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Synthesis, Stability, and X-Ray Crystallographic Structure Analysis of Spiro[1*H*-azulenium-1,1′-cycloalkane] Ions

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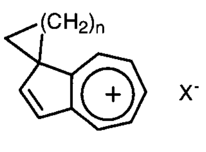
Abstract—Direct cycloalkylation of 1,6-dihydroazulene and subsequent hydride abstraction with a trityl salt gave spiro[1*H*-azulenium-1,1′-cyclopentane and -1,1′-cyclohexane] ions (**3** and **4**). On the other hand, spiro[1*H*-azulenium-1,1′-cycloheptane] ion (**5**) was synthesized from 1-acetylcyclohepta-1,3,5-triene by a sequence involving the Mukaiyama aldol reaction, the Nazarov cyclization, the Shapiro reaction, and hydride abstraction. These cations showed greater kinetic stability than the three- and four-membered ring homologues. Their pK_R+ values are far greater compared with those of the known disubstituted tropylium cations and are in the order of the number of carbon atoms at the 1 position, indicating that an inductive effect of the spiroalkyl groups, besides the π-conjugative and σ-conjugative effects, governs the thermodynamic stability. X-Ray crystallographic structure analysis of these cations was also described. © 2000 Elsevier Science Ltd. All rights reserved.

We have recently reported the synthesis and some limited physical and chemical properties of spiro[1*H*-azulenium-1,1′-cyclopropane and -1,1′-cyclobutane] ions **1**[1] and **2**,[2] the former of which has been thought to be an intermediate in solvolysis of 2-(1-azulyl)ethyl tosylate.[3] These cations seem to be suitable candidates for evaluation of the σ–π interaction[4] between a σ-orbital of the spiro ring and an electron-deficient *p*-orbital at the tropylium part because of their structural rigidity and appropriate bisected geometry. However, both cations were found to undergo facile expansion of the cyclopropane and cyclobutane rings at below room temperature or to react instantaneously with nucleophiles to give the addition products.[1,2,5] In this paper we report the synthesis and the kinetic and thermodynamic stability of spiro[1*H*-azulenium-1,1′-cyclopentane, -1,1′-cyclohexane and -1,1′-cycloheptane] ions (**3**–**5**), which are higher homologues of **1** and **2**; also, the X-ray crystallographic structure analysis of **3** and **4** is described.[6]



n = 1, X = BF_4 (**1**)
n = 2, X = BF_4 (**2a**), X = PF_6 (**2b**)
n = 3, X = BF_4 (**3a**), X = PF_6 (**3b**)
n = 4, X = BF_4 (**4a**)
n = 5, X = BF_4 (**5a**), X = ClO_4 (**5c**)

Results and Discussion

Synthesis of spiro[1*H*-azulenium-1,1′-cyclopentane and -1,1′-cyclohexane] ions (3 and 4)

The synthesis of **3** and **4** was accomplished in two steps starting from 1,6-dihydroazulene (**6**)[1,7] in a similar way to that of **1** and **2**. Spiroalkylation of **6** with 1,4-dibromobutane and 1,5-dibromopentane in the presence of sodium hydride as a base in dimethyformamide (DMF) gave **7** and **8** as a slightly air-sensitive colorless oil in 46 and 33% yields, respectively. On the other hand, the homologous hydrocarbon with a seven-membered ring was not obtained in the reaction with 1,6-dibromohexane in spite of many efforts under various conditions. Addition of a molar equivalent of a trityl salt to an acetonitrile solution of **7** and **8** at 0°C resulted in a dull-green solution, from which the cations **3b** and **4a** were isolated as green crystals in 62 and 92% yields, though the tetrafluoroborate salt **3a** was obtained as a greenish oil. These cations in the solid state did not show any appreciable change at room temperature and can be stored in a refrigerator for at least a year (Scheme 1).

Synthesis of spiro[1*H*-azulenium-1,1′-cycloheptane] ion (5)

Since spiroalkylation of **6** was hampered in the experiments leading to the seven-membered ring compound (vide supra), the cation **5** was synthesized by an alternative synthetic method, a part of which we have recently developed.[8] The

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Keywords: carbocations; spiro compounds; tropylium ion; cycloaddition; X-ray structure analysis; azulene.

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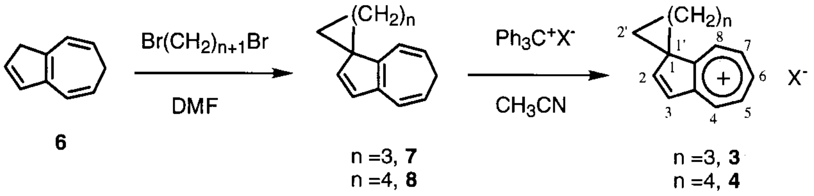
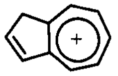


Scheme 1.

carbon skeleton required was constructed starting from 1,3,5-cycloheptatriene by a short-step sequence involving the Nazarov cyclization[9,10] as a key step, as follows. The trimethylsilyl enol ether of 1-acetylcyclohepta-1,3,5-triene (**9**),[11] prepared from 1,3,5-cycloheptatriene in two steps, was reacted with cycloheptanone under the conditions of the Mukaiyama aldol reactions[12] to give the alcohol **10** in 27% yield. Treatment of **10** with a mixture of formic acid and phosphoric acid gave the spiroalkylated tetrahydro-3-azulenone **11** in 72% yield. Tosylhydrazone of **11** was subjected to the Shapiro reaction[13] with methyllithium as a base to afford the precursor hydrocarbon **12** in 26% yield based on **11**. Hydride abstraction of **12** with a trityl salt in acetonitrile at 0°C gave **5** as greenish solids in moderate to high yields. The cation **5**, like **3** and **4**, was found to be stable at room temperature. Since other 1,1-disubstituted tetrahydro-1-azulenones can be prepared just by changing the Mukaiyama aldol reaction substrate to other ketones,[8] this protocol of the transformation from **6** into **5** will be applied to the synthesis of various 1,1-disubstituted 1*H*-azulenium ions (Scheme 2).

Physical properties of the azulenium ions

The structures of the cations **3**, **4** and **5** were fully confirmed by spectroscopic and elemental analyses. Assignments of proton and carbon signals were based on H–H COSY, HMQC, and HMBC spectra and are listed in Fig. 1. Average carbon chemical shifts of the tropylium ion part in **3**–**5** are comparable to that of **2** (δ_{ave}=155.4 ppm)[2] and are slightly greater than that of **1** (δ_{ave}=152.2 ppm)[1] and the proton chemical shifts show a similar tendency. The UV spectra of **3**–**5** in acetonitrile or 50% H_2SO_4 show three absorption maxima at around 230, 270, and 360 nm. Comparison of the wave-lengths of the long absorption maxima in 50% H_2SO_4 (**3**: 364 nm, **4**: 367 nm, **5**: 365 nm) with that of the parent azulenium ion **13** (352 nm)[14] shows clear bathochromic shifts by more than 10 nm. These shifts indicate that spiroalkylation at the 1 position of the azulenium ion reduced the HOMO-LUMO gap of this cation system. The pK_{R^+} values of **3**–**5** were determined by the UV method in 50% aqueous acetonitrile solutions to be 9.9, 10.0, and 10.4, respectively. The thermodynamic stability of these cations is comparable to that of the tris(cyclopropyl)cyclopropenium ion (pK_{R^+}= 10.0)[15] and is far greater than those of known disubstituted tropylium ions, such as 1,4-di-*t*-butyl one (**14**, 5.42),[16] 1,4-bis(cyclopropyl) one (**15**, 7.56),[16] 1,2-bicyclo[2.2.2]octano one (**16**, 8.8)[17] and cyclohepta[*a*]acenaphtalenylium ion (**17**, 8.7).[18] Reduction peak potentials for **3**–**5** measured by cyclic voltammetry were −0.41, −0.46, and −0.54 V vs SCE,[19] respectively, indicating increased reduction resistance of these cations compared with tropylium cation (−0.12[20] or −0.16 V[21] vs SCE). These properties of the cations **3**–**5** might be attributed to the effective σ–π interaction in this cationic system. The order of stability is **5**>**4**>**3**, which is the same as the order of the number of carbon atoms in the spiro saturated carbocyles. Thus, the thermodynamic stability is suggested to be governed also partly by an inductive effect of the carbocycle at the 1 position of these cations, in addition to a π-conjugative effect of the extended C–C double bond at the 2 and 3 positions and the σ-conjugative effect of the spiro ring.



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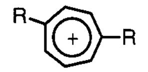
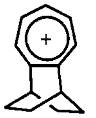


14 ; R = *t*-butyl
15 ; R = cyclopropyl



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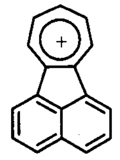

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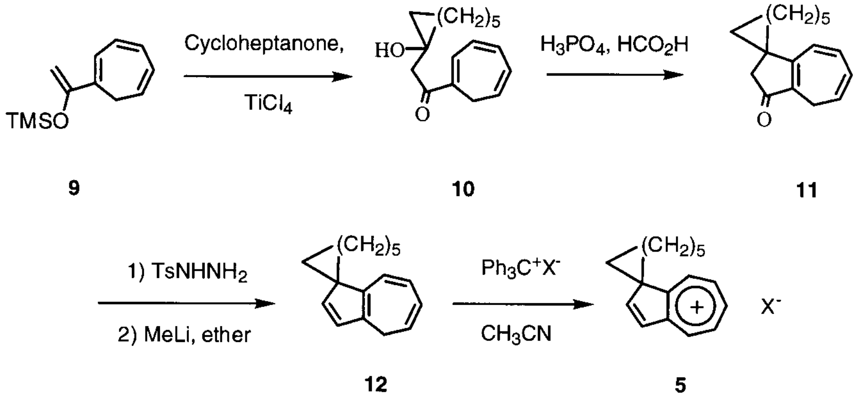


Scheme 2.

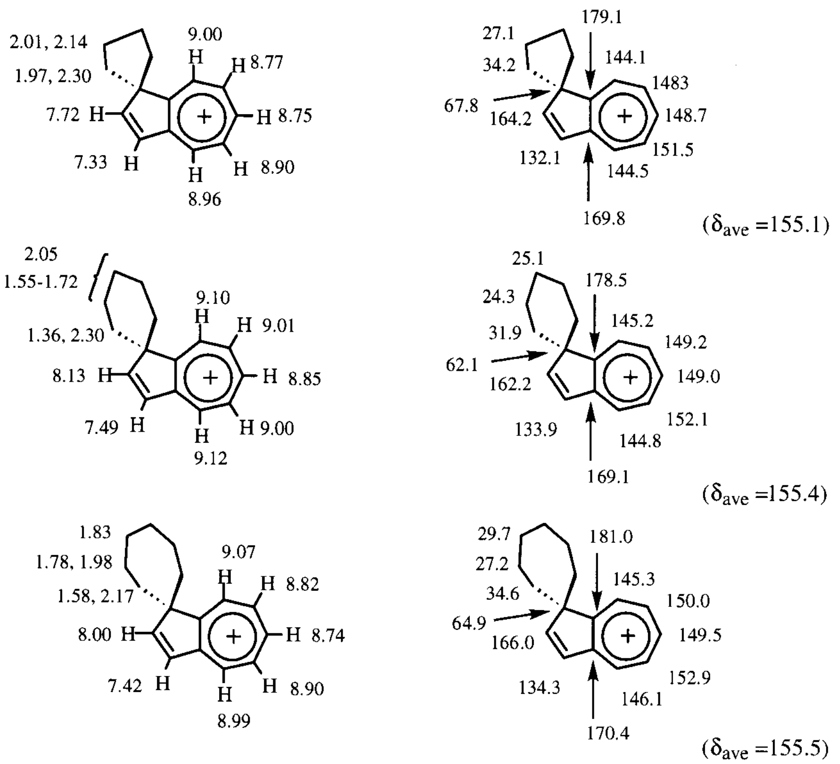


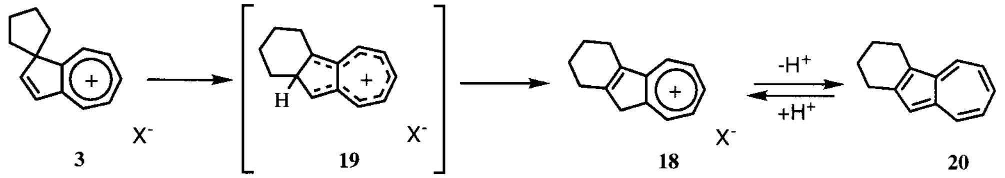
Figure 1. Proton (left) and carbon (right) shift values (δ ppm) assigned for **3**–**5**. Average carbon chemical shifts (δ ppm) of the tropylium ion part are given in parentheses.

Rearrangement of azulenium ions; kinetic stability

Although the cations **3**–**5** in solid state or solution at room temperature are stable, **3a** gradually rearranged to on heating 2,3-tetramethylene-1*H*-azulenium ion (**18**) probably via 2,3-tetramethylene-2*H*-azulenium ion (**19**) as shown in Scheme 3. The rearrangement could be monitored by ^{1}H NMR spectroscopy and its half-life was found to be 180 min at 80°C in acetonitrile-d_3. Pouring the solution of **18** into an aqueous acetone solution and extraction with hexane gave **20**[22] in a yield of 77% based on the cation **3**. The cation **5a** did not rearrange below 120°C in any solvent but on heating in tetrachloroethane solution (147°C) **5a** resulted in decomposition. However, no clear product was observed by NMR analysis in its deuterated solution. On the other hand, the cation **4a** did not show any appreciable change even under the conditions in refluxing tetrachloroethane. Thus, the order of kinetic stability of these cations is **4**>**5**>**3**. Since this order is reciprocal to the order of the ring strain[23] of cycloalkanes themselves attached at the 1 position, the kinetic stability is suggested to be dependent on the ring strain of the spiro[5.*n*]alka-1,3-diene (*n*=5–7) part of these cations.

X-Ray crystallographic structures of the azulenium ions (3b and 4a)

In spite of many efforts we have not succeeded in preparing any suitable single crystal of either **5a** or **5c**, but those of **3b** and **4a** for X-ray structure analysis were obtained by recrystallization from a mixture of ether and dichloromethane. An ORTEP drawing, crystal packing and selected bond lengths of **3b** are shown in Fig. 2. In a crystal lattice eighteen molecules of **3b** exist and six of them arrange around a hydrophobic hollow column along the c axis in such a way that two sets of three molecules hexagonally locate up and down with their C3′-C4′ ethylene parts facing each other. The cyclopentane ring of **3b** in the crystal shows an envelope conformation[24] in which the stern folds slightly to the side of the 2 position. The C–C bonds of the cyclopentane ring, the two bonds at the 1′(1) position (C1′–C2′ and C1′–C5′), are longer by 0.052–0.165 Å than the other three C–C bonds in the ring and slightly longer by 0.003–0.026 Å than the bond length (1.546 Å) of cyclopentane itself.[25] These slightly long C–C bond lengths may be due to a substituent effect and also the σ–π interaction. The part of the azulene carbon framework in the structure of **3b** is



Scheme 3.

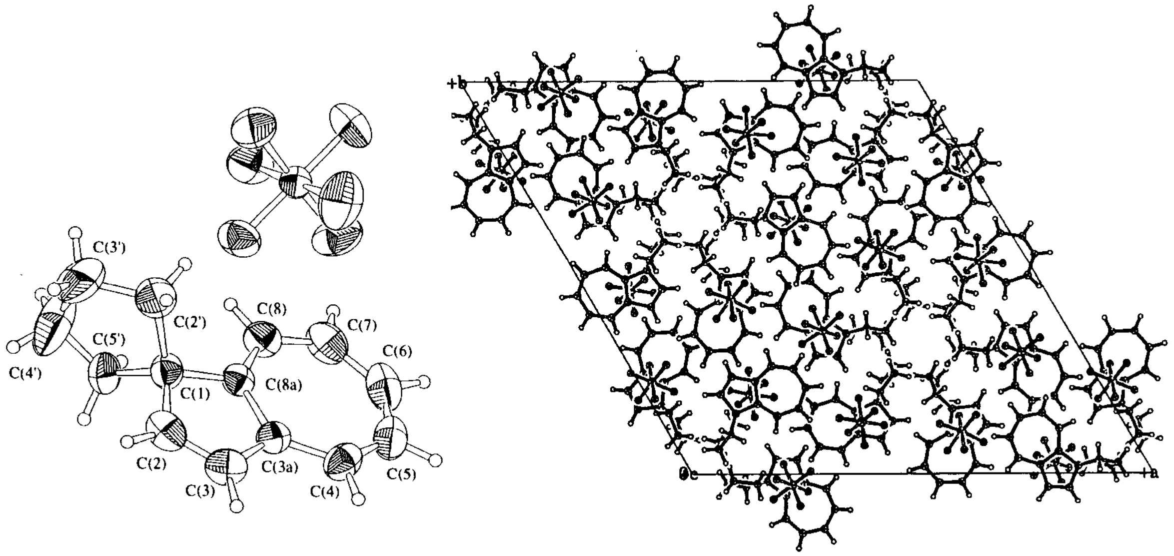


Figure 2. An ORTEP drawing and crystal packing of **3b**. Selected bond lengths and angles as follows: C1–C2; 1.496, C2–C3; 1.314, C3–C3a; 1.432, C3a–C4; 1.400, C4–C5; 1.359, C5–C6; 1.340, C6–C7; 1.372, C7–C8; 1.402, C8–C8a; 1.370, C3a–C8a; 1.412, C1′–C2′; 1.549, C2′–C3′; 1.418, C3′–C4′; 1.410, C4′–C5′; 1.497; C5′–C1′(C1); 1.575 Å. C3a–C4–C5; 128.4, C4–C5–C6; 129.9, C5–C6–C7; 129.4, C6–C7–C8; 128.0, C7–C8–C8a; 128.9, C8a–C3a–C4; 127.4°.

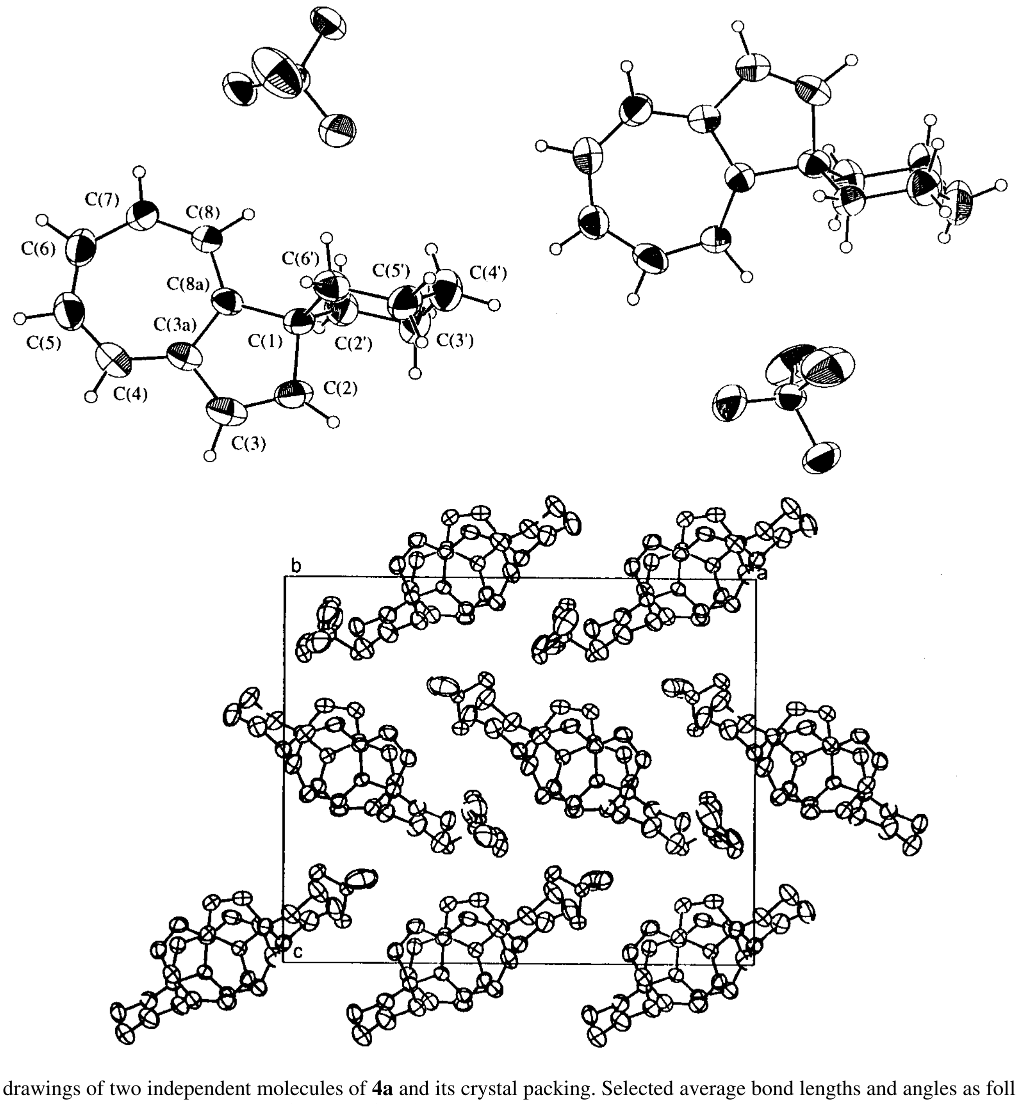
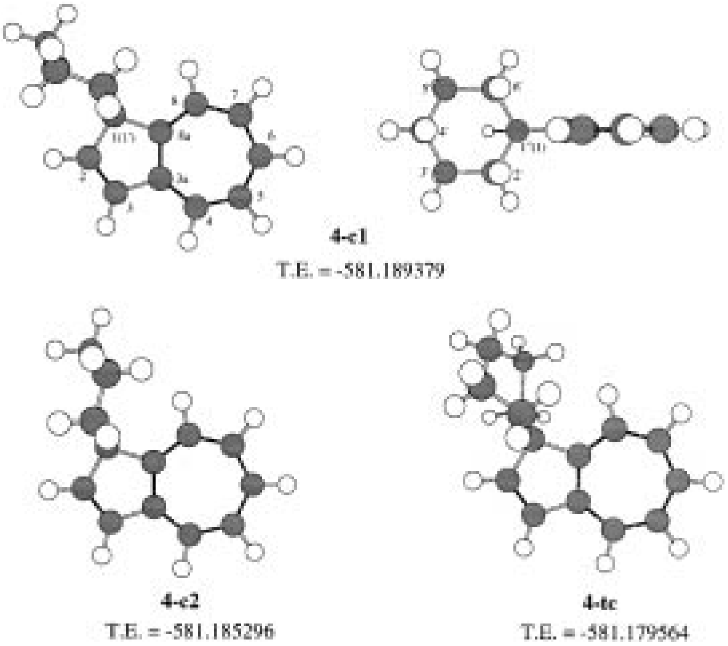


Figure 3. ORTEP drawings of two independent molecules of **4a** and its crystal packing. Selected average bond lengths and angles as follows. C1–C2; 1.54, C2–C3; 1.34, C3–C3a; 1.44, C3a–C4; 1.40, C4–C5; 1.37, C5–C6; 1.37, C6–C7; 1.37, C7–C8; 1.37, C8–C8a; 1.38, C3a–C8a; 1.41, C1′–C2′; 1.55, C2′–C3′; 1.52, C3′–C4′; 1.51 Å. C3a–C4–C5; 128.5, C4–C5–C6; 129.3, C5–C6–C7; 129.8, C6–C7–C8; 127.8, C7–C8–C8a; 129.3, C8a–C3a–C4; 127.6°.



4-c1
T.E. = -581.189379

4-c2
T.E. = -581.185296

4-tc
T.E. = -581.179564

Figure 4. MB3LYP/6-31G* optimized structures (Chem 3D output) of three conformers for the cation **4** and total energies (T.E.; in a.u.). Selected bond lengths and angles of the most stable one (**4-c1**) are as follows. C1–C2; 1.506, C2–C3; 1.353, C3–C3a; 1.447, C3a–C4; 1.407, C4–C5; 1.389, C5–C6; 1.405, C6–C7; 1.391, C7–C8; 1.407, C8–C8a; 1.386, C3a–C8a; 1.433, C1′–C2′; 1.570, C2′–C3′; 1.536, C3′–C4′; 1.535 Å. C3a–C4–C5; 128.4, C4–C5–C6; 128.9, C5–C6–C7; 128.5, C6–C7–C8; 128.9, C7–C8–C8a; 128.9, C8a–C3a–C4; 128.3°.

nearly planar; the largest torsion angle is found to be 6° through the C8–C8a–C3a–C4 atoms. The average bond angle in the seven-membered ring is 128.3° which is close to the 128.6° expected for a regular heptagon. The average C–C bond length of the seven-membered ring is 1.379 Å which is longer than that of the tropylium ion (1.35 Å) in an inclusion complex[26,27] with dibenzo-24-crown-8 and is rather close to that (1.38 Å) of acetoxytropylium bromide[28] and that (1.385 Å) of a disubstituted tropylium ion, 1,11-*o*-benzeno[2]orthocyclo[2](1,2)tropyliophane.[29] Although clear bond alternation in the seven-membered ring part as reported in tropone[27] was not observed, deviation from the average is not small—the longest bond is 1.412 Å and the shortest 1.340 Å—probably due to an effect of annelation of the cyclopentadiene part.

An ORTEP drawing and crystal packing of **4a** are shown in Fig. 3. There are two independent molecules in the crystal of **4a** with a slight difference in the bond lengths. The cyclohexane ring in both structures shows the chair conformation in which the bow folds to the side of the 2 position. The selected bond lengths of **4a** listed in Fig. 3. are average values of the two molecules. Similar structural features, seen in the crystal structure of **3b**, of the nearly planar carbon framework of the azulene moiety, the C–C bond lengths at the 1 position, and average C–C bond length and angle at the tropylium ion part are observed in **4b**. Although there are two possible chair (**4-c1** and **4-c2**) and twist chair (**4-tc**) conformations for the cyclohexane of **4**, the conformation in crystal is the most stable (**4-c1**) based on the calculation at the MB3LYP/6-31G* level of theory. Calculated total energies and the selected bond lengths and angles of those for **4** are listed in Fig. 4. The calculated bond lengths and angles agree with their X-ray counterparts to within 0.04 Å and 3°, respectively.

Summary

We have accomplished the synthesis of the title cations **3** and **4** via direct spiroalkylation of 1,6-dihydroazulene (**6**). The cation **5** has been obtained through the new synthetic sequence which involves the Mukaiyama aldol reaction, the Nazarov cyclization, the Shapiro reaction and the final hydride abstraction, starting from the silyl enol ether **9**. All of these cations are isolated as stable substances in contrast to the instability of the lower homologues, **1** and **2**, and the pK_R+ values of **3**–**5** were determined by the UV method to be 9.9, 10.0, and 10.4, respectively. This greater thermodynamic stability of **3**–**5** compared with that of the known disubstituted tropylium ions is suggested to be governed by a π-conjugative effect of the extended C–C double bond at the 2 and 3 positions and the σ-conjugative effect of the carbocycle at the 1 position, and the order of the stability seems to be derived from an inductive effect of the carbocycles at the 1 position. On the other hand, the order of kinetic stability of these cations was found to be **4**>**5**>**3**, which is suggested to be dependent on the ring strain of the carbocycles attached at the 1 position in these cations. We have also described the X-ray crystallographic structures of **3b** and **4a**, which show the nearly planar azulene carbon framework and the slight bond alternation of tropylium ion part as seen in the structure of a disubstituted tropylium ion.

Experimental

Melting points were measured on a Yanaco MP-3 and are uncorrected. IR spectra were recorded on a JASCO IR-810 and Perkin–Elmer Spectrum RX I spectrometers. UV spectra were measured on a Shimadzu UV-256FS 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 JEOL JMS-D-300 and JEOL GC-Mate mass spectrometers. Column chromatography was done with either Merck Kieselgel 60 Art 7734 or activated alumina from Wako Pure Chem. Ind. Trityl tetrafluoroborate, perchlorate and hexafluorophosphate were prepared by the reported method.[30] 1,*n*-Dibromoalkanes and cyclopentanone were purchased from Wako Pure Chem. Ind. and purified by distillation from phosphorous pentaoxide. Tosylhydrazide, phosphoric acid (85%) and formic acid (99%) were purchased from Wako Pure Chem. Ind. and were used without purification. Ethyl ether and THF were purified just before use by distillation from sodium diphenylketyl under a nitrogen atmosphere. DMF and acetonitrile were purchased from Tokyo Kasei Kogyo Co. and purified by distillation from calcium hydride. A solution of methyllithium in hexane was purchased from Kanto Chemical Co. and titrated before use. The ab initio calculations were done by using the MULLIKEN (ver. 2.0.0, 1995, IBM Co.) on an IBM RS/6000-397 computer. The MB3LYP (MBecke3LYP) functional in MULLIKEN uses the local correlation function of Perdew and Wang[31] instead of the Vosko, Wilk, and Nusair functional,[32] and is very similar to the Becke3LPY density by Stephens et al.[33]

Spiro[1,6-dihydroazulene-1,1′-cyclopentane, and -1,1′-cyclohexane] (7 and 8)

To a solution of 1,6-dihydroazulene[1] (**6**, 1.00 g, 7.68 mmol) in 40 mL of DMF at 0°C was added 0.677 g (16.9 mmol) of sodium hydride in one portion and 8.48 mmol of 1,*n*-dibromoalkane dropwise. After the addition, the ice bath was removed and the reaction mixture was stirred for 20 min at room temp. Then, the resulting reaction mixture was poured into 2 M hydrochloric solution (200 mL) and extracted with hexane (100 mL×3). The combined organic layer was washed with brine, and then dried with anhydrous $MgSO_4$. After evaporation of the solvent, the residual oil was purified by chromatography (SiO_2, hexane) to give the title compound as a slightly air-sensitive colorless oil.

7. 46% yield. ^{1}H NMR ($CDCl_3$) δ=1.70 (m, 2H, H-2′, 5′), 1.81 (m, 2H, H-2′, 5′), 1.90 (m, 4H, H-3′, 4′), 2.33 (t, *J*=6.8 Hz, 2H, H-6), 5.28 (dt, *J*=9.3, 6.8 Hz, 1H, H-7), 5.29 (dt, *J*=9.3, 6.8 Hz, 1H, H-5), 6.35 (d, *J*=9.3 Hz, 1H, H-8), 6.36 (d, *J*=5.2 Hz, 1H, H-2), 6.38 (d, *J*=5.2 Hz, 1H, H-3), 6.39 (d, *J*=9.3 Hz, 1H, H-4); ^{13}C NMR ($CDCl_3$) δ=26.21 (C-3′, 4′), 28.15 (C-6), 34.13 (C-2′), 64.19 (C-1), 116.29 (C-7), 117.35 (C-5), 122.94 (C-8), 124.50 (C-4), 129.85 (C-2), 141.00 (C-3a), 143.16 (C-3), 151.32 (C-8a); IR (film) 3005 (m), 2945 (s), 2855 (m), 1448 (m), 1393 (m), 938 (w), 900 (w), 830 (w), 783 (m), 729 (m), 693 (m), 650 (m) cm^{-1}. EIMS (70 eV) *m*/*z* (rel intensity): 184 (M$^+$, 22), 157 (23), 156 (31), 155 (40), 154 (40), 143 (48), 142 (51), 141 (100), 129 (34), 128 (50), 115 (59). UV λmax (hexane) 223 nm (log ϵ=4.11), 230 (4.13), 230 (4.13), 307 (3.48). Found: *m*/*z* 184.1246. Calcd for $C_{14}H_{16}$: M, 184.1251.

8. 33% yield. ^{1}H NMR ($CDCl_3$) δ=1.22 (dm, *J*=12.8 Hz, 2H, H-2′, 6′), 1.32 (qt, *J*=12.8, 3.6 Hz, 1H, H-4′), 1.57 (qt, *J*=12.8, 3.6 Hz, 2H, H-5′, 7′), 1.69 (td, *J*=12.8, 3.6 Hz, 2H, H-2′, 6′), 1.76–1.89 (m, 3H, H-3′, 4′), 2.32 (t, *J*=6.8 Hz, 2H, H-6), 5.30 (dt, *J*=9.2, 6.8 Hz, 1H, H-7), 5.31 (dt, *J*=9.2, 6.8 Hz, 1H, H-5), 6.38 (d, *J*=9.2 Hz, 1H, H-4), 6.41 (d, *J*=9.2 Hz, 1H, H-8), 6.46 (d, *J*=5.6 Hz, 1H, H-2), 6.76 (d, *J*=5.6 Hz, 1H, H-3); ^{13}C NMR ($CDCl_3$) δ=25.17 (C-3′, 5′), 26.03 (C-4′), 28.20 (C-6), 33.48 (C-2′, 6′), 57.68 (C-1), 116.63 (C-5), 117.78 (C-7), 123.01 (C-4), 124.55 (C-8), 131.33 (C-2), 140.47 (C-3a), 141.02 (C-3), 153.97 (C-8a); IR (film) 3010 (m), 2920 (s), 2850 (m), 1655 (m), 1445 (m), 900 (w), 840 (w), 800 (m), 780 (m), 725 (m), 700 (m) cm^{-1}. EIMS (70 eV) *m*/*z* (rel intensity): 198 (M$^+$, 42), 155 (49), 101 (63), 91 (34), 59 (77), 58 (76), 43 (100). UV λ_{max} (hexane) 221 nm (log ϵ=4.01), 229 (4.01), 280 (3.26), 306 (3.42). Found: *m*/*z* 198.1385. Calcd for $C_{15}H_{18}$: M, 198.1409.

Spiro[1,8-dihydroazulene-1,1′-cycloheptane] (12)

A solution of 1.87 g (8.20 mmol) of spiro[1,6-dihydroazulene-1,1′-cycloheptane] **11**[8] and 1.53 g (8.20 mmol) of *p*-toluenesulfonohydrazide in 20 mL of dry THF was stirred at 60°C for 96 h and then was cooled. Hexane (20 mL) was added to the reaction mixture and the solids formed were filtered. These solids were purified by silica gel column chromatography with dichloromethane as eluent to give 1.70 g (52%) of the tosylhydrazone of **11** as a white powder. This sample was used in the next reaction without further purification. The Shapiro reaction of the hydrazone was run under a nitrogen atmosphere in flame-dried glassware. To a suspension of 650 mg (1.64 mmol) of the tosylhydrazone in 50 mL of dry ether at room temperature was added 137 mL (8.20 mmol) of 0.60 M methyllithium in ether dropwise via a syringe. After the first equivalent of MeLi was added, the mixture became homogeneous and pale yellow. After the second equivalent was added, the solution became dark-orange and gradually turned brown. After 12 h of continued stirring at room temperature, several drops of water were added carefully to quench the reaction. The mixture was diluted with 100 mL of ether, washed with 50 mL of water, and dried ($MgSO_4$). The yellow solution was then concentrated. The light orange oil obtained was chromatographed on silica gel with hexane to give 160 mg (45%) of **12** as a slightly air-sensitive colorless oil: ^{1}H NMR ($CDCl_3$) δ=1.36 (dd, *J*=14.0, 6.8 Hz, 2H, H-2′, 7′), 1.50–1.90 (m, 10H, H-2′, 3′, 4′, 5′, 6′, 7′), 2.64 (d, *J*=6.4 Hz, 2H, H-8), 5.34 (dt, *J*=9.6, 6.4 Hz, 1H, H-7), 6.07 (dd, *J*=9.6, 6.0 Hz, 1H, H-6), 6.13 (d, *J*=5.6 Hz, 1H, H-2), 6.38 (dd, *J*=11.2, 6.0 Hz, 1H, H-5), 6.63 (d, *J*=11.2 Hz, 1H, H-4), 6.68 (d, *J*=5.6 Hz, 1H, H-3); ^{13}C NMR ($CDCl_3$) δ=26.18 (C-4′, 5′), 27.79 (C-4), 29.31 (C-3′, 6′), 34.83 (C-2′, 7′), 58.97 (C-1), 120.71 (C-5), 125.92 (C-6), 127.29 (C-7 or 8), 127.41 (C-8 or 7), 131.48 (C-2), 132.05 (C-3a), 147.11 (C-3), 150.33 (C-8a); IR (film) 3018 (m), 2922 (s), 2851 (s), 1457 (s), 1367 (m), 947 (w), 848 (w), 7770 (m), 729 (s), 669 (s) cm^{-1}. EIMS (70 eV) *m*/*z* (rel intensity): 212 (M+, 19), 179 (22), 170 (18), 116 (18), 95 (17), 86 (31), 57 (100). Found: *m*/*z* 212.1590. Calcd for $C_{16}H_{20}$: M, 212.1570.

1,1-Spiroalkyl-1*H*-azulenium cations 3, 4, and 5

General procedure. Trityl salt (2.00 mmol) was added in one portion to a solution of 1,1-spiroalkyldihydroazulene (2.00 mmol) in 10 mL of dry acetonitrile at 0°C. After the resulting greenish reaction mixture was stirred at the same temperature for 30 min, dry Et_2O (50 mL) was added to the mixture. The precipitate formed was collected by suction filtration and recrystallized from CH_2Cl_2-ether to give the salt of title cations **3b**, **4a**, **5a**, and **5c**. On the other hand, an oil product of the cation **3a** was obtained as follows. Addition of dry ether (100 mL) to the reaction mixture gave an oil which was washed repeatedly with dry ether (50 mL) and was dried under vacuum to give **3a** as a dark-green oil.

3a. A dark-green oil, 82% yield. IR (film) 2950 (m), 2870 (w), 1498 (m), 1448 (m), 1061 (vs), 808 (m), 728 (m) cm^{-1}. UV λ_{max} (CH_3CN) 230 nm (log ϵ=4.30), 270 (4.42), 287sh (3.88), 363 (3.94). Found: *m/z* 283.1144. Calcd for $C_{14}H_{15}$: M, 283.1171.

3b. Slightly green prisms, 62% yield, mp=120–121°C (dec.). ^1H NMR ($CDCl_3$) δ=1.97 (m, 2H), 2.01 (m, 2H), 2.14 (m, 2H), 2.30 (m, 2H), 7.33 (d, *J*=5.4 Hz, 1H), 7.72 (d, *J*=5.4 Hz, 1H), 8.75 (tt, *J*=8.8, 0.4 Hz, 1H), 8.77 (t, *J*=8.8 Hz, 1H), 8.90 (t, *J*=8.8 Hz, 1H), 8.96 (dd, *J*=8.8, 0.4 Hz, 1H), 9.00 (dm, *J*=8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=27.07, 34.24, 67.80, 132.13, 144.11, 144.45, 148.32, 148.73, 151.46, 164.16, 169.79, 179.05; IR (film) 3070 (w), 2950 (m), 2870 (m), 1570 (m), 1500 (s), 1455 (s), 1370 (m), 1320 (w), 1240 (m), 1215 (m), 1180 (w), 1115 (m), 1020 (w), 985 (m), 840 (vs), 745 (m), 715 (m), 559 (s) cm^{-1}. EIMS (70 eV) *m/z* (rel intensity): 183 (M^+, 11), 182 (61), 181 (28), 165 (20), 154 (100), 153 (25), 152 (20), 141 (20), 107 (15), 69 (17), 49 (30), 28 (57). UV λ_{max} (50% H_2SO_4) 231 nm (log ϵ=4.23), 272 (4.28), 364 (4.06). Found: C, 51.23; H, 4.61%. Calcd for $C_{14}H_{15}PF_6$: C, 51.52; H, 4.50%.

4a. Green prisms, 92% yield, mp=114–115°C. ^1H NMR ($CDCl_3$) δ=1.36 (dm, *J*=12.4 Hz, 2H), 1.55–1.72 (m, 3H), 2.05 (m, 3H), 2.30 (td, *J*=12.8, 3.6 Hz, 2H), 7.49 (d, *J*=5.6 Hz, 1H), 8.13 (d, *J*=5.6 Hz, 1H), 8.85 (tt, *J*=9.8, 1.6 Hz, 1H), 9.00 (t-like, *J*=9.8 Hz, 1H), 9.01 (t-like, *J*=9.8 Hz, 1H), 9.10 (dd, *J*=9.8, 1.6 Hz, 1H), 9.12 (dm, *J*=9.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=24.30, 25.05, 31.87, 62.07, 133.86, 144.84, 145.20, 149.04, 149.21, 152.08, 162.22, 169.09, 178.47; IR (film) 3050 (w), 2930 (m), 2850 (w), 1560 (m), 1505 (m), 1495 (m), 1445 (s), 1075 (vs), 845 (m), 825 (m) cm^{-1}. EIMS (70 eV) *m/z* (rel intensity): 183 (M^+, 11), 182 (61), 181 (28), 165 (20), 154 (100), 153 (25), 152 (20), 141 (20), 107 (15), 69 (17), 49 (30), 28 (57). UV λ_{max} (CH_3CN) 230 nm (log ϵ=4.26), 270 (4.33), 360 (4.07); λ_{max} (50% H_2SO_4) 231 nm (log ϵ=4.27), 272 (4.38), 367 (3.98). Found: C, 63.37; H, 6.06%. Calcd for $C_{15}H_{17}BF_4$: C, 63.42; H, 6.03%.

5a. Greenish microcrystals, 92% yield, mp=100–103°C. IR (film) 3090 (m), 3017 (m), 2917 (s), 2858 (s), 1596 (w), 1581 (m), 1567 (s), 1539 (w), 1496 (s), 1449 (s), 1376 (s), 1326 (s), 1287 (m), 1190 (s), 1054 (brs), 878 (w), 856 (m), 820 (s), 762 (m), 736 (m), 682 (w), 624 (w), 567 (w), 534 (w), 521 (s) cm^{-1}. UV λ_{max} (CH_3CN) 227 nm (log ϵ=4.29), 268 (4.34), 362 (4.03). Found: *m/z* 211.1500. Calcd for $C_{16}H_{19}$: M, 211.1490.

5c. Green prisms, 57% yield, mp=91–92°C. ^1H NMR (CD_3CN) δ=1.58 (m, 2H), 1.78 (m, 2H), 1.83 (m, 4H), 1.98 (m, 2H), 2.17 (m, 2H), 7.42 (d, *J*=5.6 Hz, 1H), 8.00 (d, *J*=5.6 Hz, 1H), 8.74 (t, *J*=9.6 Hz, 1H), 8.82 (t, *J*=9.6 Hz, 1H), 8.90 (t, *J*=9.6 Hz, 1H), 8.99 (d, *J*=9.6 Hz, 1H), 9.07 (d, *J*=9.6 Hz, 1H); ^{13}C NMR (CD_3CN) δ=27.23, 29.73, 34.62, 64.86, 134.27, 145.32, 146.13, 149.48, 149.96, 152.93, 165.98, 170.38, 181.01; IR (film) 3086 (m), 3013 (m), 2927 (s), 2859 (s), 1595 (w), 1579 (m), 1567 (m), 1538 (w), 1494 (s), 1448 (s), 1374 (m), 1324 (m), 1302 (w), 1273 (w), 1242 (w), 1190 (m), 1085 (brs), 881 (m), 857 (m), 818 (s), 779 (m), 760 (m), 734 (m), 683 (w), 623 (s) cm^{-1}. UV λ_{max} (50% H_2SO_4) 228 nm (log ϵ=4.29), 259 (4.32), 365 (4.03). EIMS (70 eV) *m/z* (rel intensity): 211(M^+, 18), 210 (91), 182 (58), 167 (100), 154 (63), 141 (49), 128 (19), 115 (21). Found: C, 61.79; H, 6.19%. Calcd for $C_{16}H_{19}ClO_4$: C, 61.84; H, 6.16%.

Rearrangement of the cation 3a in acetonitrile; 2,3-tetramethylene-1*H*-azulenium tetrafluoroborate (18a) and 1,2,3,4-tetrahydrobenz[*a*]azulene (20)

In an NMR tube was charged a solution of **3a** (57 mg, 0.20 mmol) in 0.7 mL of acetonitrile-d_3. The spectra change was monitored by NMR analysis at a probe temperature of 80°C. ^1H NMR (CD_3CN) of **18a**; δ=1.86 (m, 4H), 2.68 (m, 2H), 2.83 (m, 2H), 4.07 (s, 2H), 8.53–8.79 (m, 5H). After 20 h, the reaction mixture was poured into a 1:1 mixture of acetone and water and extracted with hexane (10 mL×3). The combined organic layer was dried ($MgSO_4$) and then was concentrated to give a blue oil which was chromatographed on silica gel with hexane to give 22 mg (77%) of **20** as blue needles; mp=76–77°C (lit.[22] 77–78°C). ^1H NMR ($CDCl_3$) δ=1.91–1.98 (m, 4H), 3.07–3.12 (m, 4H), 7.03 (t, *J*=9.7 Hz, 1H), 7.06 (t, *J*=9.7 Hz, 1H), 7.12 (s, 1H), 7.44 (t, *J*=9.7 Hz, 1H), 8.08 (d, *J*=9.7 Hz, 1H), 8.13 (d, *J*=9.7 Hz, 1H).

X-Ray structure analysis of the cation 3b

Green prismatic crystals were obtained by recrystallization from a mixture of ether and dichloromethane. One of them having approximate dimensions of 0.34×0.20×0.20 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Cu–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 21 carefully centered reflections in the range $59.57<2\theta<59.97°$, corresponded to a trigonal hexagonal cell (Laue class: 3) with dimensions: *a*=27.726 (3) Å, *c*=10.037 (2) Å, *V*=6682 (1) $Å^3$. For *Z*=18 and Formular weight=328.24, the calculated density is 1.47 g cm^{-3}. Based on the systematic absences of hkil ($-h+k+1$ Å$\neq 3\mathbf{n}$) packing consideration, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $R\,\bar{3}$. The data were collected at a temperature of 23±1°C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 135.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.30° with a take-off angle of 6.0°. Scans of $(1.78+0.30\tan\theta)°$ were made at speeds of 64.0, 32.0°/

min (in omega) for each 2θ shell (4.0, 80.0, 100.0<135.0°). The weak reflections ($I<10\sigma$ (I)) were rescanned (maximum of 7 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 was 2:1. The diameter of the incident beam collimeter was 1.0 mm and the crystal to detecter distance was 235 mm. The computer-controlled slits were set to 3.0 mm (horizontal) and 3.5 mm (vertical). Of the 2928 reflections which were collected, 2667 were unique ($R_{\rm int}=0.017$). The intensities of three representative reflections were measured after every 150 reflections. No correction was applied. The structure was solved by direct methods and expanded using Fourier techniques. The PF_6 ion is disordered at the two locations represented by (P1, F1-F6) and (P2, F7-F12) with an occupancy ratio of 0.9: 0.1, the latter of which was refined isotopically as a rigid group. Some non-hydrogen atoms were refined. The final cycle of full-matrix least-squares refinement was based on 1472 observed reflections ($I>3.00\sigma(I)$) and 198 variable parameters and converged (largest parameter shift was <0.01 times its esd) with unweighted and weighted agreement factors of: $R=0.055$, $R_{\rm w}=0.084$. The standard deviation of an observation of unit weight was 1.41. The weighting scheme was based on counting statistics and included a factor ($p=0.096$) to downweight the intense reflections. Plots of $\Sigma\omega(|Fo|-|Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin\theta/\lambda$ and various classses of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.22 and $-0.20\ e^-/\text{Å}^3$, respectively. Tables of fractional atomic coordinated, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, United Kingdom.

X-Ray structure analysis of the cation 4a

A slightly green, single prism was obtained by recrystallization from a mixture of ether and dichloromethane. Reflections were measured on a MacSciencece MXC18K diffractometer with graphite-monochromated Cu–Kα radiation ($\lambda=1.54175$ Å). The structure was solved by the direct method and refined by the full-matrix least-squares method using the maXus program (MacScienec Inc.). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms isotopically. $C_{15}H_{17}BF_4$ (284.10), orthorhombic, $Pna2_1$, $a=18.926$ (7) Å, $b=9.844$ (4) Å, $c=15.821$ (7) Å, $V=2947.689941$ (2) Å^3, $Z=8$, $D_{\rm cald}=1.280$ g cm^{-3}, 2907 independent reflections on a crystal (0.35×0.3×0.2 mm), 2167 observed reflections [$I>3.00\sigma(I)$] used, 387 parameters, $R=0.054$, $R_{\rm w}=0.051$. Tables of fractional atomic coordinated, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, United Kingdom.

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