Bicyclo[6.3.0]**undecapentaenyl** Anion: The Next Higher Homolog of the Indenyl Anion with Exceptionally Large Ion-Pairing Effects on its Tropicity

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Abstract: The title anion 1 was generated as a fairly thermally stable species in tetrahydrofuran (THF) and dimethylsulfoxide (DMSO) by the action of several bases (sodium hydride, potassium hydride, lithium diisopropylamide, and lithium hexamethyldisilazide) with bicyclo[6.3.0]undecaappropriate pentaenes. Variable-temperature ¹H NMR spectra of **1**·Li⁺ in [D₈]THF reveal that the anion exhibits exceptionally large ion-pairing effects; proton chemical shifts vary by more than 1 ppm as a function of ion-pairing conditions. Thus, anion 1, in a contact ion pair (Li⁺ at ambient temperature in THF), behaves as an aromatic cyclopentadienyl anion that is perturbed only slightly by the electronic effects of a paramagnetic cyclooctatetraene (COT), whereas **1** in a separated ion pair (Li⁺ at low temperatures in THF or at ambient temperature in DMSO) behaves as an overall paratropic species with a 12 π -electron periphery. ¹³C NMR spectroscopy indicates no major skeletal rearrangement and only small variations of the electron density. The variable tropicity of **1** can be as-

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Introduction

Bicyclo[6.3.0] undecapentaenyl anion **1** is a derivative of cyclopentadienyl anion **3**, fused with COT. It is the next

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cribed to small conformational changes of the molecule. In addition to its unusual, tunable tropicity, anion 1 can also serve as a versatile building block for the synthesis of cyclopentanoid conjugated systems fused to a fully unsaturated eight-membered ring. A theoretical calculation predicts that the 10-position of **1** should have the highest electron density. In agreement with this prediction, the reactions of **1** with electrophiles occur predominantly at the 10-position. The corresponding ferrocene, two fulvenes, two diazo derivatives, and a COT-fused azulene were obtained by the reactions of 1 with appropriate electrophiles.

higher homolog of indenyl anion 2. Despite its simple and fundamental structure, anion 1 has not previously been characterized well. In contrast to 2, a rigid [4n+2] annuleno-[4n+2]annulene system, anion **1** represents a flexible [4n]annuleno[4n+2]annulene system.^[1,2] Benzocyclooctatetraene (benzoCOT) $4^{[2]}$ which is an isoelectronic relative of 1, exhibits little antiaromatic character as a peripheral conjugated system because its COT ring largely deforms from planarity.^[3] On the other hand, compound 1 is an anionic system and electron repulsion should promote delocalization of the negative charge throughout the entire molecule. This tendency should increase the $4n \pi$ -electron character of the overall molecule and perturb the electronic properties of the cyclopentadienyl anion moiety as a [4n+2] π -electron system. The counterbalance between the partial aromatic character of the five-membered ring and the peripheral antiaromatic character should determine the overall electronic and magnetic properties of 1.^[4,5] One of the other isoelectronic relatives of 1, the bicyclo[6.5.0]tridecahexaenyl cation 5, suffers from valence isomerization to a tricyclic isomer 6 by a symmetry-allowed pericyclic ring-closure reaction to escape antiaromatic destabilization.^[6] Spectral data for 1 provide no evidence for the presence of tricyclic isomer 7. Although anion 1 remains bicyclic, contrary to 5, it shows exceptionally large ion-pairing effects in the ¹H NMR spectra ($\Delta \delta > 1$ ppm). We describe and discuss herein these ion-pairing effects. Moreover, anion 1 can serve

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as a versatile synthetic building block for cyclopentanoid compounds fused with an unsaturated eight-membered ring. The synthesis and some properties of fulvene, azulene, diazo, and ferrocene derivatives are described.



Results and Discussion

Generation of 1 and NMR Spectroscopy Studies

Six structural isomers of bicyclo[6.3.0]undecapentaene (8– 13) all represent promising precursors to anion 1. Among them, four isomers 8, 9, 11, and 12 are known. Dürr and Scheppers previously prepared bicyclo[6.3.0]undeca-1(8),2,4,6,9-pentaene (8) and bicyclo[6.3.0]undeca-1(11),2,4,6,9-pentaene (9) by the reaction of benzene and cyclopentadienylidene, generated in situ from photodecomposition of diazocyclopentadiene 14 (Scheme 1).^[7] Treatment



Scheme 1. Synthesis of structural isomers of bicyclo-[6.3.0] undecapentaene, which are all promising precursors to anion 1. Py = pyridine, THF = tetrahydrofuran.

of a mixture of pentaenes 8 and 9 with Py afforded 1,4,6,8,10-bicyclo[6.3.0]undecapentaene (12) in high yield. Results indicate that anion 1 forms reversibly as an intermediate and undergoes reprotonation at the 3-position to give 12.

The optimized structure and electron densities of **1** have been calculated by the PM3 method.^[8,9] The results predict





Figure 1. Optimized structures of anion 1 from PM3 calculations. a) Top view and electron density. b) Side view and dihedral angle between bonds C2-C3 and C4-C5.

that the anion possesses a nonplanar structure (Figure 1), with a dihedral angle between the C2–C3 and the C4–C5 bonds of 123.1°. Moreover, the electron density at the 10-position of **1** is the highest, whereas those of the 3- and 6-positions are the second highest. Thus, compound **12** is not the product expected from kinetically favored protonation of **1**, but appears to be formed under conditions of thermo-dynamic control. Scott and Brunsvold prepared bicyclo-[6.3.0]undeca-1(11),3,5,7,9-pentaene (**11**) from 7-iodobicyclo[5.3.1]undeca-1,3,5,9-tetraene through a skeletal rearrangement.^[10]

In the first published attempt to prepare anion 1, Schonleber reported that treatment of 12 with *n*BuLi afforded butyl adduct 15 instead of 1 (Scheme 1).^[11] Thus, compound 12 behaves as a pentafulvene derivative. This result indicates that bicyclo[6.3.0]undecapentaenes without a pentafulvene moiety should be better choices as precursors to anion 1.

Bicyclo[6.3.0]undecapentaenyl anion **1** was generated as deep purple solutions from **8** or **9** under several basic conditions (*n*-butyllithium, lithium diisopropylamide (LDA), lithium hexamethyldisilazide (LHMDS), NaH, KH in [D₈]THF, and KH in [D₆]DMSO; Figure S1 in the Supporting Information). ¹H and ¹³C NMR spectra reveal the clean formation of **1** because the signals are reasonably assignable to the structure of **1**. The anion is fairly stable thermally under inert gas atmospheres; no spectral change was observed upon heating the anion solution at 50 °C for 6 h. To our surprise, however, the ¹H NMR spectrum of **1**·Li⁺ in [D₈]THF at 21 °C differed drastically from that of **1**·Li⁺ in [D₆]DMSO at 22 °C (Figure 2).

In [D₈]THF at 21 °C, the average chemical shifts of the five-membered ring protons (H9–H11) and the eight-membered ring protons (H2–H7) of 1·Li⁺ are δ =5.12 and 4.77 ppm, respectively. This value for the five-membered ring protons is shifted only 0.22 ppm upfield from that of cyclopentadienyl anion 3 (δ =5.34 ppm).^[12] Thus, the effect of any paratropic ring currents associated with peripheral conjugation does not seem to be large under these conditions. On the other hand, compared with the average chemical

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Figure 2. ¹H NMR spectra (500 MHz) of 1 Li^+ a) in [D₆]DMSO and b) in [D₈]THF at 21 °C.

shifts of the eight-membered ring protons of **4** ($\delta = 6.09 \text{ ppm}$),^[4] the value for **1**·Li⁺ in [D₈]THF ($\delta = 4.77 \text{ ppm}$) is shifted by 1.32 ppm to higher magnetic field. This result indicates that the eight-membered ring protons are highly sensitive to local ring current effects.

In [D₆]DMSO at 22 °C, the average chemical shifts of the five-membered ring protons and the eight-membered ring protons of 1·Li⁺ are $\delta = 4.38$ and 3.65 ppm, respectively. The anion behaves as an overall paratropic species under these conditions.

It is noteworthy that the proton chemical shifts of $1\cdot Li^+$ in $[D_8]$ THF exhibit exceptionally large changes with temperatures. The chemical shifts at -50 °C appear at about 1 ppm higher magnetic field than those at 38 °C (Figure 3 and Figure S2 in the Supporting Information), and the spectra closely resemble those in $[D_6]$ DMSO (Table 1). On the other hand, the ¹H NMR spectra of $1\cdot$ Na⁺ and $1\cdot$ K⁺ in $[D_8]$ THF show much smaller variations with temperatures. In light of other studies on ion-pairing effects in solution,^[13] $1\cdot$ Na⁺, $1\cdot$ K⁺, and $1\cdot$ Li⁺ in $[D_8]$ THF at ambient temperatures appear to be contact ion pairs, whereas $1\cdot$ Li⁺ in $[D_8]$ THF at -50 °C and 1 in $[D_6]$ DMSO appear to be solvent-separated ion pairs.^[14] In the case of $1\cdot$ Li⁺ in $[D_8]$ THF, the equilibrium shifts strongly with temperature (Scheme 2).

¹³C NMR spectroscopy data for **1** under various conditions are summarized in Table 2. The chemical shifts of the five-membered ring carbon atoms (C1 and C8–C11) appear at higher field than those of the eight-membered ring carbon atoms (C2–C7). The chemical shifts of the eightmembered ring carbon atoms are almost the same as those of **4**,^[4] which indicates that the negative charge is mainly localized on the five-membered ring carbon atoms. The C10 carbon resonates at the highest magnetic field, which is consistent with theoretical calculations. The chemical shift of C2,7 remains almost constant under all conditions, which clearly excludes the possibility of structural change based on



Figure 3. Temperature-dependent chemical shift change of protons of $1-Li^+$ in $[D_8]THF$.

Table 1. ¹H NMR (100 MHz) spectroscopy data for 1.

Solvent	Cation	Т [°С]	H- 9,11 [ppm]	H-10 [ppm]	H-2,7 [ppm]	H-3,6 [ppm]	H-4,5 [ppm]	$\delta_{ m av}$ [ppm]
[D ₈]THF	Li ^[a,b]	21	5.07	5.22	5.30	4.40	4.62	4.89
	Li	-50	4.37 ^[d]		4.06	3.20	3.6 ^[e]	3.87
	Na	38	4.99	5.10	5.00	4.06	4.34	4.65
	Na	-45	4.78	4.90	4.68	3.76	4.09	4.39
	Κ	38	5.07	5.22	5.14	4.19	4.47	4.77
	Κ	-50	4.92	5.05	4.85	3.90	4.22	4.54
[D ₆]DMSO	Li ^[a,c]	21	4.39	4.37	4.07	3.22	3.66	3.89
	Na	38	4.43 ^[d]		4.14	3.27	3.71	3.94
	Κ	38	4.45 ^[d]		4.17	3.27	3.75	3.97

[a] 500 MHz NMR spectroscopy. [b] J(2,3) = 12.3 Hz, J(3,4) = 6.6 Hz, J(3,5) = 0.0 Hz, J(4,5) = 13.5 Hz, J(9,10) = 3.2 Hz. [c] J(2,3) = 12.7 Hz, J(3,4) = 8.1 Hz, J(3,5) = 0.0 Hz, J(4,5) = 13.1 Hz, J(9,10) = 3.1 Hz. The coupling constants were determined by using the gNMR (version 4.1) iterative program. [d] A sharp singlet. [e] Overlapped with the solvent signals.



Scheme 2. The equilibrium, which shifts strongly with temperature, results in the formation of $1-Li^+$ in [D₈]THF.

Table 2. ¹³C NMR (22.5 MHz) spectroscopy data and PM3 electron densities of 1.

Solvent	Cation	Т [°С]	C-1,8 [ppm]	C-2,7 [ppm]	C-3,6 [ppm]	C-4,5 [ppm]	C- 9,11 [ppm]	C-10 [ppm]	δ_{av} [ppm]
[D ₈]THF	Li	50	116.6	133.7	120.5	130.2	117.8	107.7	122.3
	Li	-50	118.3	134.2	127.3	129.2	114.1	108.5	123.1
	Na	28	116.7	133.7	123.0	129.0	117.4	108.8	122.6
	K	28	117.4	133.8	123.6	129.4	118.1	110.9	123.2
[D ₆]DMSO	Na	40	117.4	133.4	126.3	130.1	112.4	109.2	122.6
electron density		1.185	0.946	1.240	1.081	1.210	1.253		

valence isomerization to **7**. The chemical shifts of C3,6 and C9,11 exhibit relatively large changes with the ion-pairing equilibrium, which indicates that some degree of negative charge at C3,6 moves to C9,11 as the contact ion pair shifts

to the solvent-separated ion pair. The variations are relatively small ($\Delta \delta = 4$ -8 ppm), and the charge redistribution is opposite to the direction suggested by changes in the ¹H NMR chemical shifts of H3,6.^[15]

As expected from the theoretical calculations mentioned above, the eight-membered ring of **1** possesses a tub form. Any conformational change should be reflected in the values of the coupling constants of the eight-membered ring protons. It is known that the coupling constant J(3,4) of deeply bent **4** is 1 Hz.^[2c] As the eight-membered ring is flattened, this coupling constant should increase.

The coupling constants of **1** are not first order, so they were obtained by computer simulation of the experimental spectra by using the gNMR (version 4.1) iterative program (Figures S3 and S4 in the Supporting Information). The coupling constant of J(3,4) increases from 6.6 to 8.1 Hz as the contact ion pair changes into the solvent-separated ion-pair. According to the Karplus equation,^[16] this variation indicates roughly a 10° change (from 130 to 140°) of dihedral angles between the C2–C3 (C5–C6) and C4–C5 bonds; the tub shape of **1** flattens in the solvent-separated ion pair, although the conformational change is not so large. The most interesting aspect is that such a small conformational change gives rise to such an exceptionally large tropicity change.

Indenyl anion 2, cyclopentadienyl anion 3, and other aromatic anions also show solvent effects in ¹H NMR spectra under similar conditions, but the variations of the signals range within ± 0.2 ppm.^[17] To the best of our knowledge, only a few poly-, di-, and tetranions of macrocyclic annulenes^[18] or polycyclic compounds^[19,20] show such large solvent effects ($\Delta \delta > 1$ ppm). Thus, anion 1 is the first example of a monoanion to exhibit such behavior. The pronounced sensitivity is probably due to the delicate counterbalance between local aromatic and peripheral antiaromatic character of the anion.

Reactions of the Bicyclo[6.3.0]undecapentaenide Ion with Various Electrophiles

Fulvenes

Undecafulvene derivatives (11-methylideneundeca-1,3,5,7,9pentaene) are the next higher homologs of heptafulvene because the undecapentaenyl cation is a peripherally aromatic 10 π -electron system. For example, the methano[11]annulenyl cation is a stable aromatic compound.^[21] On the other hand, the bicyclo[6.3.0]undecapentaenyl cation, which is a [4n]annuleno[4n]annulene, has not been well characterized so far.^[7] High reactivity would be expected for the four π electron cyclopentadienyl cation subunit.^[7,22] If the contribution of the antiaromatic cyclopentadienyl cation emerges stronger than that of aromatic peripheral undecapentaenyl cation, these bicyclic undecafulvenes should exhibit characteristics similar to those of pentafulvenes.

Reactions of cyclopentadienyl anion **3** with acetone and with dimethylformamide (DMF)/dimethyl sulfate (Vilsmeier) complex afford 6,6-dimethyl- and 6-*N*,*N*-dimethylaminofulvenes, respectively.^[23,24] Similar treatment of **1** affords the corresponding undecafulvene derivatives **16** and **17** in moderate yields (Scheme 3). The reactions occur predominantly at the 10-position, in accordance with the calculated electron density distribution in **1**. Fulvene **16** forms modestly thermally stable, bright-red crystals, whereas **17** is a relatively labile, dark-red solid that decomposes on silica gel at room temperature. Therefore, chromatographic purification was carried out at 0°C.



Scheme 3. Preparation of undecafulvenes 16 and 17.

It has been known that protonation on the *exo*-methylene carbon atoms of heptafulvene and methanoundecafulvene derivatives produce the corresponding tropylium and methano[11]annulenyl cations.^[25,26] Attempts to generate a stable cation from fulvene **16** by dissolving it in trifluoroacetic acid or trifluoromethanesulfonic acid at low temperatures, however, simply resulted in polymerization of **16**. Although fusion of the COT moiety causes batho- and hyperchromic effects in the absorption spectra of these new fulvenes, their properties are essentially consistent with those of the corresponding pentafulvenes.

Cycloocta[a]azulene 18

Anion 1 was subjected to the Hafner azulene synthesis by using bisimmonium salt 19 to afford the corresponding azulene derivative 18.^[27] The extended fulvene 20 formed intermediately as a dark reddish purple solution. Because 20 was sensitive to oxygen, the next reaction was conducted without chromatographic purification. A brief aqueous workup was performed, however, to quench the excess potassium hydride; without this quenching procedure the yield of 18 decreased drastically. Heating 20 at 220 °C in quinoline gave cycloocta[a]azulene (18) as a deep greenish solid, together with 2-phenylazulene (21)^[28] and a trace amount of azulene (22). When pure 18 was heated at 220 °C in quinoline, compounds 21 and 22 were not obtained. Scheme 4 outlines pathways that could account for the formation of 18, 21, and 22. One factor that makes it difficult to formulate a mechanism for the formation of azulene is that the oxidation state of azulene is different from that of 18 and 21; these two hydrocarbons can be formed by the loss of HNMe₂, whereas 22 and benzene (which is most likely to be the other byproduct) cannot be formed that way. There are not enough hydrogen atoms left to form azulene and benzene if nitro-



Scheme 4. Preparation of cycloocta[*a*]azulene **18** and a proposed mechanism for the formation of 2-phenylazulene **21** and azulene **22**.

gen is lost as HNMe₂. We propose loss of the nitrogen substituent as Me–N=CH₂, with addition of a hydrogen atom to the hydrocarbon, rather than loss of a hydrogen atom. The final step in this mechanism ([2+2] cycloreversion to form two aromatic rings) is precedented in the known facile thermal fragmentation of the benzene [2+2] dimer into two molecules of benzene.^[29]

Azulene derivatives exhibit a characteristic weak but long-wavelength absorption band that arises from an intramolecular charge-transfer transition.^[30] The long-wavelength absorption band of **18** appears in the $\lambda = 600-750$ nm range (Figure S5 in the Supporting Information). Fusion of the COT moiety causes a bathochromic shift of about 50 nm. The NMR spectroscopy assignments of **18**, together with those of azulene (**22**),^[31] are shown in Figure 4. The chemical shifts of the seven- and five-membered ring protons of **18** appear at 0.25 (average) and 0.96 ppm higher magnetic fields than those of the corresponding protons of **22**. These relatively large upfield shifts are contrary to those of benzo-COT **4**.^[4] The eight-membered ring protons of **18** are observed at lower magnetic field than those of **4**; the anisotropic effect of the azulene moiety presumably accounts for the exceptionally low magnetic field resonances of the 1- and 6protons ($\delta \approx 6.70$ ppm). The degree of variation in the chemical shifts of the eight-membered ring protons is not as large as those of the azulene protons of 18. In agreement with the general character of other macrocyclic [4n]annuleno[4n+2]annulenes, the chemical shifts of protons on the $4n\pi$ ring are not as sensitive to fusion of a $(4n+2)\pi$ ring system.^[32]

10-Diazobicyclo[6.3.0]undeca-1(11),2,4,6,8-pentaene **23**

Diazocyclopentadiene 14 is known as an inordinately stable diazo compound.[33] Treatment of 1 with p-toluenesulfonylazide^[34] in the presence of diethylamine affords the relatively stable diazo compound 23 in 30% vield, together with a small amount of the 9-diazo compound 24. Compound 23 can be purified by column chromatography on silica gel and is obtained as a dark reddish oil. On the other hand, compound 24 is labile and gradually decomposes during column chro-

matography on silica gel, even at 0°C. Consequently, compound 24 has not yet been obtained as a pure sample. IR spectra of 23 and 24 exhibit characteristic absorptions of diazo groups at $\tilde{v}=2075$ and 2085 cm⁻¹, respectively. The chemical shift of the *ipso* carbon of 23 is observed at $\delta =$



Figure 4. ¹H NMR chemical shifts of azulenes 18 and 22 and benzoCOT 4 in CDCl₃.

75.49 ppm. Roberts and co-workers demonstrated that a plot of the ¹³C NMR chemical shifts of *ipso* carbon atoms against those of the anions of the hydrocarbon atoms, corresponding to replacement of the C=N₂ group by CH₂, showed a linear correlation (R^2 =0.9362; Figure S6 in the Supporting Information).^[35] The values of **23** and **1**·Li⁺ fit this relationship well.

The reaction of **23** with triphenylphosphine gives complex **25**, which decomposes on silica gel to yield bicyclo-[6.3.0]undeca-1(11),2,4,6,8-pentaen-10-one hydrazone (**26**) in 69% yield (Scheme 5).^[36] The same hydrazone was also ob-



Scheme 5. Synthesis of the corresponding 10-diazo derivative **23** and hydrazone **26** and structures of 9-diazo derivative **24**, triphenylphosphine complex **25**, and 10-carbene **27**.

tained in 33% yield by reduction of **23** with LiAlH₄ in THF.^[22] Irradiation of **23** with a high-pressure mercury lamp promotes the extrusion of N₂ to afford bicyclo[6.3.0]undeca-1(11),2,4,6,8-pentaenylidene (**27**). The characterization of carbene **27** in an argon matrix has been published previous-ly.^[37] Further chemistry of **23** will be reported in due course.

Bis(cyclooctatetraenocyclopentadienyl)iron 28

The corresponding ferrocene derivative was obtained in 59% yield from $\mathbf{1}$ and FeCl₂ by means of the standard pro-



cedure.^[38] Ferrocene **28** is composed of thermally labile orange crystals. It decomposes at around 80 °C and on silica gel at room temperature; chromatographic purification was performed at 0 °C. The coupling constant of J(3,4) determined by

computer simulation is 5.0 Hz. The value is intermediate between those of **1** and **4**. Thus, the depth of the tub-shaped structure of **28** appears to be intermediate between that of **1** and **4**.

Conclusion

The title anion **1** was obtained as a thermally fairly stable species in THF and DMSO by treatments of bicyclo-[6.3.0]undecapentaenes **8** and **9** with appropriate bases. Variable-temperature ¹H NMR spectra of **1**·Li⁺ in $[D_8]$ THF re-

vealed exceptionally large chemical shift changes ($\Delta \delta >$ 1 ppm) with temperature. Moreover, the proton chemical shifts showed drastic changes as a function of solvent $([D_8]THF versus [D_6]DMSO)$, even at ambient temperature. According to previous studies, the large chemical shift changes could be ascribed to ion-pairing effects, that is, differences between solvent-separated and contact ion pairs. Thus, anion 1 in a contact ion pair (Li⁺ at ambient temperature in THF) behaved as an aromatic cyclopentadienide ion slightly perturbed by the effects of a paramagnetic COT, whereas 1 in a separated ion pair (Li⁺ at low temperatures in THF or ambient temperature in DMSO) was an overall paratropic species in which the magnetic properties were dominated by a 12 π -electron periphery. ¹³C NMR spectra showed no evidence for skeletal rearrangement and relatively small variations in the electron densities. A relatively small conformational change appeared to cause the large change in the paratropic properties. In addition to its unusual, tunable tropicity, anion 1 could also serve as a versatile building block for the synthesis of cyclopentanoid conjugated systems fused to a fully unsaturated eight-membered ring. A theoretical calculation predicted that the 10-position of 1 should have had the highest electron density and the reactions of 1 with electrophiles did occur predominantly at the 10-position. Corresponding ferrocene, fulvenes, diazo, and azulene derivatives were prepared by the reaction of 1 with appropriate electrophiles.

Experimental Section

General

¹H and ¹³C NMR spectra were recorded on Varian XL-100, JNM-FX90Q, or Bruker-Biospin DRX-500 instruments. Spectra are reported (in δ) referenced to Me₄Si. Unless otherwise noted, CDCl₃ was used as the solvent. Data are reported as follows: chemical shift, multiplicity (s = singlet, d=doublet, t=triplet, m=multiplet, br=broad), coupling constant (in Hz), and integration. IR spectra were observed on Hitachi EPI-G3 or Jasco FT-IR-3 spectrometers. Electronic spectra were obtained on a Hitachi U-3400 instrument and are reported in nanometers (log ε ; sh= shoulder). Mass spectral analyses were performed on a JEOL JMS-O1SG-2 instrument. Only the more intense or structurally diagnostic mass spectral fragment ion peaks are reported. Melting points were determined on a Mettler FP-2 apparatus and are uncorrected. Column chromatography was carried out on Merck silica gel 60, 70–230 mesh ASTM, or neutral alumina activity II-III, 70–230 mesh ASTM.

All solvents were dried by conventional procedures. Reactions involving air-sensitive reagents were carried out under nitrogen or argon atmospheres.

NMR Spectral Measurements of Bicyclo[6.3.0]undecapentaenyl Anion 1 in $[D_8]THF$

Solutions of **8** (15 mg) in $[D_8]$ THF (0.1 dm³) were added to solutions of LHMDS (15 mg) or a suspension of NaH (15 mg) or KH (15 mg) in $[D_8]$ THF (0.2 dm³) in NMR spectroscopy tubes (i.d. = 5 mm) at -50 °C under argon. The tubes were capped with rubber septa and shaken for a few minutes to give deep-purple solutions. The resulting samples were examined by NMR spectroscopy measurements.

NMR Spectral Measurements of 1 in [D₆]DMSO

LHMDS (15 mg), NaH (15 mg), and KH (15 mg) were dissolved in $[D_6]DMSO$ (0.2 dm³) in NMR spectroscopy tubes (i.d. = 5 mm) at room

temperature under argon. The solutions were heated at 60–70 °C for a few minutes to give solutions of dimsyl anion. A solution of **8** (15 mg) in [D₆]DMSO (0.1 dm³) was added to each solution. After being purged with argon, the tubes were capped with rubber septa and shaken for a few minutes to give deep-purple solutions. The resulting samples were examined by NMR spectroscopy measurements.

10-(Isopropylidene)bicyclo[6.3.0]undeca-1(11),2,4,6,8-pentaen-10-ylidene (16)

*n*BuLi (1.5 dm³, 1.6 mol L⁻¹, 2.4 mmol) was added at -78 °C under Ar to a solution of diisopropylamine (0.35 dm³) in THF (10 dm³). The mixture was allowed to warm to 0°C in an ice bath and stirred for 30 min at that temperature. A solution of pentaene 8 (320 mg, 2.25 mmol) in THF $(4\,dm^3)$ was added to the resulting LDA solution. The dark-purple reaction mixture was stirred at 0°C for 30 min and acetone (5 dm³) was then added. The purple color of the solution immediately turned to orange. After being stirred for 30 min, the mixture was diluted with hexane (10 dm³) and quenched with water. The organic layer was separated, washed with brine, and dried over anhydrous MgSO4. The solvent was evaporated under reduced pressure. The residue was charged on silica gel and purified by column chromatography (hexane/CH2Cl2 (98:2) as the eluent) to give 16 (230 mg, 57%) as red needles (from hexane). M.p. 75.0–75.8 °C; IR (KBr): $\tilde{\nu}$ =2980 (w), 1635 (m), 1615 (m), 853 (s), 698 (s), 485 cm⁻¹ (s); UV/Vis (cyclohexane) (log ε): λ_{max} =232 sh (3.83), 289 (4.52), 300 (4.73), 312 (4.73), 376 (3.52), 397 (3.54), 421 (3.56), 449 (3.53), 485 nm (3.30); ¹H NMR (100 MHz, CDCl₃): $\delta = 2.07$ (s, 3H), 5.65–5.80 (m, 4H), 6.35 (br d, 2H), 6.56 ppm (s, 2H); ¹³C NMR (22.5 MHz, CDCl₃): $\delta = 22.3, 123.4, 125.0, 126.3, 131.4, 138.7, 141.4, 144.0 \text{ ppm};$ elemental analysis calcd (%) for C₁₄H₁₄: C 92.26, H 7.74; found: C 92.10, H 7.74.

10-(N,N-Dimethylaminomethylidene)bicyclo[6.3.0]undeca-1(11),2,4,6,8-pentaen-10-ylidene (17)

A mixture of DMF (0.8 g) and dimethylsulfate (1.3 g) was heated at 60°C for 3 h to prepare the Vilsmeier complex (10 mmol). A solution of pentaene 8 (670 mg, 4.7 mmol) in THF (5 dm³) was added to a solution of LDA prepared from diisopropylamine (0.75 dm³) and *n*BuLi (3.2 dm³, 1.6 mol L⁻¹, 2.4 mmol) in THF (20 dm³) at -78 °C under Ar. The mixture was stirred for 30 min. The Vilsmeier complex (10 mmol) was added to the solution of the anion and the mixture was stirred for 2 h. The solution was then diluted with toluene (20 dm³). The organic layer was separated, washed with brine, and dried over anhydrous MgSO4. The solvent was evaporated under reduced pressure. The residue was charged on silica gel and purified by column chromatography (hexane/AcOEt (1:1) as the eluent) at 0°C to give 17 (345 mg, 48%) as red needles. M.p. 158.0-159.0 °C; MS (EI) m/z (%): 197 (100) [M]⁺, 182 (17) [M-15]⁺, 171 (50); IR (KBr): $\tilde{v} = 2980$ (w), 1610 (vs), 1368 (s), 1250 (m), 965 cm⁻¹ (m); UV/ Vis (CH₃CN) (log ε): $\lambda_{max} = 262$ (3.89), 337 (4.64), 390 sh (4.08), 470 nm sh (3.51); ¹H NMR (100 MHz, CDCl₃): $\delta = 3.17$ (s, 6H), 5.35–5.55 (m, 4H), 6.05-6.20 (m, 3H), 6.30 (m, 1H), 6.75 ppm (s, 1H); elemental analysis calcd (%) for $C_{14}H_{15}N$: C 85.24, H 7.66, N 7.10; found: C 85.10, H 7.69, N 6.98.

Cycloocta[a]azulene 18

Pentaene **8** (510 mg, 3.5 mmol) was added to a suspension of KH (300 mg, 7.5 mmol) in THF (2 dm³) in an ice bath under Ar. After vigorous foaming, the resulting purple reaction mixture was diluted with THF (6 dm³). The mixture was stirred for 30 min in an ice bath and cooled to -50 °C. Immonium salt **19** (700 mg, 2.8 mmol) was added to the reaction mixture. The mixture was allowed to warm to room temperature and was stirred for 30 min. The color of the solution turned to dark reddish purple. The mixture was cooled to 0 °C and quenched with water (0.5 dm³). After vigorous foaming, quinoline (25 dm³) was added. The mixture was diluted with hexane. The organic layer was washed with hydrochloric acid (20 mL, 2 molL⁻¹) three times, water, and brine. The solvent was evaporated under reduced pressure. The residue was charged on silica gel and purified by column chromatography to give **22** (10 mg)

from elution with hexane as deep-green needles, **21** (51 mg, 9%) from elution with hexane/CH₂Cl₂ (98:2), and **18** (247 mg, 44%) from elution with hexane/CH₂Cl₂ (90:10). M.p. 85.0–86.0°C; MS (EI) *m*/*z* (%): 204 [*M*]⁺, 203 (68), 202 (53), 178 (86); IR (KBr): \hat{v} =3000 (w), 1633 (w), 1575 (m), 1488 (m), 664 cm⁻¹ (m); UV/Vis (cyclohexane) (log ε): λ_{max} =296 (4.44), 307 (4.45), 332 sh (4.40), 396 (3.55), 620 (2.45), 667 sh (2.41), 730 nm sh (2.00); ¹H NMR (500 MHz, CDCl₃): δ =5.70 (dd, *J*=4.4, 12.1 Hz, 1H), 5.75 (dd, *J*=4.3, 12.2 Hz, 1H), 6.08–6.12 (m, 2H), 6.75 (d, *J*=12.2 Hz, 1H), 6.80 (d, *J*=12.1 Hz, 1H), 6.97 (s, 1H), 7.00 (t, *J*=9.5 Hz, 1H), 7.02 (t, *J*=9.5 Hz, 1H); ¹³C NMR (125.8 MHz, CDCl₃): δ =119.0, 123.5, 124.3, 124.9, 127.3, 129.9, 130.9, 131.6, 132.4, 132.7, 134.0, 136.0, 137.2, 138.6, 142.5, 149.6 ppm; elemental analysis calcd (%) for C₁₆H₁₂: C 94.08, H 5.92; found: C 93.93, H 5.90.

10-Diazobicyclo[6.3.0]undeca-1(11),2,4,6,8-pentaene (23)

Diethylamine (1.5 dm³) was added to a mixture of pentaene 8 (740 mg, 5.2 mmol) and TsN₃ (2.0 g) in THF (15 dm³) in an ice bath under Ar. The mixture was stirred for 3 h, diluted with hexane (20 dm³), and quenched with water. The organic layer was separated, washed with a 10% aqueous solution of NaOH, water, and brine; and dried over anhydrous MgSO4. The solvent was evaporated under reduced pressure. The residue was charged on silica gel and purified by column chromatography (hexane as the eluent) to give recovered pentaene (277 mg), 24 (95 mg, 11%), and **23** (230 mg, 26%) as an orange oil. **23**: MS (EI) m/z (%): 164 $[M]^+$ (42), 140 (56), 139 (100); IR (KBr): v=3000 (m), 2075 (s), 1480 (m), 1352 (m), 816 cm⁻¹ (m); UV/Vis (CH₃CN) (log ε): $\lambda_{max} = 225$ (4.01), 290 (4.33), 353 nm (3.94); ¹H NMR (100 MHz, CDCl₃): δ = 5.50–5.60 (m, 2H), 5.68 (m, 2H), 6.15 (d, J=12.0 Hz, 2H), 6.41 ppm (s, 2H); ¹³C NMR (22.5 MHz, CDCl₃): $\delta = 75.5$, 120.2, 127.7, 127. 8, 127.9, 130.3 ppm. **24**: Orange oil; IR (KBr): $\tilde{\nu} = 3000$ (m), 2942 (w), 2085 (s), 1300 (m), 650 cm⁻¹ (w); ¹H NMR (100 MHz, CDCl₃): $\delta = 5.55 \sim 6.20$ (m, 7H), (5.67, (d, J=4.5 Hz, 1 H)), 6.75 ppm (d, J=4.5 Hz, 1 H).

Bicyclo[6.3.0]undeca-1(11),2,4,6,8-pentaen-10-one Hydrazone (26)

Triphenylphosphine (250 mg, 1 mmol) was added to a solution of **23** (178 mg, 1 mmol) in CH₂Cl₂ (5 dm³) at room temperature. The solvent was evaporated under reduced pressure. The residue was charged on silica gel and purified by column chromatography (toluene/ether (99:1) as the eluent) to give hydrazone **26** (120 mg, 69%) as dark-red needles. M.p. 116.8–117.2 °C; MS (EI) *m*/*z* (%): 170 (100) [*M*]+, 154 (91), 139 (42); IR (KBr): $\tilde{\nu}$ =3450 (m), 3310 (m), 1560 (s), 1385 (s), 1095 cm⁻¹ (s); UV/Vis (CH₃CN) (log ε): λ_{max} =295 sh (4.56), 326 (4.78), 404 sh (3.71), 425 (3.72), 450 sh (3.70), 480 nm (3.56); ¹H NMR (100 MHz, CDCl₃): δ = 5.85–6.40 (m, 6H), 6.44 (s, 2H), 6.45–6.60 ppm (m, 2H) ; elemental analysis calcd (%) for C₁₁H₁₀N₂: C 77.49, H 5.84, N 16.33; found: C 77.62, H 5.92, N 16.46.

Alternative Route to Hydrazone 26

Compound **23** (190 mg, 1.1 mmol) was added to a suspension of LiAlH₄ (100 mg) in diethyl ether (6 dm³) in an ice bath under Ar. The mixture was stirred for 1.5 h at 0°C, quenched with water (0.5 dm³), and stirred for another 1.5 h. Anhydrous MgSO₄ was then added to the mixture. The solid was filtered and the filtrate was condensed under reduced pressure. The residue was charged onto silica gel and purified by column chromatography (toluene/ether (99:1) as the eluent) to give hydrazone **26** (63 mg, 33%).

$Bis(1,8,9,10,11-\eta^5-bicyclo[6.3.0]$ undecapentaenyl)iron (28)

A suspension of anhydrous FeCl₃ (1 g) and iron powder (100 mg) in THF (30 dm³) was heated at reflux for 4 h to prepare a solution of FeCl₂ in THF. Pentaene **8** (1.0 g, 11.7 mmol) was added to a suspension of KH (1.0 g, 25 mmol) in THF (0.5 dm³) in an ice bath under Ar. After vigorous foaming, the purple reaction mixture was diluted with THF (5 dm³). The mixture was stirred at 0°C for 30 min to prepare the solution of FeCl₂ in THF by using a syringe. The mixture was heated at reflux for 2 h under Ar, cooled to room temperature, and diluted with hexane. The

organic layer was then separated, washed with water and brine, and dried over anhydrous MgSO₄. The solvent was evaporated under reduced pressure. The residue was charged onto charged onto silica gel and purified by column chromatography (hexane) to give recovered **8** (240 mg) and ferrocene **28** (851 mg, 59%) as orange plates. M.p. 80°C (decomp); ¹H NMR (100 MHz, CDCl₃): δ =4.09 (d, *J*=2.6 Hz, 2H), 4.44 (t, *J*= 2.6 Hz, 1H), 5.55 (m, *J*=3.1, 1.6 Hz, 2H), 5.84 (m, *J*=11.5, 3.1, 1.6 Hz, 2H), 6.20 ppm (d, *J*=11.5 Hz, 2H); ¹³C NMR (22.5 MHz, CDCl₃): δ =74.1 (two signals overlapped), 82.2, 127.9 (two signals overlapped), 129.0 ppm; IR (KBr): $\tilde{\nu}$ =1628 (brs), 1212 (m), 830 (s), 799 (s), 664 cm⁻¹ (s); UV/Vis (cyclohexane) (log ε): λ_{max} =260 (4.35), 289 (4.20), 385 sh (3.40), 455 nm sh (3.14); elemental analysis calcd (%) for C₂₂H₁₈Fe: C 78.28, H 5.38, found: C 78.12, H 5.36.

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