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Synthesis, stability and molecular structure of novel hydrocarbon cations consisting of a tropylium cation and two spiro[4.5]deca-2,4-dienes

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Abstract—Two novel hydrocarbon cations with a tropylium ion ring fused by two spiro[4,5]deca-2,4-dienes, **9** and **10**, were synthesized by a six-step sequence starting from 1,6- and 1,5-diacetyl-1,3,5-cycloheptatrienes, respectively. The p$K_R$$^+$ values of **9** and **10** were found to be the same at 13.2, providing a new access to highly stable cations. The density functional calculations predict that both **9** and **10** have cyclohexane rings with the chair conformation spread toward molecular edges as the most stable structure. The crystal packing and structure of **9** including dichloromethane were also elucidated by X-ray crystallographic analysis. © 2003 Elsevier Science Ltd. All rights reserved.

Komatsu and Ito reported the synthesis of stable hydrocarbon cations **1**[1] and **2**[2] with p$K_R$$^+$ values of 13.0 and 14.3, respectively. Recently, triarylmethyl cations with heteroatomic substituents, such as **3** and **4**, were found to show much greater stability with values of more than 20.[3–5] Hydrocarbon cation **1** consists of a tropylium cation and bicyclo[2.2.2]octenes, and the stability of **1** can be ascribed to not only the inductive effects but also the $\sigma-\pi$ conjugative effects of the bicyclooctene moieties. On the other hand, hydrocarbon cation **2** has $\pi-\pi$ conjugation throughout all of the substituted azulenes, though all of the three azulene rings cannot be coplanar concomitantly.[2] The stability of **2** can be ascribed to the extended $\pi-\pi$ conjugation and the inductive effects of the *t*-butyl groups. Meanwhile, we reported that spiroalkylated azulenium ions **5a–c**[6] show greater thermodynamic stability compared with various disubstituted tropylium cations, such as 1,4-bis(cyclopropyl)tropylium ion (**6**, p$K_R$$^+$=7.63),[7] 1,2-bicyclo[2.2.2]octenotropylium ion (**7**, 8.82),[8] and cyclohepta[*a*]acenaphtylenium ion (**8**, 8.7).[9] The effect of fusion of a spiro[4,*n*]alka-2,4-diene unit to a tropylium cation ring on its stability can be attributed to the $\pi-\pi$ conjugation at the 2,3 position and $\sigma-\pi$ conjugation between the electron-deficient p orbitals and the $C_{sp3}-C_{sp3}$ σ-bonds at the 1 position, in addition to an inductive effect of the spiro carbocycles. Thus, **5a–c** should be regarded as a hybrid type of tropylium cation stabilized by $\pi-\pi$ and $\sigma-\pi$ conjugations. The cations, dispiro[cyclohexane-1,1′-(1′,7′-dihydrocyclopenta[*f*]azulenium)-7′,1″-cyclohexane] perchlorate

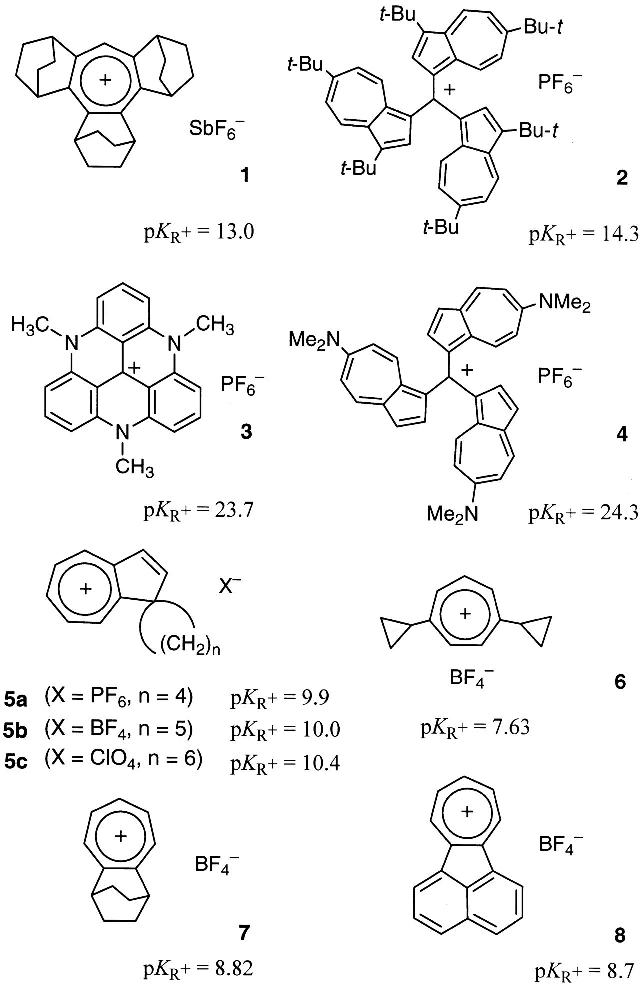

Chart 1.

Keywords: carbenium ions; azulenes; cyclohexanes; sprio compounds; X-ray crystal structures.

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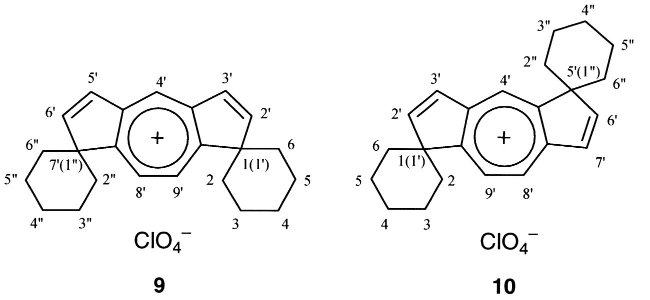


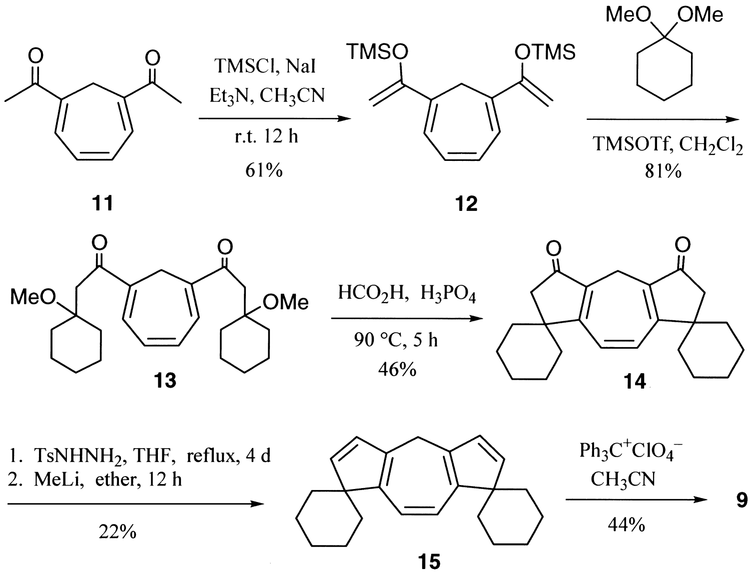
Chart 2.

(**9**) and dispiro[cyclohexane-1,1′-(1′,5′-dihydrocyclopenta[*f*]azulenium)-5′,1″-cyclohexane] perchlorate (**10**), whose tropylium ring is fused by two spiro[4,5]deca-2,4-diene units, are expected to show greater stability than **5**. In this paper we describe the synthesis of these two isomeric hydrocarbon carbocations, their thermodynamic stability, and also the crystal packing and structure of **9** (Charts 1 and 2).[10]

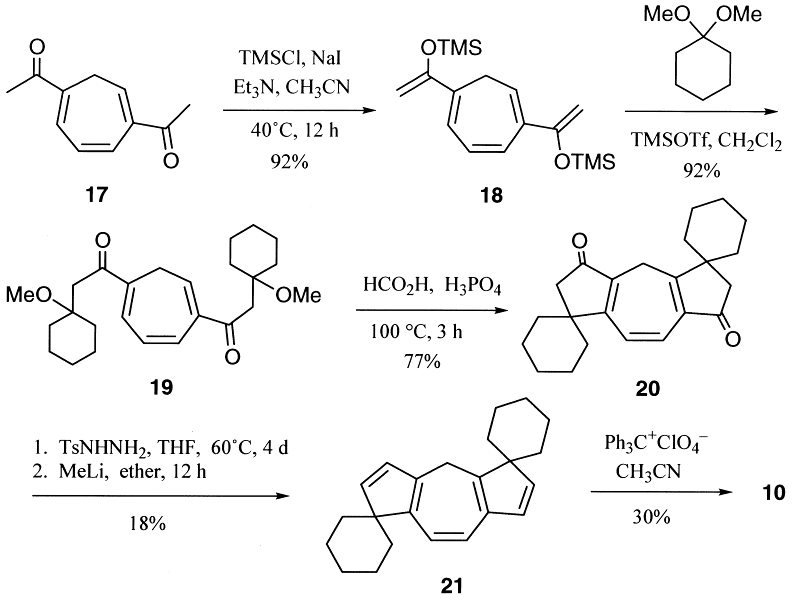
1. Results and discussion

1.1. Synthesis of dispiro[cyclohexane-1,1′-(1′,7′-dihydrocyclopenta[*f*]azulenium)-7′,1″-cyclohexane] perchlorate (9) and dispiro[cyclohexane-1,1′-(1′,5′-dihydrocyclopenta[*f*]azulenium)-5′,1″-cyclohexane] perchlorate (10)

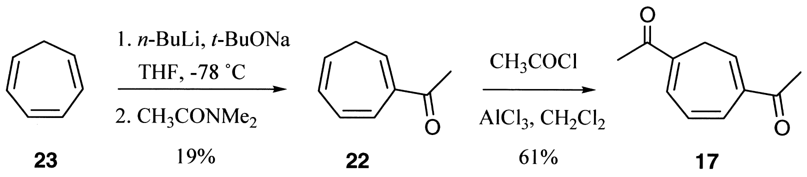
The synthesis of **9** was accomplished from 1,6-diacetyl-1,3,5-cycloheptatriene (**11**)[11] by the method which we had developed for **5c**. The trimethylsilyl enol ether **12** was treated in the presence of trimethylsilyl triflate with



Scheme 1.



Scheme 2.



Scheme 3.

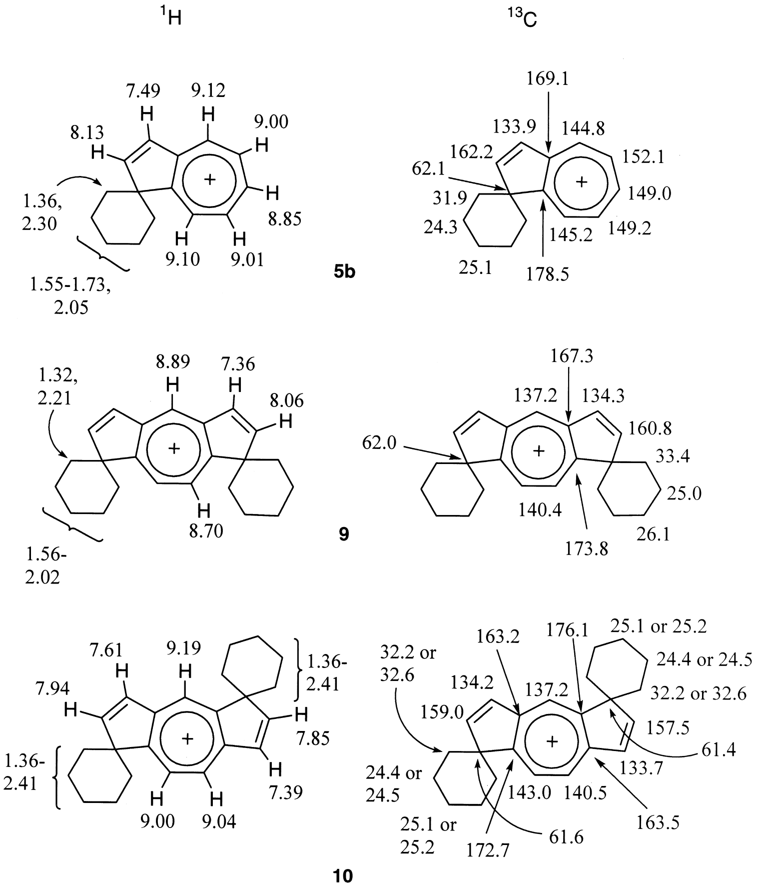


Figure 1. Proton (left) and carbon (right) chemical shift values (δ ppm) assigned for **5b**, **9** and **10**.

1,1-dimethoxycyclohexane to give **13** in 81% yield,[12] while the attempted aldol reaction of **11** with cyclohexanone in the presence of titanium chloride[13] gave none of the desired aldol product. The double Nazarov cyclization[14] of **13** in a mixture of formic acid and phosphoric acid afforded the tricyclic diketone **14** in 46% yield. The Shapiro reaction[15] of tosylhydrazone of **14** and subsequent hydride abstraction of **15** with trityl perchlorate gave **9** as yellow microcrystals in 10% yield based on **14**. The cation **9** was found to be fairly stable and it can be stored without appreciable change at room temperature for at least a year (Scheme 1).

The synthesis of **10** was carried out in the same manner starting from 1,5-diacetyl-1,3,5-cycloheptatriene (**17**) through compounds **18–21** as shown in Scheme 2. The cation **10** was obtained as stable brownish-yellow crystals. The starting material **17** was prepared by the regioselective Friedel–Crafts acetylation of 2-acetyl-1,3,5-cycloheptatriene (**22**) as seen in the acetylation of 1-acetyl-1,3,5-cycloheptatriene into **11**.[11] Although **22** has been known, the reported method by Linstrumelle[16] is not suitable for preparing it in a multi-gram quantity. In this study, **22** was obtained in one pot from 1,3,5-cycloheptatriene **23** by the regioselective lithiation of the 2 position[17] and subsequent acetylation with *N*,*N*-dimethylacetamide (Scheme 3).

1.2. Physical properties of 9 and 10

The structures of **9** and **10** were fully characterized by spectroscopic and elemental analyses. The assignment of the proton and carbon signals for **9**, **10** and known **5b** is shown in Figure 1. The average chemical shifts of 8.15 and 8.27 ppm for the olefinic protons of **9** and **10**, respectively, are slightly lower than that (8.67 ppm) of **5b**, and the same is

Table 1. Absorption maxima (nm) in the electronic spectra of **5b**, **9** and **10** in acetonitrile

Cation	λ_{max} (log ε)		
5b[a]	230 (4.24)	270 (4.33)	360 (4.07)
9	232 (4.03)	297sh (4.33), 311 (4.46)	364 (4.03), 383 (4.10)
10	238 (3.96)	282 (4.30), 306 (4.14)	381sh (3.99), 401 (4.12)

[a] Taken from Ref. 6.

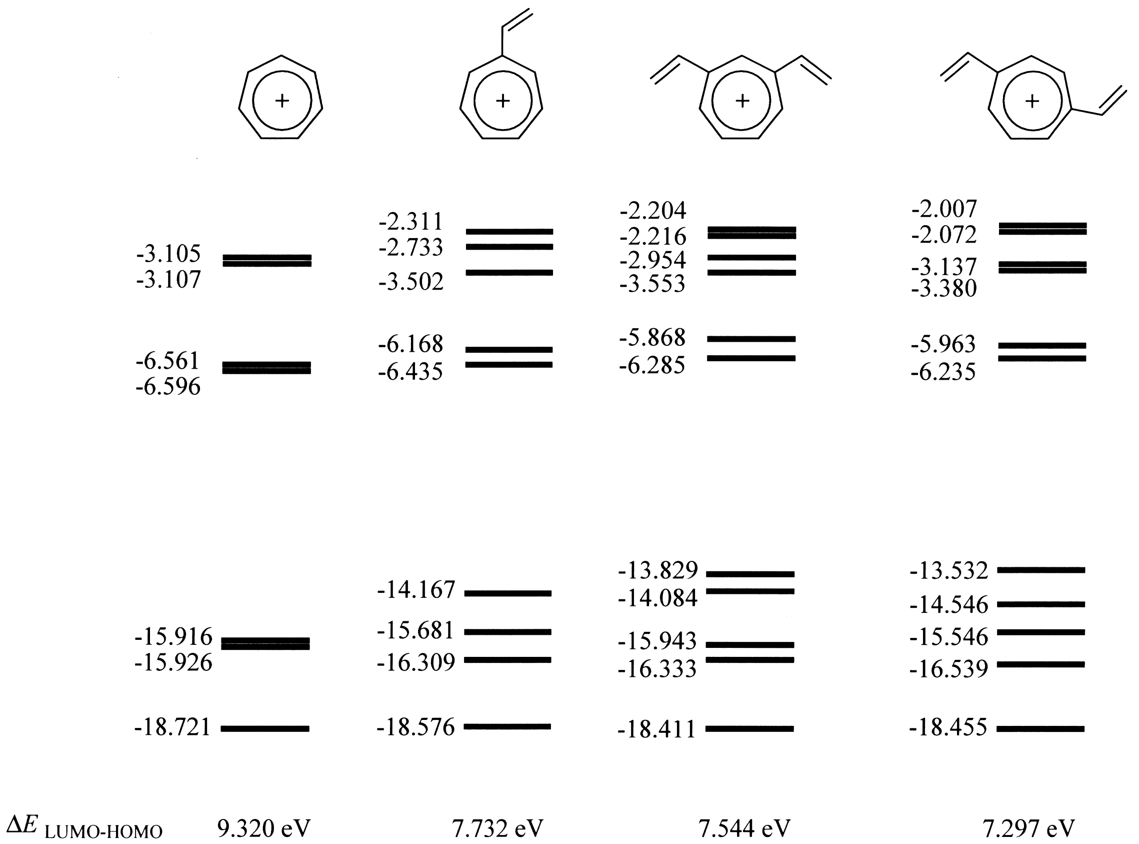


Figure 2. π-Molecular orbitals of the tropylium, vinyltropylium, 1,3-divinyltropylium and 1,4-divinyltropylium cations calculated by the PM3 method (energy level in eV) and their HOMO–LUMO gaps.

true for the ^{13}C NMR chemical shifts of 144.0 and 144.2 ppm for the secondary trigonal carbons of **9** and **10** which are slightly smaller than that (148.1 ppm) of **5b**. Comparison of the shift values of the cyclopenetaazulene skeleton hydrogens and carbons except the sp$_3$-hybridized carbons and the 4′ position in **9** and **10** with those of the corresponding precursor hydrocarbons shows clear down field shift; the average field shifts are 1.56 and 1.65 ppm for hydrogens and 18.0 and 19.5 ppm for carbons in **9** and **10**, respectively. It is worthy to note that the five-membered secondary carbons at the 2′ and 6′ positions in **9** and **10** resonate at lower field of 157.5–160.8 ppm compared with the other secondary carbons. These results indicate the delocalization of the positive charge over the skeletal carbons of the additionally fused spiro[4,5]deca-2,4-diene unit. The ^{1}H NMR spectrum of **9** shows five bands of signals in a range of 1.32–2.21 ppm for the hydrogens at the cyclohexane rings, while that of **10** indicates unresolved signals except the signals of the 2 (6) and 2″ (6″) positions in the similar region because of its less symmetrical structure. The axial–axial vicinal coupling (13.3 Hz) and the axial–equatorial vicinal coupling constant (3.3 Hz)[18] observed between these protons of **9** suggest that **9** has cyclohexane rings with a fixed chair conformation, as observed in the crystal structure of **9** (vide infra).

Table 2. The pK_R^+ values and reduction peak potentials of various cations

Cation	pK_R^+	Reduction potential	
		V vs SCE	V vs Ag/Ag$^+$
1	13.0		−1.12[a]
2	14.3		−0.91, −1.72[b]
5a	9.9	−0.41	
5b	10.0	−0.46	
5c	10.4	−0.54	
9	13.2	−0.65	
10	13.2	−0.52	

[a] Taken from Ref. 1.

[b] Taken from Ref. 2.

The UV spectra of **9** and **10** in acetonitrile show five bands, while the spectrum of **5b** shows three sharp bands (Table 1). The longest wavelength absorption maxima of **9** and **10** are

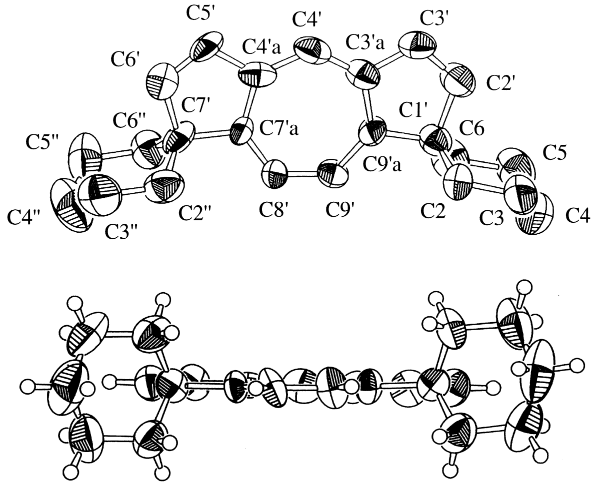


Figure 3. ORTEP drawings of the cation **9**. The perchlorate counter anion and the dichloromethane included are omitted.

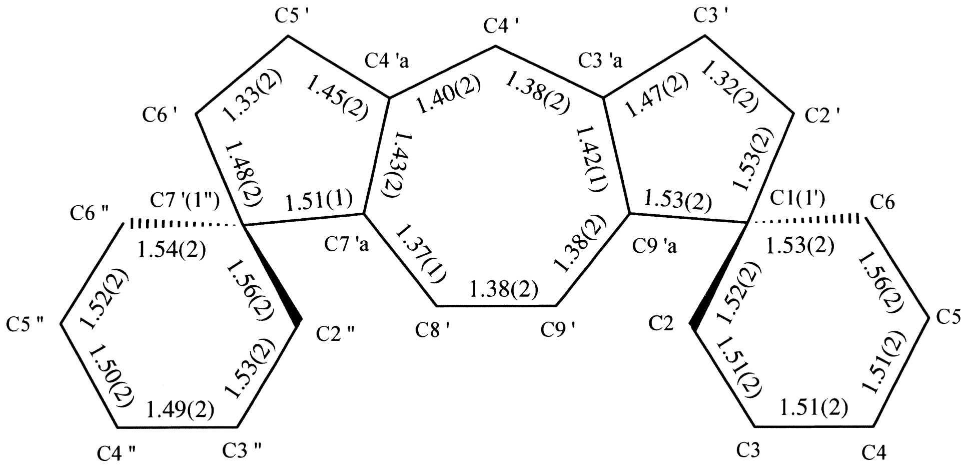


Figure 4. Bond lengths (Å) in the crystal of the cation **9**.

shifted by 23 and 41 nm to longer wavelength compared with that of **5b**. It is only natural that these shifts are mainly due to π–π conjugation of another C–C double bond around the tropylium cation ring. The dependence of the degree of the shift on the position of the double-bond around a tropylium ring can be rationalized by the following molecular orbital calculations of 1,3- and 1,4-divinyltropylium cations as simplified models for **9** and **10**, respectively. Figure 2 shows π-molecular orbitals of tropylium, vinyltropylium, and 1,3- and 1,4-divinyltropylium cations calculated by the semiempirical PM3 method. Both of the degenerated LUMO and HOMO are split in the substituted cations, and the largest splitting of HOMO and the next HOMO is expected in the 1,4-divinyltropylium cation. While the energy level of LUMO is not changed much by vinyl substitution, the level of HOMO slightly increases one by one by the substitution. The HOMO–LUMO gap is expected to be the smallest in 1,4-divinyltropylium cation among them, thus accounting for the greater shift of **10** in the UV spectrum.

The pK_R^+ values of **9** and **10** were determined by the UV method in buffered 50% aqueous acetonitrile solutions to be the same at 13.2. The reversibility in the pK_R^+ determination was confirmed by resumption of the spectra of **9** and **10** from the high pH solution up to 60% of the original intensity upon acidification with a few drops of concd H_2SO_4. The thermodynamic stability of **9** and **10** is comparable to that of **1** and slightly less than that of **2**. The difference (6.1) in the values between **5b** (10.0)[6] and the tropylium ion (3.9)[7] is far greater than that (3.2) between **9** or **10** and **5b**. Thus, a saturation effect of electronic stabilization by the spirodecadiene to the tropylium cation is clearly shown. Reduction peak potentials for **9** and **10** measured by cyclic voltammetry was −0.65 and −0.52 V vs SCE, respectively, designating increased reduction reluctance of **9** and **10** compared with **5b** (Table 2).[6]

1.3. X-Ray crystallographic analysis of 9 and density functional calculations of 9 and 10

The molecular structure of **9** was elucidated by X-ray crystallographic analysis. Single crystals of **9** containing dichloromethane were obtained by recrystallization from a mixture of ether, hexane and dichloromethane. In spite of many efforts single crystals of **10** have not been obtained. The structure was solved and refined in the space group $P2_1/n$ with four pairs of **9** and dichloromethane per unit cell. ORTEP drawings of **9** without the counter anion and the solvent are shown in Figure 3 and bond lengths in Figure 4. The structure shows C_1 symmetry, and the dihydrocyclopenta[*f*]azulenyl skeleton is nearly planar; the greatest torsion angle of 4° was observed through the C1(1′)–C9′a–C3′a–C4 carbons. Mean deviation from the least-squares plane of the dihydrocyclopenta[*f*]azulene framework is 0.0271 Å and the longest distance from the plane is observed to be 0.0854 Å long for the C1(1′) carbon (Table 3). The fairly planar carbon framework should be related to effective delocalization of the positive charge in **9**. The average C–C bond length of the seven-membered ring is 1.39 Å, which is longer than that (1.35 Å) of the tropylium ion in an inclusion complex with dibenzo-24-crown-8[19] and is rather closer to those of substituted tropylium ions, such as acetoxytropylim ion (1.38 Å)[20] and 1,11-*o*-benzeno[2]-orthcyclo[2](1,2)tropyliophane (1.385 Å).[21] Deviation from the average in the crystal structure of **9** is less than 0.04 Å. The average bond angle of the seven-membered ring is 128.1°, which is close to the 128.6° expected for a regular heptagon. One may expect that when the σ–π conjugation in **9** is effective, the C_{sp3}–C_{sp3} single bonds of the cyclohexane ring at the spiro juncture should be elongated. In the crystal structure of **9**, the average C_{sp3}–C_{sp3} bond distance (1.54 Å) at the C1(1′) and C7′(1″) carbons is indeed

Table 3. Deviation (Å) from the least-squares plane of the cyclopenta-[*f*]azulene in **9**

Carbon	Distance	esd
1(1′)	0.0854	0.0120
2′	−0.0095	0.0130
3′	−0.0473	0.0131
3′a	−0.0242	0.0137
4′	−0.0193	0.0145
4′a	−0.0026	0.0145
5′	0.0448	0.0119
6′	0.0300	0.0300
7′(1″)	−0.0073	0.0122
7′a	−0.0241	0.0118
8′	−0.0269	0.0116
9′	−0.0174	0.0121
9′a	0.0131	0.0127

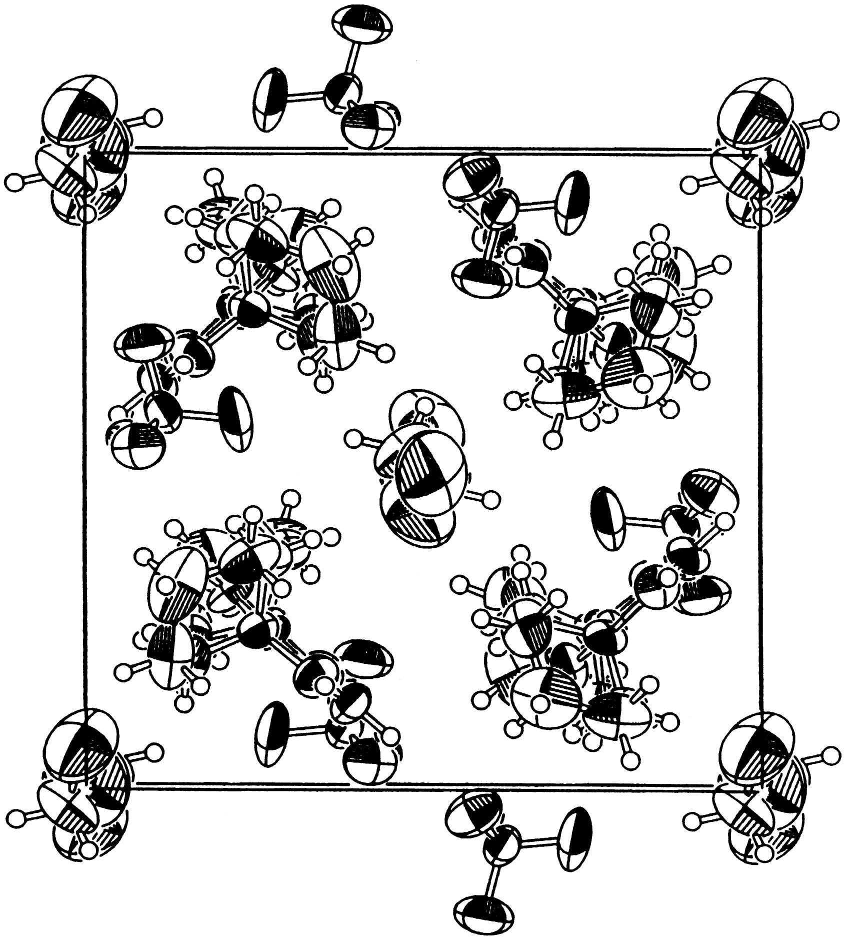


Figure 5. The crystal packing of **9** viewed along the *c*-axis.

greater than that (1.52 Å) of the other bonds in the cyclohexane rings, implying the $\sigma-\pi$ conjugation of **9**, though further comparison with bond length data of related compounds is necessary to confirm this.

The crystal packing of **9** along the *c*-axis is shown in Figure 5. Four molecules of **9** are located around the *c*-axis centered in the unit cell with symmetry of rotation–reflection. Thus, the two facing cations at the opposite angular positions are upside down against each other, making space at the middle of the cell along the axis where the two dichlromethanes are filled. Other dichloromethanes are at the unit cell edges and surrounded also by the cations in other cells. Such large space was not observed in the crystal cells of **5a** and **5b**.[6] A perspective view piled with five cells along the *c*-axis is shown in Figure 6.

As been expected by ^{1}H NMR analysis, the crystal structure clearly shows that the two cyclohexane rings of **9** have a chair form whose seats and backs are spread to the side of the molecular edges. This conformation was found to be the most stable among three possible conformers, **A**, **B** and **C** in Figure 7, two of which have at least one chair-formed cyclohexane ring folded inside the molecule, on the basis of the hybrid molecular orbital calculations at the B3LYP/6-31G* level of theory. Similar calculations for **10**, whose crystal structure is unknown, were also carried out. Among four possible chair form isomers, **D**, **E**, **F** and **G**, the conformer **D** is expected to be the most stable. As seen for **9**, the conformer **D** has a chair form whose seats and backs are spread to the side of the molecular edges. The short atomic distances less than 2.2 Å between the axial hydrogen of the cyclohexane ring and the hydrogen at the seven-membered ring observed in **B**, **C**, **E**, **F** and **G**, like 1,3-diaxial interaction, may be one reason to account for their instability (Fig. 8).

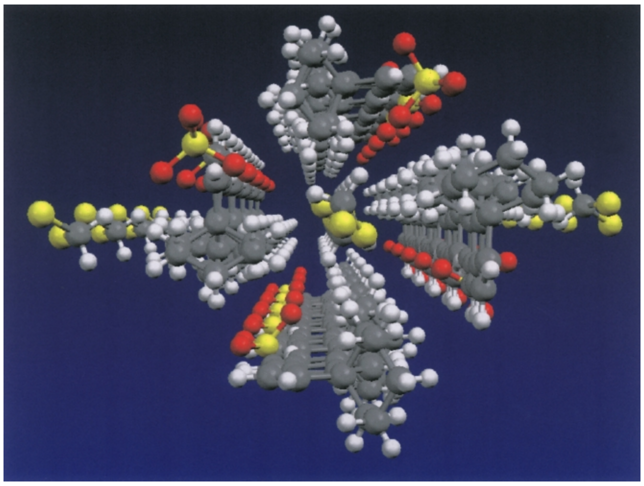
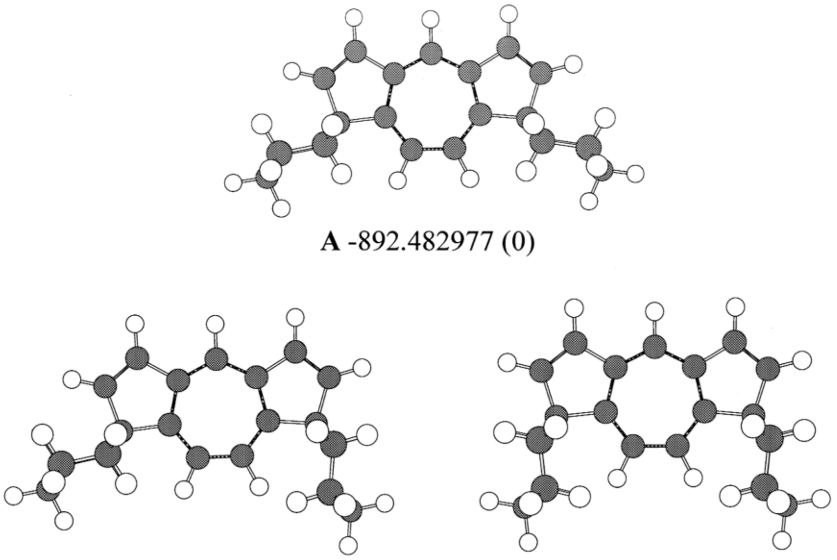


Figure 6. A perspective view along the *c*-axis.

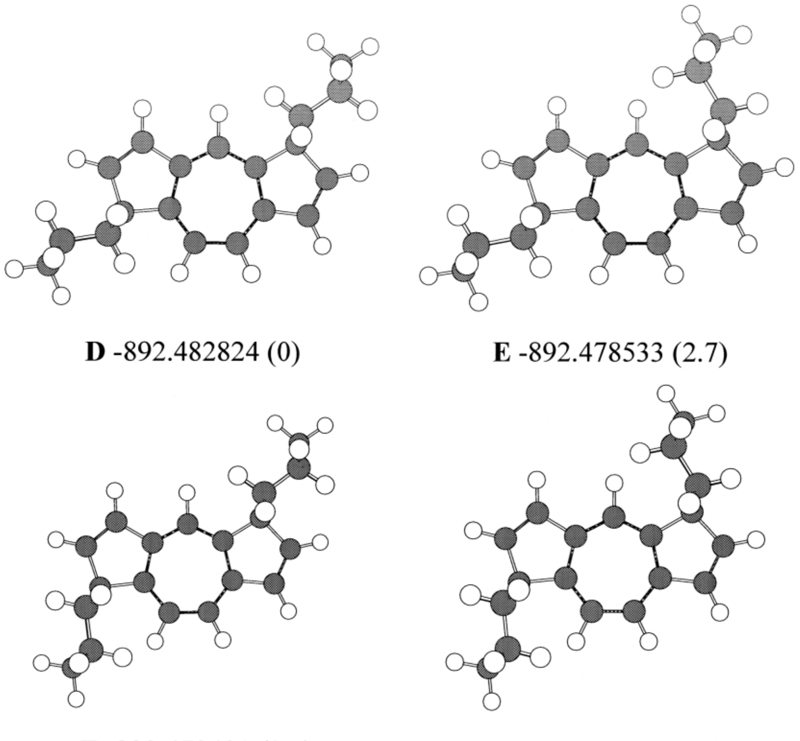


A -892.482977 (0)

B -892.478777 (2.6)

C -892.474571 (5.3)

Figure 7. Possible conformers (Chem3D output) having a chair form cyclohexanes for **9** and their total energies (in a.u.) calculated at the B3LYP/6-31G* level of theory. The relative energies (in kcal/mol) to the most stable conformer are in parentheses.



D -892.482824 (0)

E -892.478533 (2.7)

F -892.478481 (2.7)

G -892.474264 (5.4)

Figure 8. Possible conformers (Chem3D output) having a chair form cyclohexanes for **10** and their total energies (in a.u.) calculated at the B3LYP/6-31G* level of theory. The relative energies (in kcal/mol) to the most stable conformer are in parentheses.

2. Summary

In summary, we have established an efficient synthetic route to the tropylium cations fused with two spiro[4,5]-decana-2,4-diene units, **9** and **10**. Two isomeric diacetyl-1,3,5-cycloheptatrienes were converted into **9** and **10** by a sequence involving the Mukaiyama–Noyori aldol reaction, the Nazarov cyclization, the Shapiro reaction, and the final hydride abstraction. The cations **9** and **10** show enhanced thermodynamic stability comparable to that of **1**, providing a new access to highly stable hydrocarbon cations. The effect of fusion with a spiro[4,5]decana-2,4-diene unit at the tropylium cation on stability has been clearly indicated by the present results of both **9** and **10**, though a saturation effect also is shown in plural fusions. We have also demonstrated the X-ray crystal structure of **9**, as the first example of highly stable hydrocarbon cations.

3. Experimental

3.1. General

Melting points were measured on a Yanaco MP-3 and are uncorrected. IR spectra were recorded on a Perkin–Elmer Spectrum RX I spectrometer. UV spectra were measured on a Shimadzu UV-1600 spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 Hz) were recorded with tetramethylsilane as an internal standard on a JEOL α400. Mass spectra were measured on a JEOL GC-Mate mass spectrometers. Cyclic voltammogram was recorded on a Yanako P1100 instrument. Column chromatography was done with Merck Kieselgel 60 Art 7734. Ethyl ether and THF were purified just before use by distillation from sodium diphenylketyl under a nitrogen atmosphere. Trimethylsilyl triflate, 1,1-dimethoxycyclohexane, acetonitrile and HMPA were purchased from Tokyo Kasei Ind. Co. and were used after appropriately distillation. A solution of *n*-butyllithium in hexane from Aldrich Co. and a solution of methyllithium in ether from Kanto Chem. Inc. were used after titration. Sodium *t*-butoxide was purchased from Wako Chem. Co. and was used without purification. 1,6-Diacetyl-1,3,5-cycloheptatriene (**11**) was prepared by the Vogel method.[11] Trityl perchlorate was prepared according to the method in the literature.[22] The density functional calculations were conducted by using the Gaussian 94 (Revision E.1, Gaussian, Inc., Pittsburg, Pa, 1995) on an IBM RS6000-G94RevE computer. Semiempirical molecular orbital calculations were done by using the MOPAC program (ver. 6.02) on an IBM RS/6000-397 computer.

3.1.1. 1,6-Bis(1-trimethylsilyloxyethenyl)-1,3,5-cycloheptatriene (12) and 1,5-bis(1-trimethylsilyloxyethenyl)-1,3,5-cycloheptatriene (18). A solution of 19.2 ml (150 mmol) of trimethylsilylchloride was added dropwise to a solution of 8.80 g (50. 0 mmol) of **11** and 42.0 ml (304 mmol) of triethylamine, followed by addition of a solution of 22.5 g (150 mmol) of sodium iodide in 150 ml of acetonitrile. After being stirred at room temperature for 12 h, the reaction mixture was slowly poured into a cold mixture of 100 ml of hexane and 500 ml of water. The aqueous layer was extracted with hexane (100 ml×2). The combined organic layer was washed with brine and dried with anhydrous K_2CO_3. After evaporation of the solvent, the residual dark brown oil was purified by distillation to give 9.76 g (61% yield) of **12** as a pale yellow oil. Bp=110–115°C/2 mm Hg. ^{1}H NMR (CDCl$_3$) δ=0.18 (s, 18H), 2.53 (s, 2H), 4.45 (d, J=1.5 Hz, 2H), 4.82 (d, J=1.5 Hz, 2H), 6.65 (m, 4H); ^{13}C NMR (CDCl$_3$) δ=0.3, 29.2, 93.9, 123.0, 130.1, 130.8, 155.3. IR (liq. film) ν (cm^{-1}) 3043w, 3014w, 2960m, 2901w, 1612m, 1580s, 1504m, 1356m, 1294s, 1253s, 1216s, 1102m, 1042w, 1016s, 847vs, 749s, 691w; MS (70 eV) *m*/*z* (rel. intensity) 320 (M$^+$, 17), 305 (9), 215 (9), 205 (6), 147 (12), 115 (6), 75 (23), 74 (9), 73 (100); UV λ_{max} (methanol) 245 nm (log ε=4.48), 321 (3.77). Found: 320.1627. Calcd for $C_{17}H_{28}Si_2O_2$: M, 320.1628.

The compound **18** was obtained as a pale yellow oil in 92% yield from **22** in the same manner. Bp=115°C/2.5 mm Hg. ^{1}H NMR (CDCl$_3$) δ=0.21 (s, 18H), 2.56 (d, J=7.7 Hz, 2H), 4.28 (d, J=1.2 Hz, 1H), 4.48 (d, J=1.5 Hz, 1H), 4.82 (d, J=1.5 Hz, 1H), 4.82 (d, J=1.2 Hz, 1H), 5.85 (t, J=7.7 Hz, 1H), 6.48 (d, J=5.7 Hz, 1H), 6.63 (dd, J=11.5, 5.7 Hz, 1H), 6.79 (d, J=11.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=0.03, 0.07, 18.2, 92.3, 93.8, 122.2, 122.3, 129.0, 131.1, 132.4, 135.6, 154.9, 155.4. IR (liq. film) ν (cm^{-1}) 2960s, 1611m, 1584m, 1418w, 1327m, 1286s, 1252s, 1219m, 1086m, 1021s, 846s, 688w; MS (70 eV) *m*/*z* (rel. intensity) 320 (M$^+$, 8), 248 (12), 205 (35), 115 (10), 73 (100); UV λ_{max} (methanol) 231 nm (log ε=4.19), 284 (3.76). Found: 320.1593. Calcd for $C_{17}H_{28}Si_2O_2$: M, 320.1628.

3.1.2. 1,6-Bis(3-methoxyl-3,3-pentamethylenepropionyl)-1,3,5-cycloheptatriene (13) and 1,5-bis(3-methoxyl-3,3-pentamethylenepropionyl)-1,3,5-cycloheptatriene (19). To a solution of 1.60 g (5.00 mmol) of **12** and 1.66 g (11.0 mmol) of 1,1-dimethoxycyclohexane in 15 ml of dichloromethane at −78°C under nitrogen atmosphere was added 92 μl (0.50 mmol) of trimethylsilyl triflate. After being stirred at the same temperature for 12 h, the reaction mixture was poured into water and was extracted with ether (30 ml×3). The combined organic layer was washed with a saturated sodium hydrogencarbonate solution and dried with anhydrous Na_2SO_4. After evaporation of the solvent, the residual oil was purified by silica gel chromatography to give 1.62 g (81% yield) of **13** as a yellow oil. ^{1}H NMR (CDCl$_3$) δ=1.21 (m, 4H), 1.51 (m, 12H), 2.89 (s, 4H), 2.99 (s, 2H), 3.19 (s, 6H), 6.94 (m, 2H), 7.12 (m, 2H); ^{13}C NMR (CDCl$_3$) δ=21.7, 24.7, 25.4, 34.1, 44.7, 48.8, 75.8, 132.1, 133.8, 135.9, 198.0. IR (liq. film) ν (cm^{-1}) 2933s, 2857s, 2827m, 1663s, 1591m, 1513m, 1456m, 1362m, 1305m, 1256m, 1191m, 1148m, 1073s, 945w, 927w, 869w, 849w, 742m, 694w, 669w, 607w; MS (70 eV) *m*/*z* (rel. intensity) 400 (M$^+$, 8), 368 (23), 336 (17), 279 (20), 272 (56), 240 (32), 256 (30), 212 (15), 161 (15), 149 (32), 113 (100), 81 (64), 69 (26); UV λ_{max} (methanol) 245 nm (log ε=4.48), 256sh (4.41), 312 (4.09). Found: 400.2570. Calcd for $C_{25}H_{36}O_4$: M, 400.2613.

The compound **19** was obtained as yellow oil from **18** in 92% yield in the same manner. ^{1}H NMR (CDCl$_3$) δ=1.3–1.6 (m, 12H), 1.73 (t-like, 4H), 1.84 (t-like, 4H), 2.77 (d, J=7.6 Hz, 2H), 2.82 (s, 2H), 2.85 (s, 2H), 3.16 (s, 3H), 3.21 (s, 3H), 6.46 (t, J=7.6 Hz, 1H), 6.84 (dd, J=11.5, 5.9 Hz, 1H), 7.07 (d, J=5.9 Hz, 1H), 7.45 (d, J=11.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=21.7 (2C), 25.30, 25.31, 27.0, 34.3, 34.4, 44.3, 44.5, 48.7, 48.8, 75.6 (2C), 130.3, 132.8, 133.0, 133.2, 134.4, 140.7, 198.1, 198.6. IR (liq. film) ν (cm^{-1}) 2933s, 2858s, 1721s, 1656s, 1600m, 1534, 1446s, 1365s, 1308s, 1192s, 1074s, 927m, 753m, 610w; MS (70 eV) *m*/*z* (rel. intensity) 400 (M$^+$, 9), 368 (25), 336 (47), 272 (55), 241 (82), 212 (68), 177 (13), 149 (32), 145 (37), 113 (100), 81 (65); UV λ_{max} (methanol) 240 nm (log ε=4.14), 295 (3.63). Found: 400.2600. Calcd for $C_{25}H_{36}O_4$: M, 400.2613.

3.1.3. Dispiro[cyclohexane-1,1′-(1′,2′,3′,4′,5′,6′,7′-heptahydrocyclopenta[*f*]azulene-3′,5′-dione)-7′,1″-cyclohexane] (14) and dispiro[cyclohexane-1,1′-(1′,2′,3′,4′,5′,6′,7′-heptahydrocyclopenta[*f*]azulene-3′,7′-dione)-5′,1″-cyclohexane] (20). To a solution of 1.60 g (4.00 mmol) of **13** in 30 ml of formic acid was added 30 ml of 85% phosphoric acid. After being stirred at 90°C for 5 h, the reaction mixture was poured into 200 ml of cold water and was extracted with chloroform (50 ml×3). The combined organic layer was washed with a saturated sodium hydrogencarbonate solution and brine, and was dried with anhydrous Mg_2SO_4. After evaporation of the solvent, the residual solids were purified by recrystallization from a mixture of dichloromethane and hexane to give 620 mg (46% yield) of **14** as creamy white prisms. Mp >250°C (dec.) ^{1}H NMR ($CDCl_3$) δ=1.21 (m, 2H), 1.30 (m, 8H), 1.56 (m, 4H), 1.75 (m, 6H), 2.34 (s, 4H), 3.00 (s, 2H), 6.96 (s, 2H); ^{13}C NMR ($CDCl_3$) δ=16.1, 23.5, 25.3, 35.8, 44.3, 46.8, 131.1, 135.6, 170.7, 205.2. IR (liq. film) ν (cm^{-1}) 3030w, 2935s, 2854s, 1691s, 1619m, 1556m, 1455m, 1406m, 1367m, 1329m, 1296w, 1265m, 1195m, 1092m, 992m, 919w, 818m, 754m; MS (70 eV) *m/z* (rel. intensity) 336 (M$^+$, 100), 293 (5), 279 (7), 141 (7), 115 (6), 81 (5); UV λ_{max} (methanol) 238 nm (log ε=4.31), 249 (4.31), 275sh (4.22), 317 (3.68). Bis(2,4-dinitrophenylhydrazone) of **14**; Red prisms. Mp>300°C. Found: C, 60.05; H, 5.28; N, 15.78%. Calcd for $C_{35}H_{36}N_8O_8$: C, 60.34; H, 5.21; N, 16.08%.

The compound **20** was obtained as a pale yellow oil in 77% yield from **19** in the same manner. ^{1}H NMR ($CDCl_3$) δ=1.15–1.34 (m, 12H), 1.75 (m, 8H), 2.38 (s, 2H), 2.40 (s, 2H), 6.77 (d, J=11.5 Hz, 1H), 7.03 (d, J=11.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=21.2, 23.2, 23.5, 24.8, 25.2, 34.2, 35.9, 44.4, 46.0, 47.0, 47.1, 126.1, 128.9, 129.8, 135.5, 173.5, 179.5, 204.3, 205.7. IR (liq. film) ν (cm^{-1}) 2928s, 2855w, 1694s, 1617m, 1450m, 1316m, 1190w, 1025w, 919w, 850w, 754s, 667w; MS (70 eV) *m/z* (rel. intensity) 336 (M$^+$, 100), 281 (14), 240 (19), 165 (13), 141 (19), 115 (14); UV λ_{max} (methanol) 250 nm (log ε=4.16), 293 (3.63). Found: 336.2093. Calcd for $C_{23}H_{28}O_2$: M, 336.2089.

3.1.4. Dispiro[cyclohexane-1,1′-(1′,4′,7′-trihydrocyclopenta[*f*]azulene)-7′,1″-cyclohexane] (15) and dispiro[cyclohexane-1,1′-(1′,4′,5′-trihydrocyclopenta[*f*]azulene)-5′,1″-cyclohexane] (21). A solution of 2.98 g (8.87 mmol) of **14** and 3.30 g (17.7 mmol) of tosylhydrazide in 40 ml of THF was stirred at 60°C for 96 h. The solvent was evaporated and the residual solids were washed well with ether to give the crude hydrazone product. This sample was suspended in 200 ml of ether. To this at 0°C under nitrogen atmosphere was added dropwise 65 ml (71 mmol) of 1.1 M methyllithium etheral solution. After 4 h, the mixture became homogeneous and the color of the solution turned dark-red. The mixture was stirred at room temperature for 12 h. Then, the reaction mixture at 0°C was quenched carefully with 4 ml of water and was poured into water and extracted with ether (100 ml×2). The organic layer was dried with anhydrous $MgSO_4$. After evaporation of the solvent, the residual red oil was purified by silica gel chromatography with hexane as eluent to give 601 mg (22% yield) of **15** as an air-sensitive pale yellow oil. ^{1}H NMR ($CDCl_3$) δ=1.00 (dm, J=13.2 Hz, 4H), 1.32 (qt, J=13.2, 3.3 Hz, 2H), 1.52 (qt, J=13.2, 3.3 Hz, 4H), 1.68 (td, J=13.2, 3.3 Hz, 4H), 1.72–1.84 (m, 6H), 3.19 (s, 2H), 6.21 (d, J=5.4 Hz, 2H), 6.35 (s, 2H), 6.89 (d, J=5.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=25.9, 26.0, 26.7, 33.3, 58.0, 123.2, 133.6, 133.8, 144.8, 150.0. IR (liq. film) ν (cm^{-1}) 3052w, 2925s, 2855s, 1661w, 1490w, 1449s, 1378w, 1269w, 1124w, 1031w, 996w, 918w, 901w, 844m, 803w, 745m, 726s; MS (70 eV) *m/z* (rel. intensity) 304 (M$^+$, 100), 303 (71), 291 (21), 205 (27), 191 (43), 165 (36), 91 (20); UV λ_{max} (hexane) 253sh nm (log ε=3.69), 287 (3.80), 276 (3.87), 363 (4.00). Found: 304.2191. Calcd for $C_{23}H_{28}$: M, 304.2218.

The compound **21** was obtained as an air-sensitive pale yellow oil in 18% yield from **20** in the same manner. ^{1}H NMR ($CDCl_3$) δ=0.95–1.05 (m. 4H), 1.27–1.92 (m, 16H), 3.04 (s, 2H), 6.21 (d, J=5.6 Hz, 1H), 6.29 (d, J=5.6 Hz, 1H), 6.42 (d, J=11.2 Hz, 1H), 6.45 (d, J=11.2 Hz, 1H), 6.66 (d, J=5.6 Hz, 1H), 6.90 (d, J=5.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=24.9, 25.2, 26.2, 26.9, 29.4, 29.7, 34.8, 57.1, 58.0, 122.3, 127.9, 129.3 (2C), 129.4, 131.7, 140.3, 142.3, 143.8, 152.6. IR (liq. film) ν (cm^{-1}) 2925s, 2854s, 1652w, 1541w, 1506w, 1448m, 1034w, 762w, 668w; MS (70 eV) *m/z* (rel. intensity) 304 (M$^+$, 44), 290 (100), 261 (20), 247 (31), 205 (19), 191 (30), 165 (21), 141 (11), 91 (12), 69 (13); UV λ_{max} (hexane) 235 nm (log ε=4.14), 243 (3.83), 274sh (3.54), 284sh (3.54), 339 (3.29). Found: 304.2207. Calcd for $C_{23}H_{28}$: M, 304.2191.

3.1.5. Dispiro[cyclohexane-1,1′-(1′,7′-dihydrocyclopenta[*f*]azulenium)-7′,1″-cyclohexane] perchlorate (9) and dispiro[cyclohexane-1,1′-(1′,5′-dihydrocyclopenta[*f*]azulenium)-5′,1″-cyclohexane] perchlorate (10). To a solution of 300 mg (0.987 mmol) of **15** in 5 ml of acetonitrile was added 338 mg (0.990 mmol) of trityl perchlorate. The mixture was stirred at room temperature for 0.5 h. To the reaction mixture at 0°C was added 25 ml of ether. Solids formed were collected by filtration and recrystallized from a mixture of dichloromethane and ether to give 176 mg (44% yield) of **9** as yellow microcrystals. Mp=217–218°C. ^{1}H NMR (CD_3CN) δ=1.32 (dm, J=13.2 Hz, 4H), 1.56 (qt, J=13.2, 3.3 Hz, 2H), 1.72 (qt, J=13.2, 3.3 Hz, 4H), 1.91–2.02 (m, 6H), 2.21 (qt, J=13.2, 3.3 Hz, 4H), 7.36 (d, J=5.6 Hz, 2H), 8.06 (d, J=5.6 Hz, 2H), 8.70 (s, 2H), 8.89 (s, 1H). IR (KBr) ν (cm^{-1}) 2928s, 1651m, 1532m, 1487m, 1458m, 1422m, 1359m, 1085vs, 867w, 846w, 791w, 764m, 701m, 622s; MS (70 eV) *m/z* (rel. intensity) 303 (M$^+$, 37), 302 (100), 273 (21), 259 (14), 247 (19), 217 (21), 202 (19), 191 (26), 165 (11), 69 (11). Found: C, 65.69; H, 6.72%. Calcd for $C_{23}H_{27}ClO_4$ $0.2H_2O$: C, 65.84; H, 6.53%.

The cation **10** was obtained as a brownish-yellow crystals in 30% yield from **21** in the same manner. Mp=181–182°C. ^{1}H NMR (CD_3CN) δ=1.36 (m, 4H), 1.65 (m, 6H), 2.01 (m, 6H), 2.22–2.41 (m, 4H), 7.39 (d, J=5.6 Hz, 1H), 7.61 (d, J=5.6 Hz, 1H), 7.85 (d, J=5.6 Hz, 1H), 7.94 (d, J=5.6 Hz, 1H), 9.00 (d, J=9.9 Hz, 1H), 9.04 (d, J=9.9 Hz, 1H), 9.19 (s, 1H). IR (KBr) ν (cm^{-1}) 2924s, 2854s, 1493m, 1446s, 1295m, 1078s, 806s, 758s, 699s, 606m; MS (70 eV) *m/z* (rel. intensity) 303 (M$^+$, 31), 302 (100), 273 (20), 259 (24), 247 (30), 217 (42), 202 (42), 191 (50), 165 (20), 69 (20). Found: C, 68.38; H, 6.93%. Calcd for $C_{23}H_{27}ClO_4$: C, 68.56; H, 6.75%.

3.1.6. 2-Acetyl-1,3,5-cycloheptatriene (22). In a 500-ml round-bottom flask at −10°C under nitrogen atmosphere was charged 100 ml of 1.5 M *n*-butyllithium hexane solution. At the same temperature the solvent was removed under vacuum. To the residue at −78°C was added 250 ml of THF, followed by addition of 14.4 g (150 mmol) of sodium *t*-butoxide and 13.8 g (150 mmol) of 1,3,5-cycloheptatriene. After this mixture was stirred at −78°C for

24 h, 14.4 g (165 mmol) of *N*,*N*-dimethylacetamide at −50°C was added to the mixture. Then, the cooling bath was removed, and the mixture was stirred at room temperature for 2 h. The resulted reaction mixture was poured into water and was extracted with ether (100 ml×3). The combined organic layer was washed with a saturated sodium hydrogencarbonate solution and brine, and was dried with anhydrous $MgSO_4$. After evaporation of the solvent, the residual oil was purified by flash silica gel chromatography with ether–hexane (1:9) as eluent to give 3.99 g (19% yield) of **22**[16] as a colorless oil. ^1H NMR ($CDCl_3$) $\delta=2.37$ (s, 3H), 2.38 (t, $J=7.3$ Hz, 2H), 5.48 (dtd, $J=9.3$, 7.3, 1.7 Hz, 1H), 6.23 (ddd, $J=9.3$, 5.4, 0.7 Hz, 1H), 6.35 (t, $J=7.3$ Hz, 1H), 6.73 (ddd, $J=11.5$, 5.4, 1.7 Hz, 1H), 7.21 (dd, $J=11.5$, 0.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) $\delta=26.4$, 27.7, 120.9, 127.6, 127.7, 129.3, 131.9, 138.7, 198.1.

3.1.7. 1,5-Dicetyl-1,3,5-cycloheptatriene (17). A suspension of 33.0 g (250 mmol) of aluminium chloride in 100 ml of dichloromethane was refluxed with vigorous stirring. To this was added dropwise 17.3 g (220 mmol) of acetylchloride, followed by addition of 13.4 g (100 mmol) of **22**. This mixture was refluxed for 4 h and was cooled to −20°C. To this was added dropwise 10 ml of acetic acid in such manner that the temperature of the reaction mixture did not exceed 0°C, and then 50 ml of water was added carefully. The resulted reaction mixture was poured into water and was extracted with chloroform (100 ml×3). The combined organic layer was washed with a saturated sodium hydrogencarbonate solution and brine, and was dried with anhydrous K_2CO_3. After evaporation of the solvent, the residual oil was purified by alumina chromatography to give 10.9 g (61% yield) of **17** as a pale yellow oil. ^1H NMR ($CDCl_3$) $\delta=2.37$ (s, 3H), 2.40 (s, 3H), 2.79 (d, $J=7.6$ Hz, 2H), 6.53 (tm, $J=7.6$ Hz, 1H), 6.85 (dd, $J=11.5$, 5.8 Hz, 1H), 7.10 (d, $J=5.8$ Hz, 1H), 7.48 (dd, $J=11.5$, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) $\delta=22.5$, 26.0, 26.2, 130.3, 132.6, 132.7, 133.6, 134.2, 139.2, 197.0, 197.3. IR (liq. film) ν (cm^{-1}) 3025m, 2927m, 1666s, 1603m, 1538m, 1430m, 1256s, 1211s, 1020m, 975m, 774m; MS (70 eV) *m*/*z* (rel. intensity) 176 (M^+, 100), 161 (22), 133 (15), 105 (22), 91 (36), 63 (18); UV λ_{max} (hexane) 236 nm (log $\varepsilon=4.15$), 292 (3.59). Found: 176.0836. Calcd for $C_{11}H_{12}O_2$: M, 176.0837.

3.2. Determination of pK_R+ values

The UV spectra in various pH of 50% aqueous acetonitrile solutions were measured by exactly the same method of Komatsu et al.[1] Observed absorbance at the longest absorption maxima at 383 nm for **9** and at 400 nm for **10** was plotted against pH to give a classical titration curve, whose midpoint was taken as the pK_R+. Accuracy is ±0.1.

3.3. Cyclic voltammetry

A standard three-electrode cell configuration was employed using a glassy carbon disk working electrode, a Pt wire auxiliary electrode, and an Ag wire as an Ag/Ag+ quasi-reference electrode. The reference electrode was calibrated at the completion of each measurement on a saturated calomel electrode (SCE). Cyclic voltammetry was measured in an acetonitrule solution with tetrabutylammonium perchlorate as a supporting electrolyte and a scan rate of 0.1 V/s at 25°C. The peaks of **9** and **10** are irreversible.

3.4. X-Ray structural analysis of dispiro[cyclohexane-1,1′-(1′,7′-dihydrocyclopenta[*f*]azulenium)-7′,1″-cyclohexane] perchlorate (9)

Pale yellow prismatic crystals of **9** containing dichloromethane were obtained by recrystallization from a mixture of hexane, ether and dichloromethane. One of them having approximate dimensions of $0.50\times0.50\times0.50$ mm^3 was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation and a rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $22.32<2\theta<24.99°$, corresponded to a primitive monoclinic cell with dimensions: $a=12.513(3)$ Å, $b=13.079(3)$ Å, $c=15.013(3)$ Å, $\beta=93.27(2)°$, $V=2453.0(9)$ Å^3. For $Z=4$ and formular weight=487.85, the calculated density is 1.32 g/cm^3. Based on the systematic absences of $h01$:$h+1\neq2n$ and $0k0$:$k\neq2n$, the space group was uniquely determined to be $P2_1/n$ (# 14). The data were collected at a temperature of 23°C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 60.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.26° with a take-off angle of 6.0°. Scans of $(1.63+0.30\tan\theta)°$ were made at speeds of 32.0°/min (in omega). The weak reflections ($I<10.0\sigma(I)$) were rescanned (maximum of five scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 235 mm. The computer-controlled slits were set to 3.0 mm (horizontal) and 3.0 mm (vertical). Of the 7757 reflections which were collected, 7156 were unique ($R_{int}=0.023$). The intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. The linear absorption coefficient, μ, for Mo Kα radiation is 4 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.88 to 1.00. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 916 observed reflections ($I>3.00\sigma(I)$) and 280 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of: $R=0.054$, $Rw=0.067$, and $R1=0.054$ for $I>3.0\sigma(I)$ data. The standard deviation of an observation of unit weight was 1.54. The weighting scheme was based on counting statistics and included a factor ($p=0.050$) to downweight the intense reflections. Plots of $\sum w(|F_o|-|F_c|)^2$ vs $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.13 and -0.17 e$^-$/Å^3, respectively. Tables of fractional atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, United Kingdom (CCDC 172674).

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