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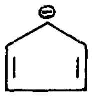
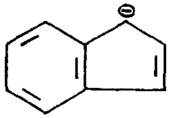
A REMARKABLY STABLE AROMATIC ANION, CYCLOPENT[e]AZULENIDE

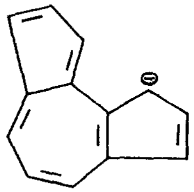
Zen-ichi Yoshida,* Mitsuhiro Shibata, and Toyonari Sugimoto
Department of Synthetic Chemistry, Kyoto University
Yoshida, Kyoto 606, JAPAN

Summary: The titled anion was obtained by *n*-butyllithium treatment of a mixture of 1H- and 3H-cyclopent[e]azulenes in THF at -30°C. The ^{1}H- and ^{13}C-nmr spectra indicate a considerably large peripheral π-conjugation due to an aromatic 14π electron structure.

The π conjugation mode in anionic polycyclic systems is of considerable interest. For example, indenide is a more unstable anion compared with cyclopentadienide, where a benzene unit fusion to the latter disrupts 6π electron conjugation of cyclopentadienide ring and does not afford a peripheral 10π electron system.[1] In contrast with this, we now found that an azulene unit fusion to cyclopentadienide stabilizes a resultant anionic spieces, cyclopent[e]azulenide (**1**) due to a peripheral 14π electron conjugation.



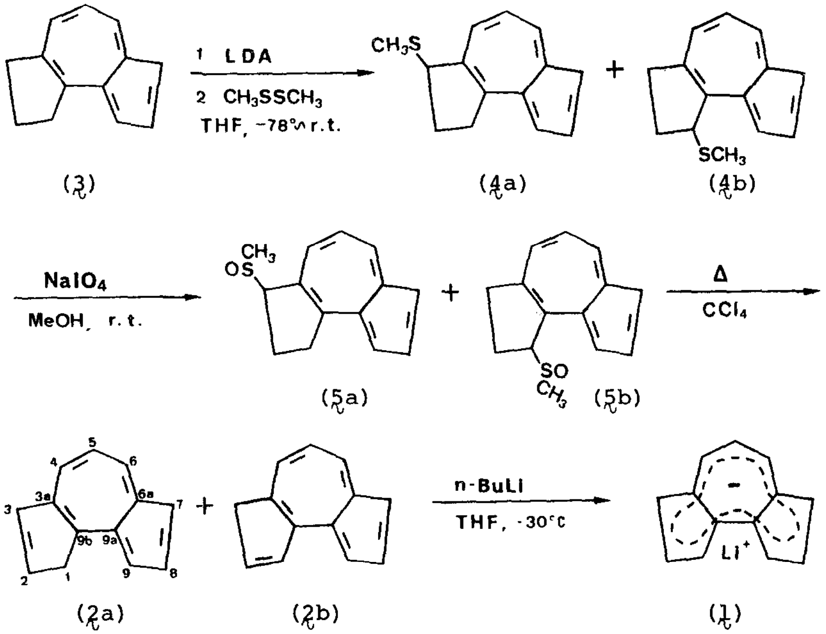




(**1**)

The conjugated acid of **1**, cyclopent[e]azulene (**2**) was readily synthesized from 4,5-cyclopentenoazulene (**3**)[2] according to Scheme 1. Thus, **3** was treated with an equimolar lithium diisopropylamide, followed by reaction with dimethyl disulfide to give *ca.*1:1 mixture of 3'- and 5'-methylthio-substituted derivatives ((**4a**) and (**4b**))[3] in 35% yield. Sodium metaperiodate oxidation of the mixture in methanol at r.t. afforded the corresponding sulfoxides ((5a) and (5b))[3] in almost quantitaive yield. Subsequent refluxing of the sulfoxides in CCl_4 and purification by column chromatography on alumina gave a mixture of 1H- and 3H-regioisomers of 2 ((2a) and (2b)) as a blue oil[3,4] in 41% yield. The ratio of 2a and 2b in the mixture[5] was

Scheme 1



determined to be 3:7 from the 400 MHz ^{1}H-nmr spectrum ($CDCl_3$): 2a δ 8.20 (d, 1H, H_6, J=9.8Hz), 7.81 (t, 1H, H_8, J=3.7Hz), 7.60 (d, 1H, H_4, J=9.8Hz), 7.36 (d, 1H, H_7 or H_9, J=3.2Hz), 7.21 (d, 1H, H_7 or H_9, J=2.4Hz), 7.08 (t, 1H, H_5, J=9.8Hz), 6.80 (dt, 1H, H_3, J=5.6, 1.8Hz), 6.40 (dt, 1H, H_2, J=5.6, 2.2Hz) and 4.06 (t, 2H, H_1, J=2.0Hz); 2b δ 8.29 (d, 1H, H_6, J=9.5Hz), 7.83 (t, 1H, H_8, J=3.7Hz), 7.67 (d, 1H, H_4, J=9.8Hz), 7.53 (dtd, 1H, H_1, J=5.6, 1.8, 0.7Hz), 7.48 (d, 1H, H_7 or H_9, J=3.9Hz), 7.33 (d, 1H, H_7 or H_9, J=2.9Hz), 7.00 (t, 1H, H_5, J=9.8Hz), 6.95 (dt, 1H, H_2, J=5.6, 2.1Hz) and 3.73 (bs, 2H, H_3).

When 2 was reacted with an equimolar *n*-butyllithium in d_8-THF at -30°C, the solution immediately turned from blue to reddish purple,[6] whose ^{1}H- and ^{13}C-nmr spectra showed the formation of 1. Under a thoroughly oxygen-free condition 1 remained unchanged even at r.t. for a long time (>1 week). Table I summarizes the nmr spectral data. Both the spectra revealed

Table I. The ^{1}H- and ^{13}C-nmr spectral data of **1** in d_8-THF at -30°C.

	^{1}H-nmr, δ (ppm)	^{13}C-nmr (ppm)	
$H_{1,9}$	6.26 (bd, 2H, J=4.2Hz)	$C_{1,9}$	103.2
$H_{2,8}$	6.69 (t, 2H, J=4.2Hz)	$C_{2,8}$	124.2
$H_{3,7}$	6.60 (bd, 2H, J=4.2Hz)	$C_{3,7}$	109.5
$H_{4,6}$	7.56 (d, 2H, J=9.6Hz)	$C_{4,6}$	133.3
H_5	6.05 (t, 1H, J=9.6Hz)	C_5	107.9, $C_{9a,9b}$ 135.3, $C_{3a,6a}$ 132.3

no change also when measured at -65°C. Obviously, **1** has a C_{2v} symmetry space group. The chemical shift values were compared with those of azulene (Fig. 1).[7] As seen from Fig. 1a, all the protons of **1** shift by 0.2 ∿ 1.1 ppm to a higher magnetic field as compared with those of azulene. In particular, the shifts of H_1, H_2 and H_5 protons are remarkable. The tendency of shift to a higher magnetic field was also observed for all the carbons, among which the C_1 and C_5 atoms revealed a largest shift (*ca.* 15 ppm) (see Fig. 1b). These results indicate a considerably large π-conjugation on a peripheral framework due to an aromatic 14π electron structure. Further evidence can be provided by the appearance of diamagnetic ring current on **1**. Thus, when compared with the ^{1}H-chemical shift (δ 5.2 ∿ 5.9) of phenalenide (**6**),[8] a non-aromatic, tricyclic anionic system with an isoelectronic structure to **1**, all the

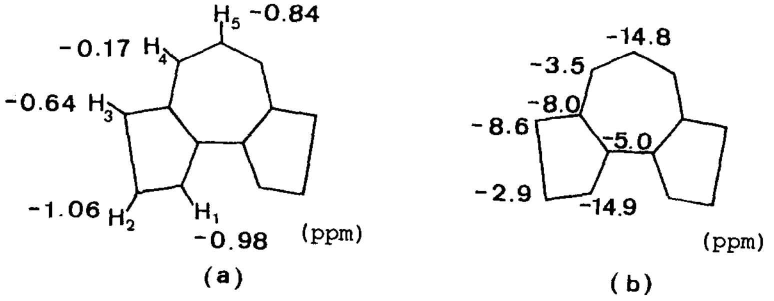
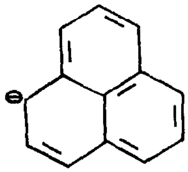


Fig. 1 The difference in ^{1}H- (a) and ^{13}C- (b) chemical shift values between **1** and azulene.

protons of 1 appear in a fairly lower magnetic field (δ 6.1 ∿ 7.6).

An average pK_a of 2 was approximately estimated by reference to acidities of other compounds. By the reaction of 2 with an equimolar lithium cyclopentadienide in THF at -78°C was obtained a reddish purple solution as observed above. Treatment of the solution with an excess of methyl iodide afforded a mixture of 1- and 3- methyl-substituted derivatives of 2[9] in quantitative yield. While, the use of lithium malononitrile as a base revealed no formation of 1, thereby suggesting that an average pK_a of 2 ranges between 12 and 15, the respective pK_a's of malononitrile and cyclopentadiene. It is noteworthy that the stability of 1 presents a striking contrast to that of cyclopent[a]azuleneide (7), one of some isomers obtained by azulene unit fusion to cyclopentadienide, whose conjugated acid was estimated to have a very high pK_a value (*ca.* 22)[10] comparable with those of phenalene and indene.



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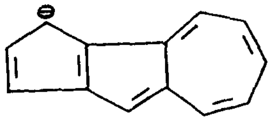

(7)

References and Notes

1. E. Buncel, "Carbanions: Mechanistic and Isotopic Aspects", Elsevier, Amsterdam (1975).
2. C. Jutz and E. Schweiger, *Synthesis*, 193 (1974).
3. All new compounds have been fully characterized by spectra (IR, NMR and Mass). Also, satisfactory elemental analyses were obtained.
4. The uv spectrum of the mixture is as follows: $\lambda_{max}^{CH_2Cl_2}$ (log ε) 266 (4.28), 294(4.36), 340(3.43), 356(3.49), 370(3.34), 384(3.10), 580(2.63), 624(2.59), and 690 nm(2.18).
5. Before purification by the column chromatography, the ratio of 2a and 2b was *ca.* 1:1, while the value changed to 3:7 for the chromatographed 2 as a result of isomerization on alumina.
6. The reddish purple solution revealed a longest wave-length absorption band near 524 nm.
7. J.-R. Llinas, D. Roard, M. Derbesy, and E.-J. Vincent, *Can. J. Chem.*, 53, 2911 (1975).
8. H. Prinzbach, V. Freudenberger, and U. Scheidegger, *Helv. Chim. Acta.*, 50, 1087 (1967).
9. From the 400 MHz nmr spectrum of the reaction mixture, the formation ratio of 1- and 3-methyl-substituted derivatives was determined to be *ca.* 6:1.
10. R. Fleischer, K. Hafner, J. Wildgruber, P. Hochmann, and R. Zahradník, *Tetrahedron*, 24, 5943 (1968).

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