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Dispiro[cyclohexane-1,1′-(1′,7′-dihydrocyclopenta[*f*]azulenium)-7′,1″-cyclohexane] perchlorate, a new highly stable hydrocarbon cation

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Abstract—The title cation was synthesized from 1,6-diacetylcyclohepta-1,3,5-triene by a six-step sequence involving an aldol reaction, the Nazarov cyclization, the Shapiro reaction and hydride abstraction, and its pK_{R+} value was found to be 13.2, providing a new access to highly stable hydrocarbon cations. © 2002 Elsevier Science Ltd. All rights reserved.

Independent studies on the synthesis of a stable hydrocarbon cation by Komatsu and Ito have provided cations **1**[1] and **2**[2] with high pK_{R+} values of 13.0 and 14.4, respectively, though X-ray crystal structure analysis of those stable hydrocarbon cations has not been achieved yet. On the other hand, triarylmethyl cations with heteroatomic substituents were recently found to show much greater stability with values of more than 19.7.[3–5] We reported that spiroalkylated azulenium ions **3a**–**c**[6] show greater thermodynamic stability compared with various disubstituted tropylium cations, such as 1,4-bis(cyclopropyl)tropylium ion ($pK_{R+}=7.56$),[7] 1,2-bicyclo[2.2.2]octenotropylium ion (8.8),[8] and cyclohepta[*a*]acenaphtalenium ion (8.7).[9] The effect of the annelation of the spiro[4,*n*]alka-2,4-diene around a tropylium ion ring on its stability can be attributed to the extended π–π conjugation at the 2,3 position and σ–π 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. The title cation **4**, whose tropylium ring is annelated doubly by two spiro[4,5]deca-2,4-dienes, is expected to show greater stability than **3**. In this letter we describe the synthesis, stability and X-ray crystal structure of **4** (Chart 1).

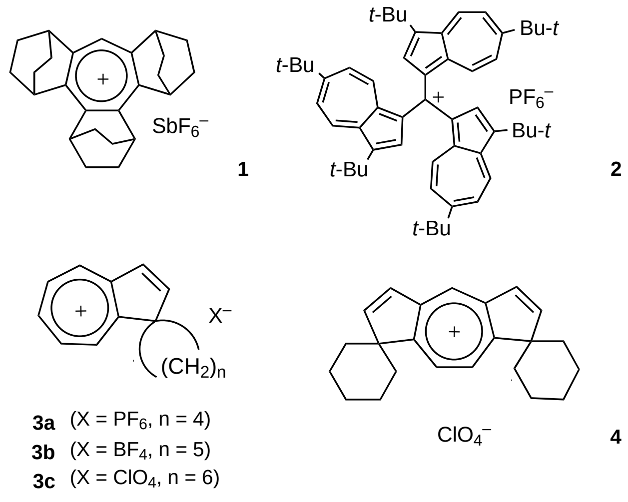

Chart 1.

The synthesis of **4** was accomplished from 1,6-diacetylcyclohepta-1,3,5-triene (**5**)[10] by the method which we had developed for **3c**. The trimethylsilyl enol ether **6** was treated in the presence of trimethylsilyl triflate with 1,1-dimethoxycyclohexane to give **7** in 81% yield,[11] while the attempted aldol reaction of **6** with cyclohexanone in the presence of titanium chloride[12] gave none of the desired aldol product. The double Nazarov cyclization[13] of **7** in a mixture of formic acid and phosphoric acid afforded the tricyclic diketone **8** in 46% yield. The Shapiro reaction[14] of tosylhydrazone of **8** and subsequent hydride abstraction with trityl perchlorate gave **4** as yellow microcrystals in 44% yield.

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

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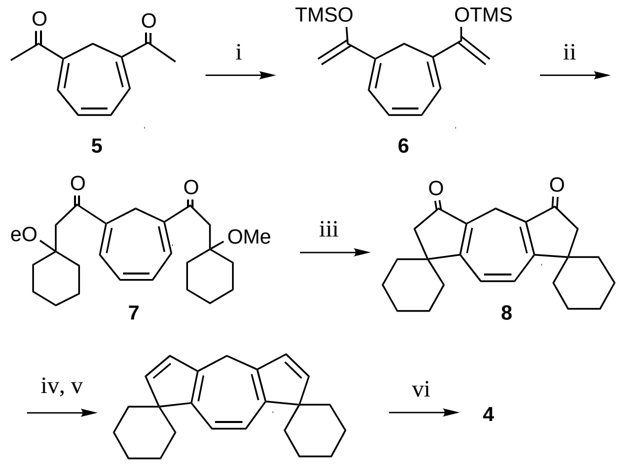
The structure of **4** was fully characterized by spectroscopic and elemental analyses.[15] The average chemical shift (8.27 ppm) of the olefinic protons of **4** is slightly lower than that (8.67 ppm) of **3b**, and the same is true for the ^{13}C NMR chemical shift (152.3 ppm) of the trigonal sp^2 carbons of **4** which is lower than that (153.8 ppm) of **3b**, indicating the delocalization of the positive charge over the skeletal carbons of the additionally annelated spiro[4,5]deca-2,4-diene unit. The pK_{R+} value of **4** was determined by the UV method in buffered 50% aqueous acetonitrile solutions to be 13.2.[16] Thus, the thermodynamic stability of **4** is comparable to that of **1** and slightly less than that of **2**. The difference (6.1) in the values between **3b** (10.0)[6] and tropylium ion (3.9)[7] is far greater than that (3.2) between **4** and **3b**. Thus, a saturation effect of electronic stabilization by the spirodecadiene to the tropylium cation is clearly shown. Reduction peak potential for **4** measured by cyclic voltammetry[17] was −0.65 V versus SCE, designating increased reduction reluctance of **4** compared with **3a**, **b**, and **c** (Scheme 1, Table 1).[6]



Scheme 1. *Reagents and conditions*: (i) TMSCl, NaI, Et_3N, CH_3CN, rt 12 h, 61%; (ii) TMSOTf, 1,1-dimethoxycyclohexane, CH_2Cl_2, 81%; (iii) HCO_2H, H_3PO_4, 90°C, 5 h; (iv) $TsNHNH_2$, THF, reflux, 4 days; (v) MeLi, ether, rt, 12 h, 22% from **8**; (vi) $Ph_3C^+ClO_4^-$, CH_3CN, 44%.

Table 1. The pK_{R+} values and reduction peak potentials of various cations

Cation	pK_{R+}	Reduction potential	
		V versus SCE	V versus Ag/Ag$^+$
1	13.0		−1.12[a]
2	14.4		−0.91, −1.72[b]
3a	9.9	−0.41	
3b	10.0	−0.46	
3c	10.4	−0.54	
4	13.2	−0.65	

[a] Taken from Ref. 1.

[b] Taken from Ref. 2.

The molecular structure of **4** was elucidated by X-ray crystallographic analysis.[18] An ORTEP drawing and the atomic distances of **4** are shown in Figs. 1 and 2, respectively. 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. The two cyclohexane rings 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, 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.[19] One may expect that when the σ–π conjugation in **4** is effective, the C_{sp3}–C_{sp3} single bonds of the cyclohexane ring at the spiro juncture should elongate. In the crystal structure of **4**, the average C_{sp3}–C_{sp3} bond distance (1.54 Å) at the C1(1′) and C7′(1″) carbons is indeed greater than that (1.52 Å) of the other bonds in the cyclohexane rings, implying the σ–π conjugation of **4**, though further comparison with bond length data of related compounds is necessary to confirm this.

In summary, we have established an efficient synthesis of the dispiro[cyclohexane-1,1′-(1,7′-dihydrocyclopenta-[*f*]azulene)-7′,1″-cyclohexane] skeleton via the double Nazarov cyclization of the cycloheptatriene derivative. The title cation **4**, obtained by subsequent hydride abstraction, shows enhanced thermodynamic stability comparable to that of **1**, providing a new access to highly stable hydrocarbon cations. We have also demonstrated the X-ray crystal structure of **4**, as the first example of highly stable hydrocarbon cations.

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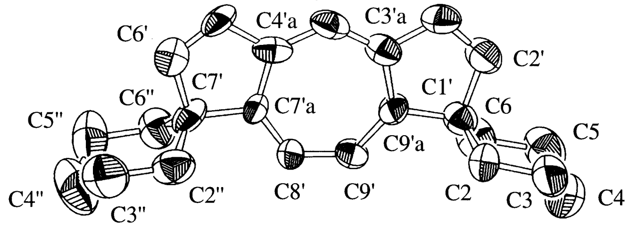

Figure 1. An ORTEP drawing of the cation **4**. The perchlorate counter anion and the dichloromethane included are omitted.

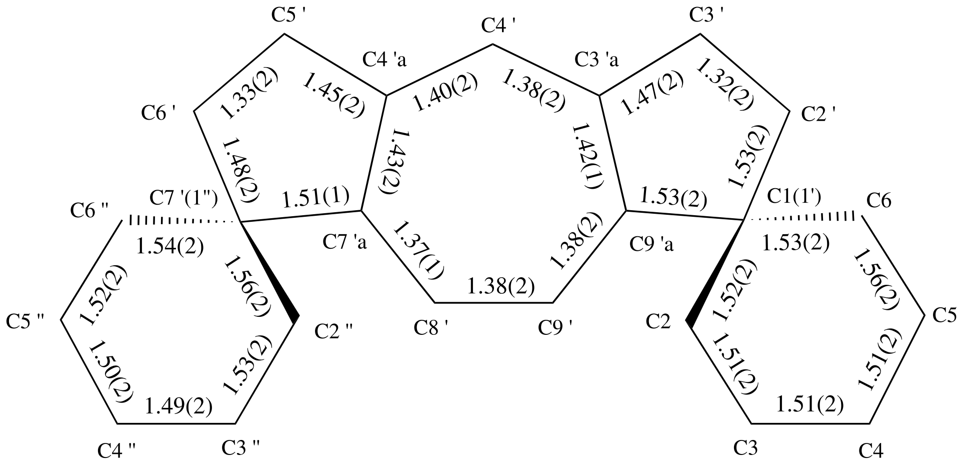

Figure 2. Atomic distances (Å) in the crystal of the cation **4**.

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15. Selected data for new compounds. **4**: mp 217–218°C; $\lambda_{\max}$ (CH_3CN)/nm 232, 297sh, 311, 364, 383; δ_H (400 MHz; CD_3CN), 1.32 (4H, dm, 12.4), 1.57 (2H, tt, 12.4, 3.4), 1.65–1.78 (4H, m), 1.90–2.02 (6H, m), 2.21 (4H, td, 12.4, 3.4), 7.43 (2H, d, 5.6), 8.06 (2H, d, 5.6), 8.79 (2H, s), 8.89 (1H, s); δ_C (100 MHz; CD_3CN), 25.0 (C3, 5, 3″, 5″), 26.1 (C4, 4″), 33.4 (C2, 6, 2″ 6″), 62.0 (C1, 1″), 134.3 (C3′, 5′), 137.2 (C3′), 140.4 (C8′, 9′), 160.8 (C2′, 6′), 167.3 (C3′a, 4′a), 173.8 (C7′a, 9′a); $\nu_{\max}$ (KBr)/cm^{-1} 2928s, 1731m, 1359m, 1085s, 867w, 764m, 622s; m/z (rel. int.) 302 (M^+, 100), 273 (13), 259 (14), 247 (19), 217 (21), 202 (19), 191 (26), 165 (11), 69 (11); EA calcd for $C_{23}H_{27}ClO_4{\cdot}0.2\ CH_2Cl_2$; C, 65.84; H, 6.53, found C, 65.69; H, 6.73. **7**: δ_H (400 MHz; $CDCl_3$), 1.21 (4H, m), 1.51 (12H, m), 1.74 (4H, m), 2.89 (4H, s), 2.99 (2H, s), 3.19 (6H, s), 6.94 (2H, m), 7.12 (2H, m); δ_C (100 MHz; $CDCl_3$), 21.7, 24.7, 25.4, 34.1, 44.7, 48.8, 75.8, 132.1, 133.8, 135.9, 198.0; $\nu_{\max}$ (liq. film)/cm^{-1} 2933s, 2856s, 1663s, 1455m, 1256m, 1147m, 1073s, 927w, 817w, 742m; m/z (rel. int.) 400 (M^+, 8), 368 (23), 336 (17), 240 (32), 149 (32), 113 (100), 81 (64), 69 (26); HRMS calcd for $C_{25}H_{36}O_2$ 400.2613, found 400.2569. **8**: Creamy white prisms. Mp >250°C (decomposed); $\lambda_{\max}$ (CH_3OH) nm 238, 249, 257sh, 317; δ_H (400 MHz; $CDCl_3$), 1.21 (2H, m), 1.30 (8H, m), 1.56 (4H, m), 1.75 (6H, m), 2.34 (4H, s), 3.00 (2H, s), 6.96 (2H, m); δ_C (100 MHz; $CDCl_3$) 16.1, 23.5, 25.3, 35.8, 44.3, 46.8, 131.1, 135.6, 170.7, 205.2; $\nu_{\max}$ (KBr)/cm^{-1} 2935m, 1691s, 1556w, 1264w, 1195m, 1092w, 919w, 754w; m/z (rel. int.) 336 (M^+, 100), 293 (5), 279 (7), 141 (7), 115 (6), 81 (5); EA of the bis(2,4-dinitrophenylhydrazone) derivative (mp >300°C), calcd for $C_{35}H_{36}N_8O_8$; C, 60.34; H, 5.21; N, 16.08, found C, 60.05; H, 5.28; N, 15.78. **9**: δ_H (400 MHz; $CDCl_3$), 1.14 (2H, m), 1.50 (8H, m), 1.56 (4H, m), 1.75 (6H, m), 3.19 (2H, s), 6.21 (2H, d, 5.4), 6.35 (2H, s), 6.89 (2H, d, 5.4); δ_C (100 MHz; $CDCl_3$), 25.9 (C3, 5, 3″, 5″), 26.7 (C4, 4″), 29.3 (C4′), 33.3 (C2, 6, 2″, 6″), 58.0 (C1, 1″), 123.2 (C2′, 6′),

133.6 (C8′, 9′), 133.8 (C3′, 4′), 144.8 (C3′a, 4′a), 150.0 (C7′a, 9′a); *m*/*z* (rel. int.) 304 (M^+, 100), 303 (71), 291 (21), 290 (68), 205 (28), 191 (43), 165 (36), 91 (20); HRMS calcd for $C_{23}H_{28}$ 304.22178, found 304.21910.

16. The reversibility in the pK_{R+} determination was confirmed by resumption of the cation spectrum up to 60% of the original intensity upon acidification with a few drops of concd H_2SO_4.
17. Cyclic voltammetry was measured in an acetonitrile solution with tetraammonium perchlorate as a supporting electrolyte. The peak of **4** is irreversible.
18. Crystal data for **4**: $C_{23}H_{27}ClO_4CH_2Cl_2$, $M=487.85$, monoclinic, $a=12.513(3)$, $b=13.079(3)$, $c=15.013(3)$ Å, $\beta=93.27$ (2)°, $V=2453.0(9)$ Å^3, $Z=4$, $D_{\text{calcd}}=1.321$ g cm^{-3}, μ(Mo-Kα)$=0.71$ mm^{-1}, $T=296$ K, space group $P2_1/n$ (no. 14), 7757 reflections measured, 7156 unique ($R_{\text{int}}=0.023$) which were used in all calculations. $R_1=0.054$ ($F^2>2\sigma$). The final $wR(F^2)$ was 0.067 (all data). CCDC deposition No. 172674.
19. The hybrid density functional calculations were done on an IBM-RS6000-G94RevE computer by using the Gaussian 94 (Revision E.1, Gaussian, Inc., Pittsburgh Pa, 1995) program.