethylene HOMO-NLUMO interaction. While the results of this perturbation calculation are certainly not quantitatively significant, they may contribute to our understanding of the origin of the bond alternation in **21**. Apparently the lone pairs on oxygen do not contribute detectably to bond alternation; evidence supporting this surmise will be presented elsewhere.

The 10,11-π bond is not the whole story, however. Dihydro compound **24** seems to have some bond localization (as judged from $^3J_{7,8}$) and the benzene *syn*-**4**, also a bicyclo[2.2.1]hepteno derivative, definitely does. Very recently Kochi has made precise electron density measurements by X-ray diffraction on *syn*-**4**.[31] They provide a basis for rationalizing the bond alternation in terms of VSEPR theory, specifically in terms of repulsion between the electrons of the annellating bonds and those of the adjacent endo and exo bonds in the π system.[32]

Bond localization in azulene lowers the symmetry of its molecular orbitals, which raises the question whether the regiochemistry of some of its reactions could be significantly influenced by the alternation. In particular, HOMO coefficients at C_1 and C_3, the most reactive sites for electrophilic substitution, differ appreciably (0.416 vs 0.537, respectively) in azulene geometry-optimized at the AM1 level. For this reason, it seemed desirable to examine the question of regiochemistry experimentally in an azulene that actually has alternating bonds. Accordingly, **21** was allowed to react with trifluoroacetic anhydride in the presence of calcium carbonate.[33] Trifluoroacetyl derivatives **28** and **29** were formed in the ratio 8:3, *contrary* to the prediction of frontier orbital theory. This result can be understood in terms of two factors. First, the NHOMO of azulene, which lies slightly less than 1 eV below the HOMO, has smaller coefficients at C_1 and C_3 (0.386 vs 0.124, respectively) but a larger difference between them in favor of C_1. The effect of the HOMO distortion is therefore roughly canceled. Preference for **28** over **29** may reflect a difference in stability of the intermediate cations, modeled as **30** and **31** for the purpose of calculation. At the HF/6-31G*//3-21G level, **30** is lower in energy than **31** by 2.42 kcal/mol.



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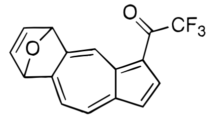
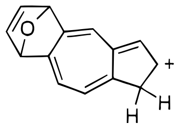
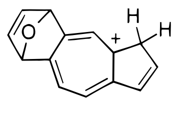


29



30



31

Conclusion

5,6-Azulyne (**12**) has been synthesized and trapped with furan to give the adduct **21**. The crystal structure of **21** reveals strongly alternating bonds in its 10-π system. Bond alternation in the azulene ring system is also apparent in the ^{1}H NMR spectrum, as there is a rough correlation between $^3J_{HH}$ and bond length in the 7-ring of azulenes. Hydrogenation of adduct **21** gave **24**, which has a smaller degree of bond localization as judged from the ^{1}H NMR spectrum. Thus, the "isolated" double bond of **21** is implicated as a cause of bond alternation. Consistent with this finding, a perturbation calculation indicates that stabilizing $\pi-\pi^*$ interactions of that bond with the azulene π system are greater in **21** than in its hypothetical bond-shift isomer. As proposed by Kochi for a bicycloannellated benzene,[31] mutual repulsion among bonding electron pairs at the ring fusion is probably also significant. Azulene's molecular orbitals are distorted somewhat by bond alternation, but FO theory predicts

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(28) Mulliken, R. S.; Rieke, C. A.; Orloff, D.; Orloff, H. *J. Chem. Phys.* **1949**, *17*, 1248.

(29) The Spartan package of programs was used. Hehre, W., Wavefunction, Inc.: 18401 Von Karman, Suite 370, Irvine, CA 92717.

(30) The value of β' was taken to be 1.44 eV, calculated as follows. The ratio of the overlap integrals for the 5,10- (and 6,11-) interaction (0.0653) to that for ethylene (0.272) was multiplied by the β for ethylene (6.00), assumed to be half the AM1 $\pi-\pi^*$ energy gap.

(31) Rathore, R.; Lindeman, S. V.; Kumar, A. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 6012.

(32) Other explanations that have been advanced for bond alternation in bicycloannellated aromatics include a tendency for π electrons to distort the σ framework (Shurki, A.; Shaik, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2205. Shaik, S.; Shurki, A.; Danovich, D.; Hiberty, P. C. *J. Mol. Struct. (THEOCHEM)* **1997**, *398−399*, 155. Hiberty, P. C.; Danovich, D.; Shurki, A.; Shaik, S. *J. Am. Chem. Soc.* **1995**, *117*, 7760), nonbonded repulsion between bridgehead atoms (Jemmis, E. D.; Kiran, B. *J. Org. Chem.* **1996**, *61*, 9006), and hyperconjugation involving the bridgehead carbon bonds (ref 7).

(33) Anderson, A. G.; Anderson, R. G. *J. Org. Chem.* **1962**, *27*, 3578.

incorrectly the regioselectivity of an electrophilic substitution on adduct **21**. Calculations suggest that the relative stability of intermediate cations may control the orientation of electrophilic attack in this case.

Experimental Section

Tetrabromothiophene,[19] 3,4-dibromothiophene (**16**),[18] and 6-dimethylaminofulvene (**18**)[21] were prepared according to literature methods. NMR spectra were recorded on a Varian Unity Plus 300 FT NMR spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 Series FTIR instrument, and UV/vis on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer. High-resolution mass spectrometric analyses were done by the Midwest Center for Mass Spectrometry at the University of Nebraska-Lincoln. Melting points were measured with a Thomas-Hoover Unimelt capillary melting point apparatus or, for **21** and **24**, a Fisher-Johns hot stage without correction. The X-ray structure determination was carried out by J.P.J.

6-Amino-5-chloroazulene (15). A solution of 1.0 g of 5,6-dichloroazulene (**13**) (5.1 mmol) in 20 mL of EtOH and 5 mL of 30% ammonia water (75 mmol) was sealed in metal bomb and heated to 160 °C for 24 h. Solvents were removed by rotary evaporator. The brown residue was dissolved in 50 mL of methylene chloride, washed with water, and dried over sodium sulfate. The extract was concentrated to 5 mL and then subjected to flash column chromatography (silica gel) using 100% hexane first. The hexane content in the eluent was gradually reduced to 2:8 hexane:methylene chloride, and 0.63 g of pure **15** was obtained as red crystals. Yield 70%, mp 87−88 °C. ^{1}H NMR ($CDCl_3$): δ 8.38 (s, H_4), 7.99 (d, $J_{7,8}$ = 10.8 Hz, H_8), 7.46 (t, $J_{1,2}$ = 3.9 Hz, H_2), 7.16 (m, H_1 and H_3), 6.55 (d, H_7), 5.17 (bs, $2H_N$). ^{13}C NMR ($CDCl_3$): δ 151.31, 138.35, 135.57, 132.72, 131.73, 131.47, 119.47, 119.33, 113.79, 109.33. IR (KBr, cm^{-1}): 3486, 3377 (N−H stretch), 1607, 1579, 1395, 1335, 946, 928, 832, 787, 752.

3,4-Dibromothiophene 1,1-Dioxide (17). To a 250-mL three-neck round-bottom flask fitted with a dropping funnel and a thermometer was added 20 mL (200 mmol) of 30% H_2O_2 and the mixture was stirred in a $CaCl_2$−ice bath (−15 to −20 °C). Trifluoroacetic anhydride (50 mL, 370 mmol) was added dropwise so that the temperature was kept below 5 °C. The solution was stirred for another 10 min, and 6 g (25 mmol) of 3,4-dibromothiophene (**16**) in 30 mL of methylene chloride was added all at once. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. Then the solution was transferred to an 1-L Erlenmeyer flask in an ice bath, and 500 mL of saturated sodium carbonate was slowly added to bring the pH up to around 5. The organic layer was separated and the aqueous layer was extracted with 40 mL of methylene chloride four times. The organic solutions were combined and washed with 30 mL of saturated sodium carbonate two times and 30 mL of water two times, then dried over $MgSO_4$. Solvents were removed on a rotary evaporator, and the remaining yellowish-orange oil was mixed with 20 mL of ethanol and stored in a refrigerator. After 12 h, pale yellow, chalky crystals were collected and washed with cold ethanol (4.7 g, 69% yield). Mp 104−106 °C (lit.[19] mp 106 °C). ^{1}H NMR ($CDCl_3$): δ 6.84 (s).

5,6-Dibromoazulene (20). To a solution of 3.04 g (11 mmol) of 3,4-dibromothiophene 1,1-dioxide (**17**) in 10 mL of chloroform was slowly added 1.35 g (11 mmol) of 6-dimethylaminofulvene (**18**), and the solution was refluxed under N_2 for 5 h. Volatiles were removed on a rotary evaporator, leaving a black tar that was stirred in 10 mL of warm hexane (40−50 °C) until all the tar turned to fine powder. The liquid and powder were loaded on a silica gel column and subjected to flash column chromatography using hexane as the eluent. Blue crystals of pure **20** were obtained (1 g, 32% yield), mp 185 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.80 (s, H_4), 7.99 (d, $J_{7,8}$ = 10.8 Hz, H_8), 7.95 (t, $J_{1,2}$ = $J_{2,3}$ = 3.8 Hz, H_2), 7.74 (d, H_7), 7.42 (d, H_1 or H_3), 7.38 (d, H_3 or H_1). ^{13}C NMR ($CDCl_3$): δ 139.63, 138.82, 137.81, 137.24, 136.10, 133.02, 126.28, 120.59, 120.55, 120.03. MS *m*/*e*: 284 (M^+), 126 ($C_{10}H_6^+$, base). IR (polyethylene, cm^{-1}): 1572, 1496, 1398, 1194, 1144, 1009, 908, 824, 754. Anal. Calcd for $C_{10}H_6Br_2$: C, 42.00; H, 2.11. Found: C, 42.01; H, 2.16.

7-Oxabicyclo[2.2.1]hepta-2,5-dieno[2,3-*f*]azulene (21). All the glassware used was dried in a 170 °C oven overnight. Tetrahydrofuran was distilled from potassium benzophenone ketyl. 5,6-Dibromoazulene (**20**) (100 mg, 0.35 mmol) in 20 mL of dry THF was stirred in a 100-mL, three-neck, round-bottom flask under dry N_2. One milliter of furan (12 mmol) was added through a 10-mL syringe packed with 5 mm of activated 4 Å molecular sieves, and the system was flushed with dry N_2 three times. Then 300 μL of 1.8 M phenyllithium (0.54 mmol) was added dropwise with stirring; stirring was continued at room temperature under dry N_2 for 6 h. Water (8 mL) was added and THF was removed on a rotary evaporator. The remaining turbid solution was extracted with 12 mL of methylene chloride three times; the combined extract was washed with 10 mL water twice, then dried over $MgSO_4$. Methylene chloride was removed on a rotary evaporator, and the residual oil was loaded onto a silica gel column. Flash column chromatography using hexane with a gradual change to 2.5% ether in hexane eluted a teal band after starting materials and products of nucleophilic attack. Solvent was removed and the residue was sublimed at 2 mmHg and 70−80 °C to give 15 mg of **21** as purple blue powder (22% yield). Mp 139.5−140 °C. ^{1}H NMR ($CDCl_3$): δ 8.15 (s, H_4), 8.10 (d, $J_{7,8}$ = 8.5 Hz, H_8), 7.71 (t, $J_{1,2} \sim J_{2,3}$ = 3.8 Hz, H_2), 7.20−7.23 (m, H_7, H_1, and H_3), 6.99−7.12 (m, $J_{10,11}$ = 3.6 Hz, $J_{9,10}$ = $J_{11,12}$ = 1.8 Hz, H_{10} and H_{11}), 5.79 (bs, H_9), 5.71 (bs, H_{12}).^{13}C NMR ($CDCl_3$): δ 155.52, 143.23, 141.62, 140.60, 139.31, 136.28, 135.75, 135.55, 127.59, 119.76, 119.49, 116.68, 86.16, 85.50. MS *m*/*e*: 194 (M^+), 165 ($M^+ - CHO$, base). IR (polyethylene, cm^{-1}): 2920, 2848, 1589, 1378, 1281, 1262, 1002, 881, 853, 802, 757. UV/vis (CH_2Cl_2): λ (ϵ) 584 (314), 633 (sh, 248), 703 (sh, 88), 429 (1007), 404 (657), 368 (sh, 2095), 368 (581), 355 (3654), 339 (3427), 287 (48699), 297 (sh, 41037). HRMS Calcd for $C_{14}H_{10}O$: 194.0732. Found: 194.0730.

7-Oxabicyclo[2.2.1]hept-2-eno[2,3-*f*]azulene (24). To a two-neck, 5-mL, round-bottom flask was added 10 mg (0.05 mmol) of 7-oxabicyclo-[2.2.1]hepta-2,5-dieno[2,3-*f*]azulene (**21**) in 2 mL of ether with <1 mg of 10% Pd on C. The system was flushed with H_2 three times, then stirred under a H_2 balloon at room temperature for 5 h. The catalyst was removed by filtration through a cotton wad, and ether was removed by aspirator. Sublimation of the remaining solid at 2 mmHg and 60−70 °C gave 9.5 mg of **24** as blue powder (94% yield). Mp 83−84 °C. ^{1}H NMR ($CDCl_3$): δ 8.30 (d, $J_{7,8}$ = 9.0 Hz, H_8), 8.28 (s, H_4), 7.85 (t, $J_{1,2}$ = $J_{2,3}$ = 3.8 Hz, H_2), 7.37 (d, H_1 and H_3), 7.17 (d, H_7), 5.54 (d, $J_{9,10exo}$ = 3.6 Hz, H_9), 5.47 (d, $J_{11exo,12}$ = 3.6 Hz, H_{12}), 2.14−2.19 (m, H_{10exo} and H_{11exo}), 1.48−1.60 (m, H_{10endo} and H_{11endo}). ^{13}C NMR ($CDCl_3$): δ 153.88, 139.99, 138.82, 137.87, 136.59, 136.33, 128.05, 118.96, 118.24, 114.49, 83.19, 82.35, 27.08, 26.48. IR (polyethylene, cm^{-1}): 2882, 2950, 2920, 2848, 1584, 1492, 1386, 1275, 1238, 1178, 1086, 1010, 974, 927, 884, 848, 814, 757, 566. UV/vis (CH_2Cl_2): λ (ϵ) 577 (305), 624 (sh, 251), 691 (sh, 89), 348 (4786), 341 (sh, 2884), 333 (3000), 282 (57480), 287 (sh, 53728), 300 (sh, 8121). HRMS Calcd for $C_{14}H_{12}O$: 196.0888. Found: 196.0882.

X-ray Structure Determination. Data collection was done at ambient temperature on a Rigaku AFC-6S Diffractometer with graphite-monochromated molybdenum Kα radiation (λ = 0.71069 Å). The structure was solved by direct methods,[34,35] and neutron scattering factors were obtained from Cromer and Waber.[36] Twenty reflections were used for the unit cell determination, corresponding to an orthorhombic cell in the space group $P2_12_12_1$ (no. 19) with these lattice parameters: a = 7.908(2) Å, b = 21.361(2) Å, c = 5.900(2) Å, V = 996.6(4) Å^3. For Z = 4 and formula weight 194.23, the calculated density was 1.294 g/cm^3. A total of 1385 reflections were measured. R = 0.043 (Rw = 0.037).

1- and 3-Trifluoroacetyl-7-oxabicyclo[2.2.1]hept-2-eno[2,3-*f*]-azulene (28 and 29). A solution of 5 mg (0.026 mmol) of **9** and 20 mg (0.2 mmol) of $CaCO_3$ in 1 mL of carbon tetrachloride (dried with 4 Å molecule sieves) protected from moisture with a drying tube was

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(34) SHELX: Sheldrick, G. M.; Kruger, C.; Goddard, R. In *Crystallographic Computing 3*; Oxford University Press: New York, 1985; pp 175−189.

(35) All calculations were carried out with the TEXSAN, TEXRAY Structure Analysis Package, version 2.1, of Molecular Structure Corporation: The Woodlands, TX.

(36) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.3.1 and 2.2A.

treated with 5.6 μL (0.039 mmol) of trifluoroacetic anhydride (TFAA). The color of the solution quickly changed from blue to red. The mixture was stirred at room temperature for 5 min and excess TFAA was then decomposed by the careful addition of 0.5 mL of 5% aqueous sodium bicarbonate with stirring. The separated red organic phase was washed three times with 0.5-mL portions of water and dried over anhydrous sodium sulfate. Solvent was removed on a steam bath, and the residue was dissolved in $CDCl_3$. ^1H NMR revealed an 8:3 mixture of **28** and **29**: δ 9.76 (s, H_4 of **29**), 9.69 (d, $J_{7,8} = 9.3$ Hz, H_8 of **28**), 8.39 (d, $J_{7,8} = 9.3$ Hz, H_8 of **29**), 8.31 (s, H_4 of **28**), 8.30−8.34 (m, H_2 of **28**), 8.10−8.14 (m, H_2 of **29**), 7.69 (d, H_7 of **28**), 7.68 (d, H_7 of **29**), 7.09−7.26 (m, H_1, H_3, H_{10}, H_{11}), 6.00 (bs, H_9 of **29**), 5.87 (bs, H_9 of **28**), 5.86 (bs, H_{12} of **29**), 5.84 (bs, H_{12} of **28**).

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Supporting Information Available: Additional information regarding the X-ray structure determination (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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