

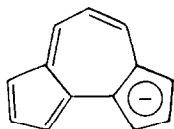
1,6- AND 2,6-DI-t-BUTYL-CYCLOPENT[f]AZULENIDE;
DOUBLE BOND LOCALIZATION IN A PLANAR 14 π -PERIMETER

Klaus Hafner* and Georg F. Thiele

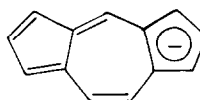
Institut für Organische Chemie der Technischen Hochschule
Petersenstr. 22, D-6100 Darmstadt

Summary: The stable diatropic 1,6- and 2,6-di-t-butyl-cyclopent[f]azulenides 9a and b are prepared and shown to be dominated by polymethide conjugation rather than by 14 π -perimeter conjugation.

For the study of models, describing the conjugation in polycyclic π -systems, symmetrical nonbenzenoid carbanions, such as cyclopent[e]azulenide (1) and cyclopent[f]azulenide (2), are of particular interest.

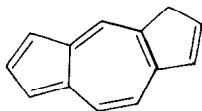


1

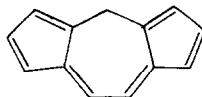


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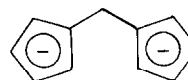
Contrary to the recently prepared cyclopent[e]azulene¹, cyclopent[f]azulene (3) is not easily available by the Ziegler-Hafner azulene synthesis. Therefore, we have chosen an approach via its 4H-tautomer 4, which could be formed by condensation of glyoxal with the methylene-dicyclopentadienide ion (5).



3

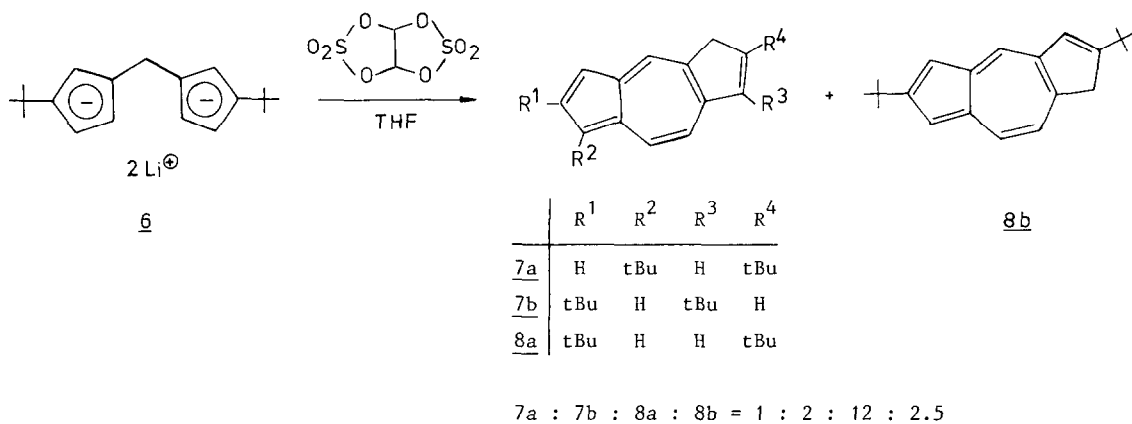


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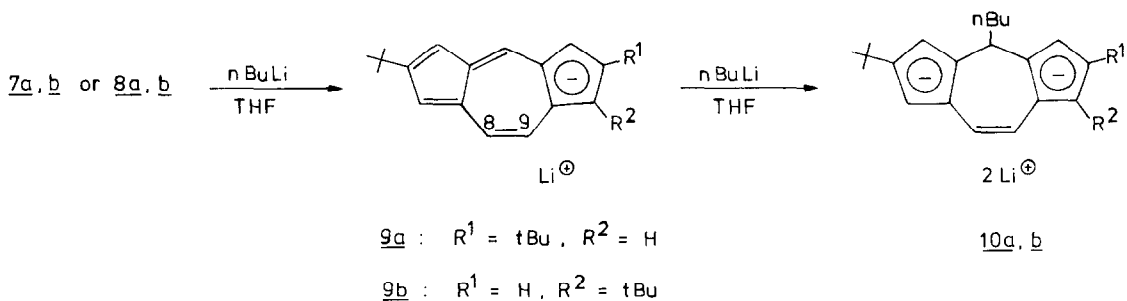


5

While attempts to prepare 3 by condensing 5 with glyoxalic sulfate have been unsuccessful so far, the di-*t*-butyl derivative 6² condenses with glyoxalic sulfate in tetrahydrofuran to give a mixture of four isomeric di-*t*-butyl-cyclop[*f*]azulenes in 5 % yield. Column chromatography with pentane on alumina separates this mixture into those of 7a,b and 8a,b.



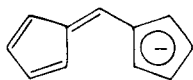
When the mixture 8a,b is treated with equimolar *n*-butyllithium in tetrahydrofuran, the colour changes immediately from blue to orange red. The ¹H-NMR spectrum indicates the formation of a single anion 9a, thus confirming the structures assigned to 8a,b. Excess *n*-butyllithium adds to the 4-position to give the dianion 10a. With the mixture 7a,b, similar unsymmetrically substituted species 9b and 10b are formed.



The simple four line ¹H-NMR spectrum of 9a shows the anion to be symmetrical, at least on the NMR time scale. The negative charge is located at the five membered rings, shifting the five ring proton signals upfield. When the extra shielding by the negative charge is taken into account, 9a appears to be as strongly diatropic as the azulene hydrocarbons 8a,b.

Solutions of 9a in tetrahydrofuran are stable at room temperature under an inert atmosphere for at least 24 hours. Upon the addition of water, the mixture 8a,b is recovered without decomposition. The hydrocarbons 8a,b are more acidic than cyclopentadiene, since they are completely deprotonated by a 1:1 mixture of cyclopentadiene and lithium cyclopentadienide in tetrahydrofuran.

π -SCF calculations³ on the parent anion 2 predict it to be symmetrical with an essentially localized double bond between C-8 and C-9. Thus it resembles the open chain analogue 11.⁴



11

A quantitative estimate of the contribution of substructure 11 to the π -system of 2 can be obtained by calculating delocalization energies with the appropriate reference states. With "pentafulvene + cyclopentadienide + conjugation across a single bond"⁵ as the reference state for 11, the delocalization energy of 11 is calculated as 22.6 kcal/mol. This will also be the contribution of substructure 11 to the π -system of 2. The remaining contribution of the 14π -perimeter conjugation can then be calculated, using "11 + localized double bond + conjugation across two single bonds" as the reference state for 2. The value of 4.7 kcal/mol thus obtained is significantly smaller than the one calculated above. Apparently, the polymethide delocalization of 11 is dominating over the 14π -perimeter delocalization in determining the electronic structure of 2, leading to double bond localization between C-8 and C-9 in the seven membered ring.

These theoretical results are confirmed by the ¹H-NMR spectra of the unsymmetrical anions 9b and 10b. Both species show similar coupling constants $J_{8,9} = 11.1$ Hz and 11.0 Hz, which are somewhat larger than those of hydrocarbons 7a,b (10.1 Hz and 10.2 Hz), where the C-8, C-9 bond is part of the delocalized azulene π -system.

Selected spectroscopic data of compounds 7 - 10⁶

UV: 8a,b: λ_{\max} (lg ϵ) (n-hexane) = 218 sh(4.14), 229 (4.08), 237 (4.06), 244 (4.00), 253 (3.84), 303 (4.83), 306 (4.81), 315 (4.66), 348 (3.69), 356 (3.77), 362 (3.84), 371 (3.97), 382 (3.94), 391 (4.26), 552 (2.42), 577 (2.51), 618 (2.45), 625 (2.45), 662 (2.07), 683 (2.01), 691 nm (2.03).

9a: λ_{\max} (n-hexane) = 428, 448 nm.

¹H-NMR: 7b: (CDCl₃) δ = 1.46(s, 9H, tBu), 1.46(s, 9H, tBu), 3.58(d, J = 2.1Hz, 2H, 3-H), 6.54(t, J = 2.1Hz, 1H, 2-H), 7.16(d, J = 1.7Hz, 1H, 5-H or 7-H), 7.23(d, J = 1.7Hz, 1H, 5-H or 7-H), 7.65(d, J = 10.4Hz, 1H, 9-H), 8.23(d, J = 10.4Hz, 1H, 8-H), 8.34 ppm(s, 1H, 4-H).
8a: (CDCl₃) δ = 1.29(s, 9H, 2-tBu), 1.45(s, 9H, 6-tBu), 3.71(s, 2H, 3-H), 6.64(s, 1H, 1-H), 7.15(s, 1H, 5-H or 7-H), 7.16(d, J = 9.7Hz, 1H, 9-H), 7.19(s, 1H, 5-H or 7-H), 8.17(d, J = 9.7Hz, 1H, 8-H), 8.26 ppm(s, 1H, 4-H).

- 9a: (THF-d₈) δ = 1.32(s, 18H, tBu), 6.27(br s, 4H, 1,3,5,7-H), 6.85(s, 2H, 8,9-H), 7.95 ppm(s, 1H, 4-H).
- 9b: (THF-d₈) δ = 1.20(s, 9H, tBu), 1.30(s, 9H, tBu), 6.28(d, J = 2.1Hz, 1H, 5-H or 7-H), 6.32(d, J = 4.1Hz, 1H, 3-H), 6.34(d, J = 2.2Hz, 1H, 5-H or 7-H), 6.56(d, J = 4.1Hz, 1H, 2-H), 6.88 (d, J = 11.1Hz, 1H, 8-H), 7.34(d, J = 11.1Hz, 1H, 9-H), 7.99 ppm (s, 1H, 4-H); all other signals hidden by solvent.
- 10a: (THF-d₈) δ = 1.14(s, 18H, tBu), 5.28(d, J = 2.7Hz, 2H, 1,7- or 3,5-H), 5.37(d, J = 2.7Hz, 2H, 1,7- or 3,5-H), 5.92 ppm(s, 2H, 8,9-H); all other signals hidden by solvent.
- 10b: (THF-d₈) δ = 3.43(t, J = 7.5Hz, 1H, 4-H), 5.14 (d, J = 3.1Hz, 1H, 3-H), 5.31(d, J = 2.7Hz, 1H, 5-H or 7-H), 5.39(d, J = 3.3Hz, 1H, 2-H), 5.39(d, J = 2.4Hz, 1H, 5-H or 7-H), 6.12(d, J = 11.0Hz, 1H, 8-H), 6.47 ppm(d, J = 11.0Hz, 1H, 9-H); all other signals hidden by solvent.

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5. The values for the "conjugation across a single bond" and a "localized double bond" have been derived from π -SCF calculations on 1,3-butadiene and 1,3,5-hexatriene with torsion angles of 90° and 180° across the C-C single bond.
6. The structures of compounds 7 - 10 have been assigned on the basis of their 300 MHz ¹H-NMR spectra (Bruker WM 300 spectrometer), using NOE difference spectroscopy when necessary. UV spectra were recorded with a Beckman UV 5240 spectrometer.

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