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X-ray Crystal Structures of Two (*deloc*-2,3,5)-1,2,3,4,5,6-Hexamethylbicyclo[2.1.1]hex-2-en-5-ylium Ions

Thomas Laube* and Christian Lohse

Contribution from the Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule Zürich, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich, Switzerland

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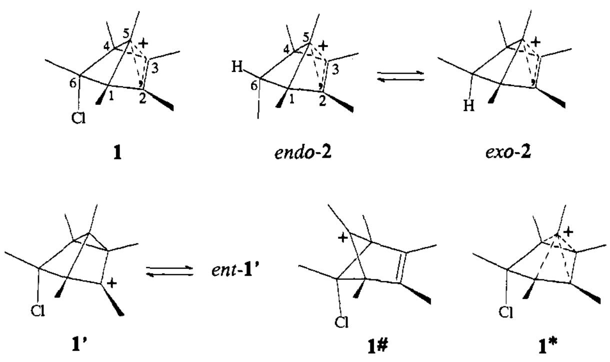
Abstract: The crystal structures of a 6-chloro-substituted and of a 6-hydrogen-substituted example for the title compound (**1** and *endo*-**2**) were determined at low temperatures, because earlier published NMR results of Hogeveen and Olah indicated the presence of a three center, two electron bond (3c, 2e bond) in such cations. While **1**·BCl_4 is (also due to the absence of heavy atoms like Sb) a rather precise structure ($R1 = 4.37\%$, $\sigma_{C-C} \le 0.003$ Å; **1** has a crystallographic mirror plane), *endo*-**2**·CF_3SO_3 has a disordered anion, and the cation *endo*-**2** was refined with an enforced mirror plane ($R1 = 12.33\%$). A third structure (*endo*-**2**·CF_3SO_3–SbF_5) is mentioned but, due to cation and anion disorder, not discussed. The structure of **1** shows an unusually strong 3c, 2e bond (C2–C3 = 1.406(1), C2–C5 = C3–C5 = 1.741(2) Å), and its displacement parameters agree with a static structure in the crystal, i.e., pairs of equilibrating ions can be excluded. The results of a new refinement of the earlier published crystal structure of the 7-norbornenyl ion **5**, which has a weaker 3c, 2e bond, are enclosed for comparison. Detailed experimental procedures are given.

The first preparations of 1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hex-2-en-5-ylium ions were reported in 1968 by the groups of Hogeveen,[1] Paquette and Olah.[2] Several of these cations were thoroughly investigated by NMR spectroscopy.[3-5] The chloro derivative **1**[6] was found to be present as one diastereomer,[3d,4,5] while **2** exists in solution as an equilibrating 3:1 mixture of the diastereomers *endo*-**2** and *exo*-**2**.[1,2,3a,b] The description of these cations with three center, two electron bonds (3c, 2e bonds) agrees with the experimental data,[3c,e] while other possibilities like equilibrating pairs of tricyclic cations (**1'** and *ent*-**1'**, a "Wagner–Meerwein pair") or a classical cation (**1#**) without 3c, 2e bonds were excluded. However, in the VB description a small contribution of a resonance structure like **1*** was found to be operative. We report here the rather precise crystal structure of **1**·BCl_4 and, due to anion disorder, the less precise crystal structure of *endo*-**2**·CF_3SO_3.

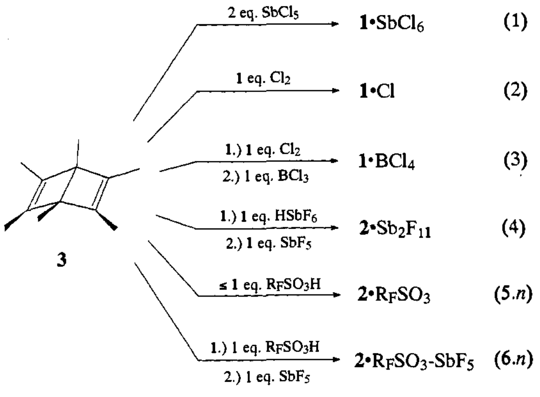
Chart 1



Results

Syntheses and Crystallizations. Our syntheses started from commercially available hexamethyldewarbenzene (**3**), see Scheme 1. The chlorination of **3** according to reactions 1[4,5] and 2[3d,4] yielded only small and intergrown crystals, while reaction 3 gave rather large, clear crystals of **1**·BCl_4 suitable for the crystal structure analysis (see Table 1 and the Experimental Section). The protonation of **3** according to reaction 4 gave only oils or bad crystals. Fluorinated sulfonic acids yielded the following crystal qualities: reaction 5.1, small and intergrown; reaction 5.2, small but suitable (the crystals contain only the *endo* diastereomer; see Table 1 and the Experimental Section); reaction 5.3,[7] small and twinned; reaction 5.4,[8] thin plates. The acidity of the sulfonic acids was enhanced[9] by the addition of 1 equiv of SbF_5, which

Scheme 1



n =	1	2	3	4
R_F =	F	CF_3	$CF_3(CF_2)_3$	C_6F_5

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1994.

(1) Hogeveen, H.; Volger, H. C. *Recl. Trav. Chim. Pays-Bas* **1968,** *87,* 385–386.

(2) Paquette, L. A.; Krow, G. R.; Bollinger, J. M.; Olah, G. A. *J. Am. Chem. Soc.* **1968,** *90,* 7147–7149.

(3) (a) Hogeveen, H.; Volger, H. C. *Recl. Trav. Chim. Pays-Bas* **1968,** *87,* 1042–1046. (b) Hogeveen, H.; Volger, H. C. *Recl. Trav. Chim. Pays-Bas* **1969,** *88,* 353–366. (c) Hogeveen, H.; Kwant, P. W. *J. Am. Chem. Soc.* **1973,** *95,* 7315–7319. (d) Hogeveen, H.; Kwant, P. W.; Schudde, E. P.; Wade, P. A. *J. Am. Chem. Soc.* **1974,** *96,* 7518–7524. (e) Hogeveen, H.; Kwant, P. W. *Acc. Chem. Res.* **1975,** *8,* 413–420.

(4) (a) Burger, U.; Delay, A. *Helv. Chim. Acta* **1973,** *56,* 1345–1347. (b) Delay-Soutter, A. Ph.D. Thesis, University of Geneva, Switzerland, 1977.

(5) Hüttel, R.; Tauchner, P.; Forkl, H. *Chem. Ber.* **1972,** *105,* 1–7.

(6) The atom numbering used here agrees with *Chemical Abstracts*. In earlier publications, the atom numbers 5 and 6 were interchanged.

(7) Nonafluorobutane-1-sulfonic acid was synthesized according to the following: Gramstad, T.; Haszeldine, R. N. *J. Chem. Soc.* **1957,** 2640–2645.

(8) Pentafluorobenzenesulfonic acid was synthesized according to the following: Sartori, P.; Bauer, G. *J. Fluorine Chem.* **1978,** *12,* 203–210.

(9) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley: New York, 1985; pp 42–48.

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Table 1. Data of the Measured Crystals[a]

	1·BCl$_4$	*endo*-**2**·CF$_3$SO$_3$	*endo*-**2**·CF$_3$SO$_3$–SbF$_5$
space group (no.)	$P2_1/m$ (11)	$Pna2_1$ (33)	Cc (9)
a (Å)	7.806(5)	15.31(2)	10.556(5)
b (Å)	10.280(2)	10.914(7)	12.444(8)
c (Å)	10.97(1)	8.840(8)	15.350(7)
α (deg)	90	90	90
β (deg)	105.70(7)	90	106.56(4)
γ (deg)	90	90	90
V (Å^3)	848(1)	1478(2)	1933(2)
sum formula	$C_{12}H_{18}BCl_5$	$C_{13}H_{19}F_3O_3S$	$C_{13}H_{19}F_8O_3SSb$
molecular weight	350.35	312.35	529.09
Z	2	4	4
F_{000}	360	656	1040
measuring temp (°C)	–165	–78	–95
d_X (g cm^{-3})	1.373	1.404	1.818
Θ_{max} (deg)	40	23	25
h_{min}, h_{max}	0, 14	–16, 0	0, 13
k_{min}, k_{max}	0, 18	0, 11	0, 16
l_{min}, l_{max}	–19, 19	–9, 9	–20, 19
no. of measured reflections	5447	2049	2328
no. of reflections ($I > 2\sigma_I$)	4675	785	1706
no. of parameters	132	106	148
no. of restraints	0	108	2
μ (mm^{-1})	0.837	0.256	1.619
extinction coefficient[b]	not significant		
weight parameter a_w[b,c]	0	0.2245	0.1000
$R1$[b,d] ($I > 2\sigma_I$)	0.0437	0.1233	0.1765
$wR2$[b,e] ($I > 2\sigma_I$)	0.1124	0.3069	0.3933
$R1$[b,d] (all data)	0.0493	0.2133	0.1776
$wR2$[b,e] (all data)	0.1145	0.4034	0.3947
comment		anion disordered; C framework of the cation with enforced m symmetry	cation and anion disordered

[a] Mo Kα radiation (λ = 0.710 69 Å, graphite monochromator) was used in all cases. [b] SHELXL-93. [c] $w = 1/[\sigma_{F_{obs}^2}^2 + (a_wP)^2]$ with $P = (\max(F_{obs}^2,0) + 2F_{calc}^2)/3$. [d] $R1 = \sum||F_{obs}| - |F_{calc}||/\sum|F_{obs}|$. [e] $wR2 = (\sum[w(F_{obs}^2 - F_{calc}^2)^2]/\sum[wF_{obs}^4])^{1/2}$.

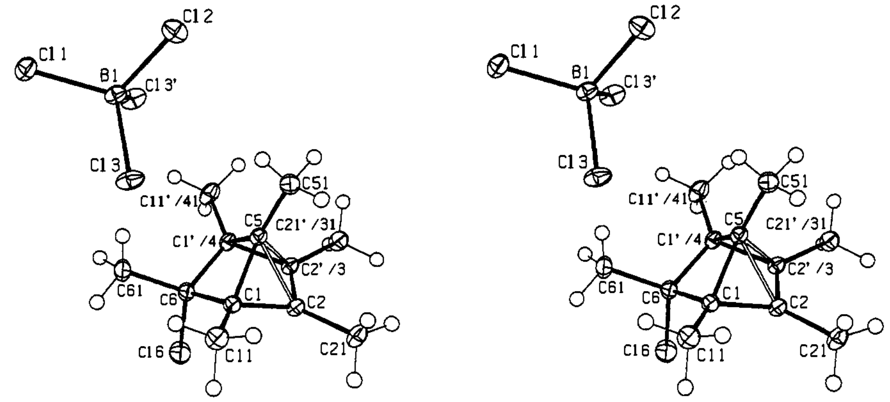

Figure 1. ORTEP stereodrawing of the crystal structure of **1**·BCl$_4$. The cation and the anion contain a common crystallographic mirror plane passing through C5, C51, C6, C61, Cl6, B1, Cl1, Cl2. The symmetry-related atoms have primed labels (′ = x, $^1/_2 - y$, z), and their "chemical" number[11] is given after the slash. The displacement ellipsoids are drawn at the 50% probability level, the hydrogen atoms are represented by spheres with a radius of 0.1 Å.

leads, due to complexation, to another set of anions.[10] The following crystal qualities were obtained: reaction 6.1, microcrystalline; reaction 6.2, suitable (see Table 1, the Experimental Section, and the supplementary material); reaction 6.3, microcrystalline; reaction 6.4, no crystals.

Crystal Structures. The crystal structure of **1**·BCl$_4$ is shown in Figure 1. The cation and the anion both contain a crystallographic mirror plane, and the observed configuration of **1** (Cl6 at C6 in *endo* position; "chemical" atom numbers[11]) agrees with the configuration assigned on the basis of NMR results.[3d,4,5] The ^{1}H NMR spectrum of **1**·BCl$_4$ in liquid SO$_2$ is (with the exception of a downfield shift of all signals by 0.34 ppm, probably due to the use of an external standard) practically identical with the spectrum of **1**·Cl in SO$_2$ reported by Delay-Soutter.[4b] The ^{13}C NMR shifts of **1**·BCl$_4$ determined by us in SO$_2$ solution deviate by +0.5 to –2.2 ppm from those of **1**·Cl measured in CH$_2$Cl$_2$ by Hogeveen et al.[3c] Therefore, it is certain that the configuration of **1** in the crystal as described here is the same as that in solution reported previously.[3c,d,4,5]

The most remarkable feature of **1** is the strong bending of the C5 bridge toward the C2–C3 bridge, see Figure 2 and Table 2. The angle between these bridges is only 75.6(1)°, and thus the C2–C5/C3–C5 distances are only 1.741(2) Å. The C2–C3 bond, a double bond in a neutral molecule without significant charge at C5 like the ketone **4**, is elongated to 1.406(1) Å if compared with a double bond (reference value[12] for a $(C_{sp^3})_2C{=}C(C_{sp^3})_2$ bond, 1.331(1) Å; elongation, 0.075(2) Å), but shortened if

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(10) Crystal structure of CF$_3$SO$_3$H·SbF$_5$: Mootz, D.; Bartmann, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1991**, *46b*, 1659–1663.

(11) The "chemical" numbers of the skeleton atoms agree with the *Chemical Abstracts* numbering of **1** as depicted in Chart 1, see also ref 6. These "chemical" numbers will be used in the discussion, Figures 2, 3, 7, and Table 2.

(12) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. in *International Tables for Crystallography, Volume C*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, 1992; pp 685–706.

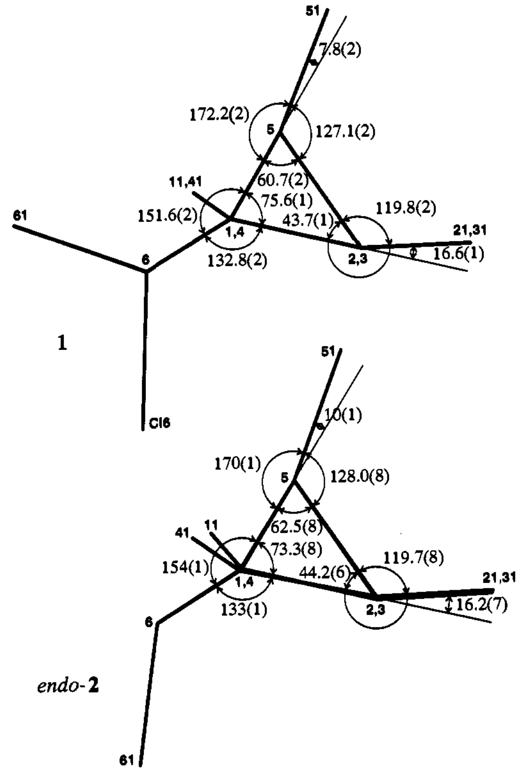
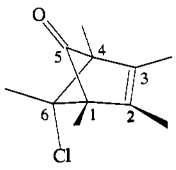


Figure 2. Newman projections of **1** and *endo*-**2** (approximately along C1–C4). The angles (in degrees) involve *P*(1,4,5), *P*(1,4,6), *P*(1,2,3,4), *P*(2,3,5), *P*(2,3,21,31), and *L*(5,51), see caption of Table 2.

compared with an unconjugated C=C—C=C bond (reference value,[12] 1.478(4) Å), i.e., C2–C3 has a partial double bond character. The atoms C2, C3, and C5 are strongly pyramidalized,[13] if one ignores the C2–C5 and C3–C5 bonds: $\Delta_{C2} = \Delta_{C3} = 0.126(2)$ Å, $\Delta_{C5} = 0.088(3)$ Å, see Table 2. The C2–C21/C3–C31 and C5–C51 bonds (1.481(2) and 1.485(2) Å) are slightly shortened by 0.022(2) and 0.018(2) Å, if they are compared with the average length[12] of a C_{sp^2}–CH_3 bond (1.503(1) Å). The C1–C11/C4–C41 bonds (1.495(1) Å) are more strongly shortened than the $C^{\delta+}$–CH_3 bonds (by 0.039(2) Å with regard to the not perfectly suitable reference value[12] for a $(C_{sp^3})_3C$–CH_3 bond, 1.534(1) Å), but the shortening may be at least partially due to a low p character of the C1 and C4 orbitals contributing to these bonds because of the unusual angles around C1 and C4. The C1–C5/C4–C5 bonds are rather long (1.560(2) Å) if compared with the C_{sp^3}–C(=O) bond in cyclobutanones[12] (1.529(4) Å, i.e., an elongation by 0.031(4) Å). The C6–Cl6 (1.802(2) Å) bond is short if compared with other X_3C–Cl (X = C, H, N, O) bonds[12] (average: 1.843(5) Å), but also here, the C hybridization in this bond may significantly contribute to the shortening.



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According to the interpretation of the NMR spectra by Hogeveen et al.,[3c,e] the positive charge in ions like **1** is mainly delocalized over C2, C3 and to a smaller amount over C5. The smallest positive charge was found on C1 and C4. In agreement with these results and the fact that nucleophiles may attack C2, C3, or C5,[3c,e] the cation **1** shows in the crystal packing a van der Waals contact between C2/C3 and an anion (C2···Cl1″ = C3···Cl1″ = 3.451(4) Å),[14] while C5 interacts only weakly with two symmetry-related Cl atoms (C5···Cl3 = C5···Cl3′ = 3.991(5) Å); perhaps the C61 methyl group prevents any closer contact between C5 and the anionic Cl atoms (see Figure 3). The crystal structure of *endo*-**2**·CF_3SO_3 is shown in Figure 4. Because of the disorder of the anion and the weak diffracting power of the small crystal, only a poor reflection/parameter ratio (3.7) was achieved, and the cation had to be refined with an enforced noncrystallographic mirror plane concerning the C atom positions and their isotropic displacement parameters. This mirror plane is justified by the *m* (C_s) symmetry of **1** and by the NMR results and several other findings on bicyclo[2.1.1]hexenyl cations.[3e] Several restraints were applied for the anion (see the Experimental Section). Therefore, the data derived from this structure are less precise and reliable, and they are presented here only in order to show that *endo*-**2** has in the crystal a rather similar structure to **1** (see Table 2 and Figure 2). The crystal packing of *endo*-**2**·CF_3SO_3 is also similar to that of **1**·BCl_4 (see Figure 5): C2 and C3 have van der Waals contact to a CF_3 group (C2···F1′ = 3.14(2), C3···F1′ = 3.15(2) Å),[16] while the distance of C5 to the next O atom is rather large (C5···O1 = 3.50(2) Å).[17]

Table 2. Selected geometrical data of the cations in **1**·BCl_4 and *endo*-**2**·CF_3SO_3[a]

	1	*endo*-**2**
C2–C3	1.406(1) [1.409]	1.43(2)
C2–C5, C3–C5	1.741(2) [1.744]	1.72(2), 1.72(2)
C1–C2, C4–C3	1.481(2) [1.483]	1.48(2), 1.48(2)
C1–C5, C4–C5	1.560(2) [1.564]	1.51(2), 1.55(2)
C1–C6, C4–C6	1.531(1) [1.534]	1.44(2), 1.51(2)
C1–C11, C4–C41	1.495(1) [1.497]	1.56(2), 1.51(2)
C2–C21, C3–C31	1.481(2) [1.483]	1.50(2), 1.49(2)
C5–C51	1.485(2) [1.488]	1.52(2)
C6–C61	1.508(3) [1.510]	1.57(2)
C6–Cl6	1.802(2)[1.806]	
C6–C1–C11, C6–C4–C41	125.6(2) [125.6]	128(1), 125(1)
C5–C1–C11, C5–C4–C41	127.4(2) [127.3]	123(1), 125(1)
C5–C1–C6, C5–C4–C6	88.7(2) [88.8]	93(1), 88.8(9)
C2–C1–C11, C3–C4–C41	121.9(2) [121.9]	117(1), 123(1)
C2–C1–C6, C3–C4–C6	107.3(2) [107.3]	110(1), 109(1)
C2–C1–C5, C3–C4–C5	69.8(2) [69.8]	70.1(9), 69.1(9)
C1–C2–C21, C4–C3–C31	125.7(2) [125.7]	128(1), 131(1)
C1–C2–C3, C4–C3–C2	104.4(2) [104.4]	102(1), 102(1)
C2–C3–C5, C3–C2–C5	66.2(2) [66.2]	65.4(8), 65.4(8)
C2–C5–C3	47.6(1) [47.6]	49.2(7)
C1–C5–C4	86.6(2) [86.6]	84.0(9)
C1–C6–C4	88.7(2) [88.7]	88(1)
C1–C5–C51, C4–C5–C51	136.1(2) [136.2]	138(1), 136(1)
C2–C5–C51, C3–C5–C51	123.5(2) [123.5]	125(1), 123(1)
C1–C6–C61, C4–C6–C61	114.6(2) [114.6]	121(1), 116(1)
C1–C6–Cl6, C4–C6–Cl6	114.1(2) [114.2]	
C61–C6–Cl6	109.5(2) [109.5]	
C2–C1–C6–C61, C3–C4–C6–C61	∓164.7(2) [∓164.7]	69(2), –75(1)
C2–C1–C6–Cl6, C3–C4–C6–Cl6	±67.9(2) [±67.9]	
|C2–*P*(1,3,21)|,|C3–*P*(2,4,31)|	0.126(2) [0.126]	0.14(1), 0.11(1)
|C5–*P*(1,4,51)|	0.088(3) [0.088]	0.12(1)
L(2,21)–*P*(1,2,3), *L*(3,31)–*P*(2,3,4)	13.1(2)	14.4(9), 11(1)
L(5,51)–*P*(1,4,5)	7.8(2)	10(1)
|C5–*P*(1,2,3,4)|	1.100(3) [1.103]	1.09(1)
L(5,51)–*P*(1,2,3,4)	83.4(1)	83.7(8)

[a] Chemically equivalent parameters are listed on the same line. Distances are given in angstroms, angles in degrees; in brackets are the values of **1** corrected for thermal motion. $P(i_1, ..., i_n)$ is the (for $n > 3$: least squares) plane defined by $Ci_1, ..., Ci_n$; $L(i_1, i_2)$ is the line through Ci_1 and Ci_2. For other angles see Figure 2.

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(13) The pyramidalization Δ is the distance of a trigonal atom from the plane through its three bonding partners.

(14) Sum of the van der Waals radii[15] of C and Cl: 1.70 Å + 1.75 Å = 3.45 Å.

(15) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

(16) Sum of the van der Waals radii[15] of C and F: 1.70 Å + 1.47 Å = 3.17 Å.

(17) Sum of the van der Waals radii[15] of C and O: 1.70 Å + 1.52 Å = 3.22 Å.

(18) Stewart, J. J. P. MOPAC, version 5.0 (integrated in SYBYL 6.0[19]). Program No. 455 from Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN.

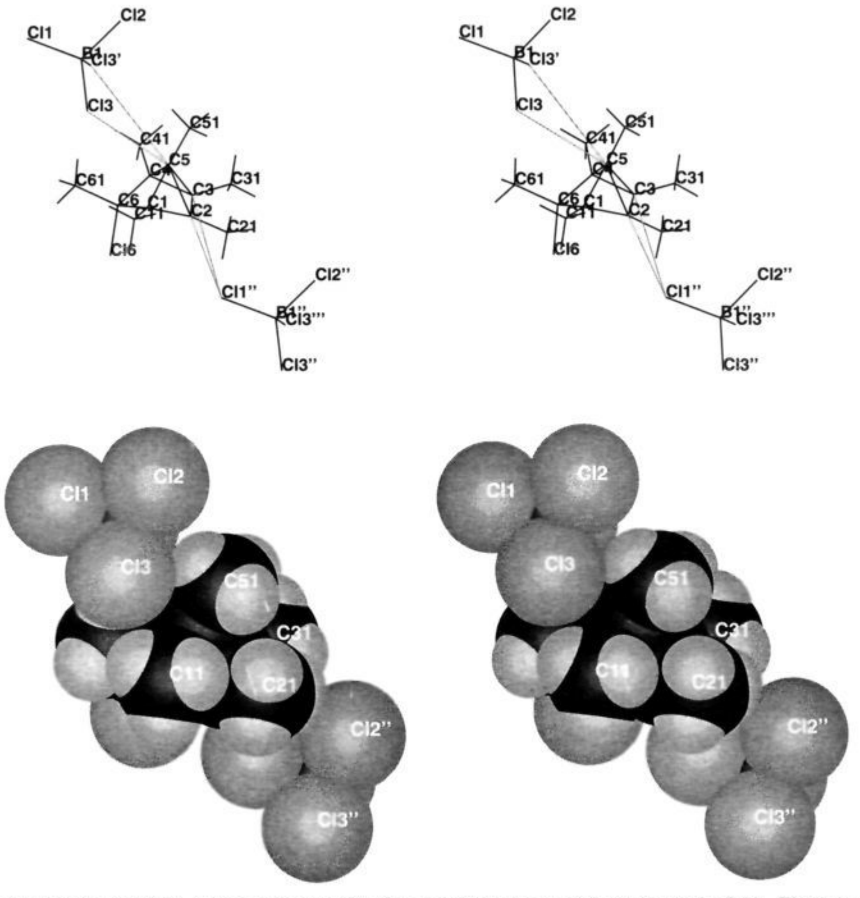

Figure 3. Stereodiagram of **1** and the two BCl_4 anions nearest to C2, C3, and C5 in the crystal structure of **1**·BCl_4. The symmetry operations are as follows: ′ = x, $^1/_2 - y$, z; ″ = x, y, $z + 1$; ‴ = x, $^1/_2 - y$, $z + 1$. Top: wire frame diagram (the shortest $C^{\delta+}\cdots Cl$ contacts are indicated by grey lines). Bottom: space-filling diagram (van der Waals radii according to Bondi[15]).

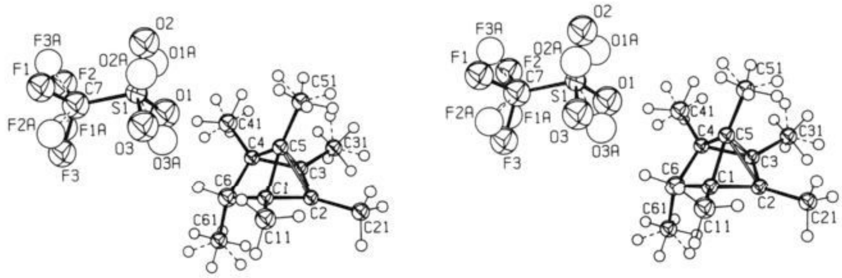

Figure 4. ORTEP stereodrawing of the crystal structure of *endo*-**2**·CF_3SO_3. Only S1 was refined anisotropically, all other atoms isotropically. The S1 displacement ellipsoid and all other non-hydrogen displacement spheres are drawn at the 50% probability level; the hydrogen atoms are represented by spheres with a radius of 0.1 Å. Bonds to the atoms of the minor orientations of the rotationally disordered CF_3, SO_3, and CH_3 groups are dashed. In the anion, the atoms of the minor orientation are drawn as white spheres and have the appendix A at their name.

The structure of *endo*-**2**·CF_3SO_3–SbF_5 shows at least 2-fold orientational disorder of the cation and of the anion. The cation is in both major orientations *endo*-configured, and the cation–anion interactions are similar to those in Figures 3 and 5 (see the supplementary material).

Discussion

The structure of **1** (and related cations) with the very long C2–C5 and C3–C5 bonds and the partial C2–C3 double bond character deviates so strongly from the structure of a neutral bicyclo[2.1.1]hexene derivative like **4** (see Figure 6) that it cannot be described as a classical ion (**1#**). An equilibrating or disordered pair of tricyclic cations **1′** and *ent*-**1′** can also be excluded because the cation and the anion behave in the crystal like rigid bodies (see the results of the thermal motion analysis in the Experimental Section). Therefore, the description with a 3c, 2e bond as depicted in the formula **1** is most suitable, and accordingly the prefix *deloc*-2,3,5 (which is used by *Chemical Abstracts*) was added to the names of all cations. From the small angle between the cationic bridges in **1** ($P(1,2,3,4)$–$P(1,4,5)$ = 75.6(1)°, see Figure 2) if compared with the 7-norbornenyl cation **5**[20,21] ($P(1,2,3,4)$–$P(1,4,7)$ = 90.4(5)°, see Figure 6) and from the partial bond lengths (**1**, C2–C5/C3–C5 = 1.741(2) Å; **5**, C2–C7 = 1.88(1), C3–C7 = 1.87(1) Å), one can conclude that the bishomoaromatic

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(19) SYBYL Version 6.0 for Sun computers, November 1992, Tripos Associates, Inc. (a subsidiary of Evans & Sutherland), St. Louis, MO 63144-2913. The programs res2dat, dat2cry, and cry2mol (Laube, T.) were used for the conversion of coordinate files in various formats to files in the "mol" format, which were read by SYBYL and then processed interactively. The generated PostScript files require some editing concerning the atom labels.

(20) Laube, T. *J. Am. Chem. Soc.* **1989**, *111*, 9224–9232.

(21) The structural data of **5** reported here stem from a new and enhanced refinement using a disorder model for the SbF_6 anion. Details and data are given in the Experimental Section and the supplementary material.

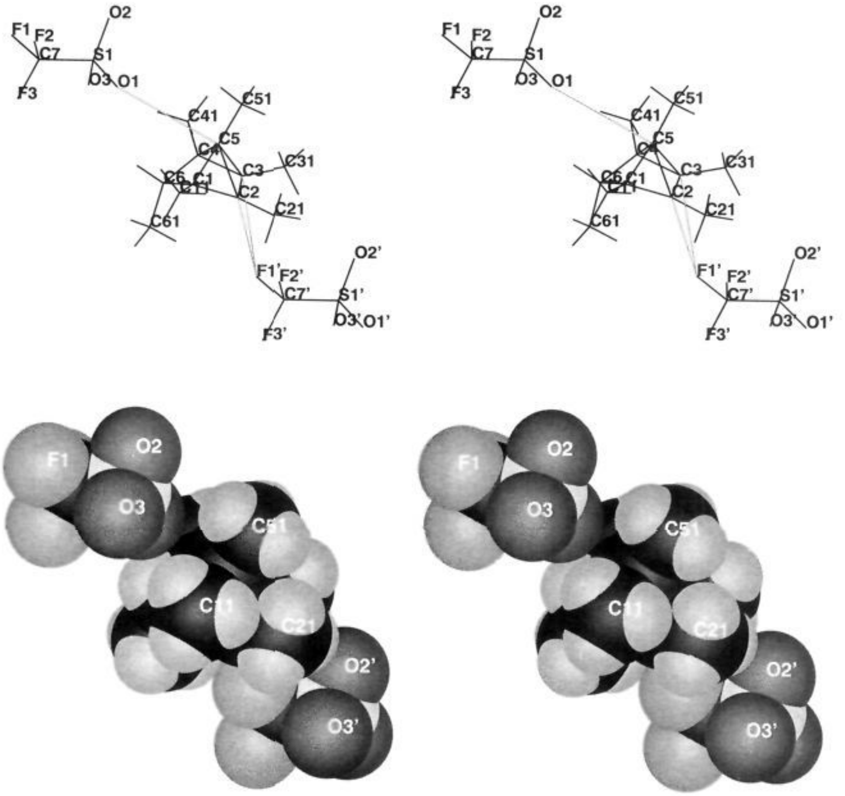
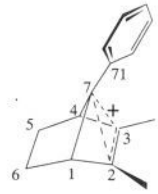


Figure 5. Stereodiagram of *endo*-**2** and the two triflate anions (major orientation) nearest to C2, C3, and C5 in the crystal structure of *endo*-**2**·CF_3SO_3. The symmetry operation (′) is *x*, *y* + 1, *z*. Top: wire frame diagram (the shortest $C^{\delta+}\cdots$Cl contacts are indicated by grey lines). Bottom: space-filling diagram (van der Waals radii according to Bondi[15]).

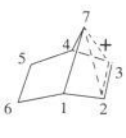
charge delocalization in **1** (CH_3 group at C5) is, as expected, stronger than in **5** (Ph ring at C7). However, the strong pyramidalization of C2 and C3 is comparable in **1** and **5**. A comparison with the ab initio structures (6-31G*) of the related unsubstituted norborn-2-en-7-ylium and norborna-2,5-dien-7-ylium ions (**6** and **7**) computed by Schleyer et al.[22] shows that the C2–C7/C3–C7 bonds in these systems (**6**, 1.756 Å; **7**, 1.719 Å) are very similar to the C2–C5/C3–C5 bonds in **1**. The boron compound **8** of Fagan et al.[23] is very similar to **5**, i.e., the bridging is weaker than in **1**.

There may be a small contribution of the resonance formula **1*** to the VB description of **1**, because the C1–C5/C4–C5 bonds are slightly elongated, and the C5–C51 bond is bent to the left side by 7.8(2)° in the Newman projection in Figure 2, so that the line through C5–C51 is nearly perpendicular to the plane *P*(1,2,3,4)–the angle between them is 83.4(1)°. It is remarkable that the analogous C7–C71 bond in **5** is slightly bent to the opposite direction (by 3.7(6)°, see Figure 6), which was interpreted[20] as an indication of the mutual approach of the p orbital axes of C2, C3, and C7. Therefore, it is possible that, despite the stronger bishomoaromatic delocalization in **1** than in **5**, the bending of C5–C51 in **1** indicates a beginning rehybridization of C5 in terms of a contribution of **1*** to the VB description of **1**. The reduction of the strength of the C1–C5/C4–C5 bonds in **1** is also reflected by the AM1 bond orders computed with the experimental geometry (see Figure 7). From the small shortenings of the C2–C21/C3–C31 and C5–C51 bonds, one must conclude that C–H hyperconjugation does not play an important role in **1** (for comparison: the average $C^+–CH_3$ length in the *tert*-butyl cation[24] is 1.442(5) Å).

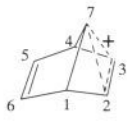
Chart 2



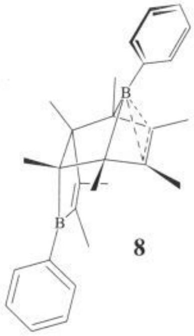
5



6



7



8

Conclusion

The precise crystal structure of the bicyclo[2.1.1]hexenylium ion **1** shows that this ion contains a 3c, 2e bond involving C2, C3, and C5. There are indications that even C1 and C4 may bear a small positive charge, i.e., the previously published results of Hogeveen et al.[3c,e] are confirmed. From the displacement parameters, it follows that **1** is a static cation in the crystal (rigid body). The contacts of **1** to the next counterions in the crystal correlate with the preferred directions of the nucleophilic attack on **1** observed in solution. The crystal structure of *endo*-**2** is similar to that of **1**, but less precise.

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[22] Bremer, M.; Schötz, K.; Schleyer, P. v. R.; Fleischer, U.; Schindler, M.; Kutzelnigg, W.; Koch, W.; Pulay, P. *Angew. Chem.* **1989**, *101*, 1063–1065; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1042.

[23] (a) Fagan, P. J.; Burns, E. G.; Calabrese, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 2979–2981. (b) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880–1889.

[24] Hollenstein, S.; Laube, T. *J. Am. Chem. Soc.* **1993**, *115*, 7240–7245.

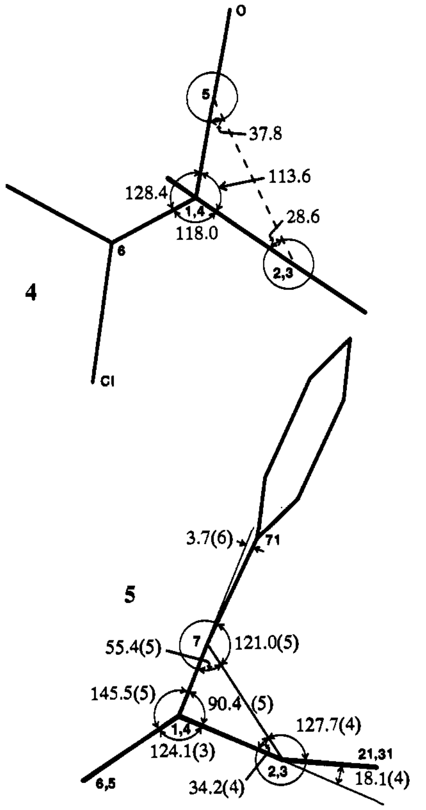

Figure 6. Newman projections of the computed structure[18,19] (MOPAC 5.0, AM1 Hamiltonian) of **4** and of the crystal structure[20,21] of **5** (both approximately along C1–C4). The angles (in degrees) involve for **4** $P(1,4,5)$, $P(1,4,6)$, $P(1,2,3,4)$, $P(2,3,5)$ and for **5** $P(1,4,7)$, $P(1,4,5,6)$, $P(1,2,3,4)$, $P(2,3,7)$, $P(2,3,21,31)$, and $L(7,71)$, see caption of Table 2.

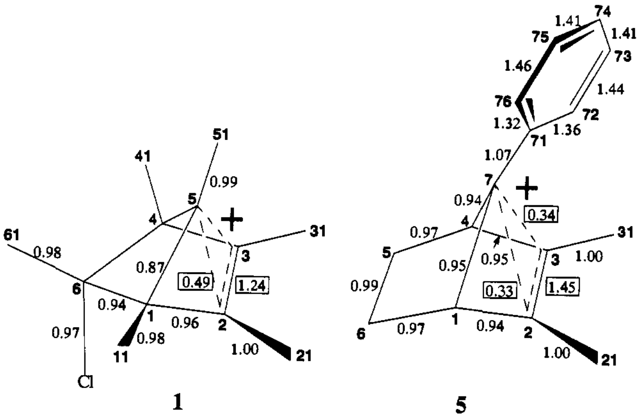

Figure 7. AM1 bond orders[18,19] of **1** (point group: *m*) and **5** (point group: 1) computed with the geometries from the crystal structures. Orders of bonds involved in the 3c, 2e bonds are framed.

Experimental Section

General. All solvents used for the carbocation experiments were distilled over P_2O_5 and stored under argon. For more details on the apparatus used for the syntheses see the experimental part in ref 25. WARNING: Because there is a remote chemical relationship between the chlorination of **3** and the bromination of norbornadiene (which caused a severe accident[26]), these experiments should be carried out under safety conditions appropriate to highly toxic compounds (i.e., small scales, no inhalation of or skin contact with the products; well-ventilated hoods, use of closed apparatuses where possible, safe waste disposal).

Synthesis According to Reaction 3 and Crystallization of (*deloc*-2,3,5)-6-*endo*-Chloro-1,2,3,4,5,6-*exo*-hexamethylbicyclo[2.1.1]hex-2-en-5-ylium Tetrachloroborate (1·BCl_4). In compartment A of the carefully dried reaction vessel (see Figure 6 in ref 25), 0.50 g of hexamethylbicyclo[2.2.0]hexa-2,5-diene (hexamethyldewarbenzene, **3**; 3.09 mmol; Aldrich) was added to 9 mL of CH_2Cl_2 under argon at –90 °C. Using a gas-tight syringe equipped with a long needle, 70 mL of chlorine gas (room temperature; 3.09 mmol; Union Carbide, purity 99.0%) was condensed into compartment B (through stopcock 1). During 1 h the liquefied chlorine was then flushed into the reaction mixture in A by a gentle argon stream. Meanwhile the solution warmed up to –60 °C. The slightly turbid mixture was cooled to –95 °C, and during 10 min 4.52 g of a BCl_3 solution (3.09 mmol; Fluka, 1 M in CH_2Cl_2) was added drop by drop (through joint 3, equipped with a septum). During the addition the reaction mixture in A turned rapidly dark alga green. The solution was slowly warmed up to –65 °C, and after filtration through a glass frit (D4), the resulting colorless solid was washed with 3 mL of precooled CH_2Cl_2 and dried in A in the high vacuum (HV) at <0.01 Torr within 3 h at –55 °C. The apparatus was refilled with argon, and the filtercake was powdered at –80 °C with a long spatula through joint 3 (flushed with argon). The whole apparatus was quickly turned around to the left by about 100°, so that the filtration vessel could now be cooled to –80 °C, and the raw powdered salt was very quickly transferred with a spatula from A into the precooled compartment C. The reaction vessel on joint 5 was replaced by an adapter with a 3-way stopcock with a septum and an argon inlet. The salt was cooled to –100 °C or lower (filtration apparatus in position I), and 12 mL of CH_2Cl_2 was very slowly added with a syringe through the 3-way stopcock on joint 5 into C. In order to avoid decomposition the salt should be dissolved in melting CH_2Cl_2. The solution was warmed up to –60 °C, stirred for 1 h, and filtered at –60 °C into D by turning the filtration apparatus into position II. A very small residue of the salt remained on the frit. The clear filtrate was collected and then quickly poured into the precooled 50 mL 2-neck flask (with an adapter fitting to a HV line on its second joint) connected to the filtration vessel at joint 6. The cooled flask was then disconnected from joint 6, stoppered, and transferred to a HV line. The solvent was slowly evaporated during 16 h at –78 °C (≈0.2 Torr). One obtains colorless irregular prisms (size: up to 1.3 mm × 1.0 mm × 0.3 mm). A photograph of the crystals is shown in figure S1 of the supplementary material.

NMR Spectra of 1·BCl_4 (Dissolved Crystals). The dry crystalline salt and a capillary with the external standard (ca. 90% CD_3COCD_3 + 10% TMS) were filled at –60 °C under dry inert gas into a NMR tube, which was then connected to a HV line, where SO_2 (Fluka, > 99.7%) was distilled into the NMR tube. After sealing off the tube, the spectra (^1H, 300 MHz; ^{13}C, 75 MHz) were recorded at –63 °C on a Varian XL-100 NMR spectrometer equipped with a variable-temperature probe. All chemical shifts (in ppm) are relative to the external Me_4Si signal. The assignment of the ^{13}C signal types was secured by DEPT (distortionless enhancement by polarization transfer); an assignment of the signals has been carried out by Hogeveen et al.[3c] The almost colorless sample turned intense purple when it warmed up after the NMR experiment. The spectra are shown in Figures S9–S11 of the supplementary material. ^{13}C NMR: δ 1.693 (CH_3), 5.460 (CH_3), 9.993 (CH_3), 22.854 (CH_3), 42.886 (C without H), 75.122 (C without H), 76.904 (C without H), 123.527 (C without H). ^1H NMR: δ 1.857 (s, 3 H), 2.022 (s, 6 H), 2.292 (s, 3 H), 2.565 (s, 6 H). Broad peaks at 0.61, 3.03, 4.82, and 5.45 ppm stem from unidentified products probably formed by decomposition.

Synthesis According to Reaction 5.2 and Crystallization of (*deloc*-2,3,5)-1,2,3,4,5,6-*endo*-Hexamethylbicyclo[2.1.1]hex-2-en-5-ylium Triflate (*endo*-2·CF_3SO_3). In the apparatus shown in Figure 6 in ref 25, a solution of 1.50 g of **3** (9.25 mmol; Aldrich) in 7 mL of CH_2Cl_2 was added slowly with a syringe (through joint 3, equipped with a septum) to a solution of 0.34 g of triflic acid (2.27 mmol; Aldrich) in 15 mL of CH_2Cl_2 in compartment A at –80 °C under argon. After bubbling argon (from B) for 90 min through the reaction mixture (the argon outlet is stopcock 2), 32 mL of $CFCl_3$ was slowly added with a syringe through joint 3. When the precipitation was completed, the slightly turbid reaction mixture was filtered (argon over-pressure from stopcock 2 and slight vacuum through stopcock 1). The mother liquor collected in B is then removed with a long needle through the septum on stopcock 1 by argon over-pressure. The resulting filtercake on the frit (almost colorless) was dried at –80 to –50 °C at <0.01 Torr (HV applied through stopcocks 1 and 2) for about 2 h. After refilling the apparatus with argon (the reaction vessel is permanently cooled), the filtercake was coarsely powdered at –80 °C with a long spatula through joint 3 (flushed with argon), and the raw powdered salt was very quickly transferred with the spatula from A into the precooled compartment C. The reaction vessel on joint 5 was replaced by an adapter with a 3-way stopcock with a septum and an argon inlet.

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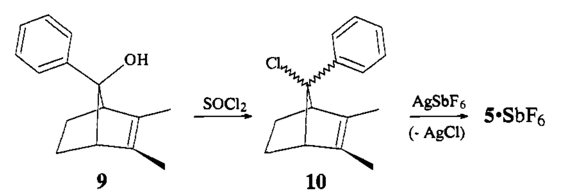
(25) Laube, T. *Helv. Chim. Acta* **1994**, *77*, 943–956.

(26) Winstein, S. *J. Am. Chem. Soc.* **1961**, *83*, 1516–1517.

Scheme 2



9 **10**

The salt was cooled to –100 °C (filtration apparatus in position I), and 7 mL of CH_2Cl_2 was very slowly added with a syringe through the 3-way stopcock on joint 5 into C. In order to avoid decomposition, the salt should be dissolved in melting CH_2Cl_2. The clear solution was slowly warmed up to –40 °C, stirred for about 1 h, and filtered at –40 °C into D by turning the filtration apparatus into position II. The clear filtrate was collected and then quickly poured into the precooled 50 mL 2-neck flask (with an adapter fitting to the HV line on its second joint) connected to the filtration vessel at joint 6. The flask was then disconnected from joint 6, stoppered, and transferred to the HV line. The solvent was slowly evaporated during 36 h at –78 °C (≈0.4 Torr). One obtains colorless intergrown prisms (some with inclusions; size: up to 0.35 mm × 0.25 mm × 0.25 mm). A photograph of the crystals is shown in Figure S12 of the supplementary material.

Synthesis According to Reaction 6.2 and Crystallization of (*deloc*-2,3,5)-1,2,3,4,5,6-*endo*-Hexamethylbicyclo[2.1.1]hex-2-en-5-ylium Pentafluorotriflatoantimonate(V) (*endo*-2·CF_3SO_3–SbF_5). The synthesis was carried out in the filtration vessel of the apparatus shown in Figure 6 of ref 25, equipped with a PTFE dropping funnel on joint 5 and a 2-neck flask (with an adapter fitting to a HV line on its second joint) at joint 6. A mixture of 0.30 g of triflic acid (2 mmol; Aldrich) and 0.434 g of SbF_5 (2 mmol; Aldrich) was added slowly from the PTFE dropping funnel to 13 mL of CH_2Cl_2 at –95 °C in compartment C (with a stirring bar). The added mixture instantly coagulated to a highly viscous, sticky oil. When the addition was completed, the PTFE dropping funnel on joint 5 was replaced by a septum, and a solution of 0.325 g of **3** (2 mmol; Aldrich) in 8 mL of CH_2Cl_2 was added slowly with a syringe at –80 °C. After being stirred for 2 h and slowly warming up to –65 °C, the orange solution was filtered by turning the apparatus to the left by about 90° (into position II). The collected filtrate was quickly poured into the precooled 50 mL 2-neck flask which was then disconnected from joint 6, stoppered, and transferred to the HV line. The solvent was slowly evaporated during 40 h at –78 °C (≈0.2 Torr). One obtains colorless prisms (some with inclusions and rough surfaces; size: up to 0.75 mm × 0.35 mm × 0.2 mm). A photograph of the crystals is shown in Figure S15 of the supplementary material.

Synthesis of 7-Chloro-2,3-dimethyl-7-phenylbicyclo[2.2.1]hept-2-ene (10).[27] After the addition of 0.6 mL of $SOCl_2$ to a solution of 0.33 g of **9**[20,28] in 15 mL of ether at 0 °C, the reaction mixture was stirred for 3 h at room temperature (according to a procedure of Coates[29]). For two times, 5 mL of benzene was added, and the solvents were evaporated. The product **10**[20,28] (one diastereomer of unknown configuration) was obtained after Kugelrohr distillation (150 °C, 10^{-2} Torr) in practically quantitative yield as a colorless wax. ^1H NMR (90 MHz, $CDCl_3$, δ in ppm (TMS)): 1.20–1.40 (m, 2 H, H_{endo}(C5), H_{endo}(C6)), 1.48 (s, 6 H, 2 CH_3), 2.20–2.50 (m, 2 H, H_{exo}(C5), H_{exo}(C6)), 3.00–3.10 (m, 2 H, H(C1), H(C4)), 7.0–7.4 (m, 5 H, arom H).

Synthesis and Crystallization of (*deloc*-2,3,7)-2,3-Dimethyl-7-phenylbicyclo[2.2.1]hept-2-en-7-ylium Hexafluoroantimonate(V) (5·SbF_6).[27] A solution of 0.558 g of $AgSbF_6$ (1.62 mmol; Aldrich) in 5.5 mL of CH_2Cl_2 was slowly added to a solution of 0.36 g of freshly prepared **10** (1.55 mmol) in 50 mL of $CFCl_3$ at –78 °C in the apparatus shown in Figure 6 of ref 25. After 30 min the precipitate was filtered off and dried at 10^{-3} Torr below –45 °C. After the addition of 15 mL of CH_2Cl_2 to the dry salt mixture, stirring, and a subsequent low-temperature filtration, the solution was cooled from -60 to -80 °C within 30 h (programmable cryostat). The crystals of **5**·SbF_6 (length up to 2 mm) were isolated by removing the mother liquor with a syringe, washed with 2 × 1.5 mL of cold CH_2Cl_2, dried at –60 °C in the HV, and mounted in Lindemann glass capillaries at 4 °C.

Crystal Selection, Mounting, Measurement, Data Reduction, and Solution (Common Procedure for 1·BCl_4, *endo*-2·CF_3SO_3, *endo*-2·CF_3SO_3–SbF_5). The dried crystals were examined and mounted under dry nitrogen at –60 °C on a self-constructed cryostage (see Figure 7 in ref 25). The X-ray measurements were carried out on an Enraf-Nonius CAD4 diffractometer (Mo Kα radiation with λ = 0.710 69 Å, graphite monochromator). The data reductions were carried out with DIFDAT[30] from the Xtal 3.2[31] system (in the case of **1**·BCl_4, an empirical absorption correction with 36 scans of the reflection $\bar{1}05$, which had $\chi \approx 90°$; minimum 1.0018, maximum 1.3377, was applied with ABSCAL[32]) and a HKLF file for the SHELX programs[33,34] was generated with LISTFC.[35] The structures of **1**·BCl_4 and *endo*-**2**·CF_3SO_3 were solved with the direct methods option of SHELXS-86;[33] the positions of the heavy atoms of *endo*-**2**·CF_3SO_3–SbF_5 were determined with the Patterson option of SHELXS-86.

Refinement of 1·BCl_4. The structure was first refined upon F^2 with SHELXL-93.[34] After several cycles of isotropic and anisotropic refinement (full matrix; $w = 1/\sigma_{F_{obs}^2}{}^2$; the extinction parameter refined to 0.006(3) and was not included in further refinements), all H's could be located in the difference density maps and refined on reasonable positions. The results of the refinement with SHELXL-93 are considered as final (*R* values: see Table 1); they are listed in the supplementary material and used for the Figures 1–3 and 7. The highest difference density maximum in the cation region (Cl6 excluded) is 0.65 e Å^{-3} (rms deviation from the mean: 0.12 e Å^{-3}). The Cl atoms are surrounded by maxima up to 1.31 e Å^{-3}. In order to obtain electron and difference density contour diagrams, the refinement (based on F^2; full matrix; $w = 1/\sigma_{F_{obs}^2}{}^2$) was repeated with CRYLSQ[36] (final *R* values: $R = 4.3\%$ (using $|F|$), $wR = 11.3\%$ (using $|F^2|$)), and the result was not significantly different from that of the SHELXL-93 refinement. The electron and difference density contour maps for 5 planes (see the supplementary material, Figures S4–S8) were generated with the program sequence FOURR,[37] SLANT,[38] CONTRS,[39] PREVUE,[40] PLOTX;[41] the density functions were analyzed with PEKPIK.[42] The difference density contour map in the mirror plane (supplementary material, Figure S4) shows that all atoms are surrounded by a pair of maxima aligned with the atomic position in the same direction. These peaks are probably due to an imperfect absorption correction. Because they are superimposed with the bond density peaks, these maps cannot be safely interpreted with regard to information about the chemical bonds. Separate thermal motion analyses of **1** and of the BCl_4 anion with

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(27) This procedure was used for the work described in ref 20.

(28) See Scheme 2.

(29) Coates, R. M. (University of Illinois at Urbana—Champaign), private communication. See also: Coates, R. M.; Kirkpatrick, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 4883–4892.

(30) Stewart, J.; Merom, R.; Holden, J.; Doherty, R.; Hall, S.; Maslen, T.; Spadaccini, N. *DIFDAT. Xtal 3.2 Reference Manual*; Hall, S. R., Flack, H. D., Stewart, J. M., Eds.; Universities of Western Australia, Geneva, and Maryland; Lamb: Perth, Australia, 1992; pp 104–110.

(31) Hall, S. R., Flack, H. D., Stewart, J. M., Eds. *Xtal 3.2 Reference Manual*; Universities of Western Australia, Geneva, and Maryland; Lamb: Perth, Australia, 1992. The program version used here contains the August 1993 updates.

(32) Watenpaugh, K.; Stewart, J. *ABSCAL. Xtal 3.2 Reference Manual*; Hall, S. R., Flack, H. D., Stewart, J. M., Eds.; Universities of Western Australia, Geneva, and Maryland; Lamb: Perth, Australia, 1992; pp 41–43.

(33) Sheldrick, G. *SHELXS-86*; University of Göttingen: Federal Republic of Germany, 1986. Sheldrick, G. M. *Acta Crystallogr.. Sect. A* **1990**, *A46*, 467–473.

(34) Sheldrick, G. *SHELXL-93*; University of Göttingen: Federal Republic of Germany, 1993. Sheldrick, G. M. *J. Appl. Crystallogr.*, in press.

(35) Hall, S. *LISTFC. Xtal 3.2 Reference Manual*; Hall, S. R., Flack, H. D., Stewart, J. M., Eds.; Universities of Western Australia, Geneva, and Maryland; Lamb: Perth, Australia, 1992; pp 153–155.

(36) Olthof-Hazekamp, R. *CRYLSQ. Xtal 3.2 Reference Manual*; Hall, S. R., Flack, H. D., Stewart, J. M.. Eds.; Universities of Western Australia, Geneva, and Maryland; Lamb: Perth, Australia, 1992; pp 93–103.

(37) Stewart, J.; Holden, J.; Doherty, R.; Hall, S. *FOURR. Xtal 3.2 Reference Manual*; Hall, S. R., Flack, H. D., Stewart, J. M., Eds.; Universities of Western Australia, Geneva, and Maryland; Lamb: Perth, Australia, 1992; pp 118–124.

(38) Spadaccini, N.; Alden R. *SLANT. Xtal 3.2 Reference Manual*; Hall, S. R., Flack, H. D., Stewart, J. M., Eds.; Universities of Western Australia, Geneva, and Maryland. Lamb: Perth, Australia, 1992; pp 303–306.

(39) Spackman, M. *CONTRS. Xtal 3.2 Reference Manual*; Hall, S. R., Flack, H. D., Stewart, J. M., Eds.; Universities of Western Australia, Geneva, and Maryland; Lamb: Perth, Australia, 1992; pp 82–87.

(40) Streltsov, V. *PREVUE.* Described in *Notes from Ozy*; Hall, S. R., Flack, H. D., Stewart, J. M., Eds.; Universities of Western Australia, Geneva, and Maryland. Vol. III, No. 8, August 1993.

(41) Hall, S.; Olthof-Hazekamp, R.; Flack, H.; Hester, J.; Bartsch, U. *PLOTX. Xtal 3.2 Reference Manual*; Hall, S. R., Flack, H. D., Stewart, J. M., Eds.; Universities of Western Australia, Geneva, and Maryland; Lamb: Perth, Australia, 1992; pp 244–246.

(42) Hall, S.; Doherty, R. *PEKPIK. Xtal 3.2 Reference Manual*; Hall, S. R., Flack, H. D., Stewart, J. M., Eds.; Universities of Western Australia, Geneva, and Maryland; Lamb: Perth, Australia, 1992; pp 232–234.

THMA11[43] (using the σ_U values for weights; assuming a rigid body) gave for **1** a weighted R for all U's of 3.5%, and for the diagonal U's of 2.8% and for the BCl_4 anion the corresponding values of 0.9% and 0.9%. The roots of the eigenvalues of the **L** and **T** tensors for **1** are 3.03°, 1.95°, 1.85° and 0.1265 Å, 0.1131 Å, 0.1068 Å, and for the BCl_4 anion 3.78°, 3.08°, 2.40° and 0.1423 Å, 0.1087 Å, 0.1072 Å. The largest difference between the mean square displacement amplitudes of bonded atoms in **1** is 0.0009(5) $Å^2$ for C1–C5 and for any atom pair 0.0024(5) $Å^2$ (Cl6···C61). All rigid body corrections of bond lengths in **1** are less than 0.0033 Å (see Table 2).

Refinement of *endo*-2·CF_3SO_3. The structure was refined upon F^2 (full matrix; for the weights see Table 1) with SHELXL-93.[34] Only S1 could be refined anisotropically. Using a SAME instruction with default standard deviations, a noncrystallographic mirror plane was enforced for the cation structure. The isotropic displacement parameters of corresponding C atoms related by this mirror plane were constrained to be equal with FVARs. In the final refinement, all H positions were computed, and the methyl H displacement parameters were constrained to be $U_{iso}(H) = 1.5U_{iso}(C)$ with regard to their C atom; for H6, $U_{iso}(H6) = 1.2U_{iso}(C6)$ was chosen. For C11 and C21, one set of H positions was refined with free rotation around the C–CH_3 bonds in each case. For the other methyl groups, two sets of H positions (rotated from each other by 60°) were refined in each case, and the major H population factors converged to the following values: C31 0.6(2), C41 0.7(2), C51 0.7(2), C61 0.7(1). For the anion, two sets of O and F positions rotated from each other by about 60° around the C7–S1 bond with free population factors were refined in each case. Using several SADI instructions with default standard deviations (same values for all C7-F*i*, S1···F*i*, C7···O*i*, S1–O*i*, neighboring F_{major}···F_{minor}, neighboring O_{major}···O_{minor} distances; i = 1, 2, 3, 1A, 2A, 3A; the indices major and minor refer to the population, see Figure 4) and using FVARs for one common displacement parameter for all O and F atoms in each case, the following major population factors were obtained: F 0.74(2), O 0.81(1). For the R values see Table 1. The highest difference density maximum in the cation region is 0.60 e $Å^{-3}$ and in the anion region 1.10 e $Å^{-3}$ (rms deviation from the mean: 0.17 e $Å^{-3}$).

Refinement of *endo*-2·CF_3SO_3-SbF_5. The structure was refined upon F^2 (full matrix; for the weights see Table 1) with SHELXL-93. Only Sb1 could be refined anisotropically. Disorder models were used for the cation and the anion. For the Figures S17 and S18 in the supplementary material, only the major orientation of the anion was drawn (F1–F5, population = 0.74(5)). Two orientations of the cation (both with *endo* configuration at C6; populations: 0.66(6) and 0.34(6)) were refined with several common C atoms. No H positions were calculated. There are two very high difference density peaks in the anion region (13.24 and 10.84 e$Å^{-3}$), indicating additional anion orientations; in the cation region, the highest difference density peak has 1.75 e $Å^{-3}$ (rms deviation from the mean 0.49 e $Å^{-3}$).

New Refinement of 5·SbF_6. The structure was refined upon F^2 with SHELXL-93.[34] (full matrix; $w = 1/[\sigma_{F_{obs}^2}{}^2 + (0.1613P)^2 + 3.3123P]$ with $P = (\max(F_{obs}{}^2,0) + 2\,F_{calc}{}^2)/3$). A disorder model for the anion was used, so that two sets of positions for F2 to F5 were refined (population of the major orientation: 0.88(1)). All H positions were calculated; the H's at C5 and C6 had one common displacement parameter in each case; for the C21 and C31 methyl groups, each two sets of positions (rotated from each other by 60°) were refined (major H populations at C21 0.52(8), at C31 0.73(11)). With 3814 reflections and 229 parameters, one obtains for $I > 2\sigma_I$: $R1$ = 7.57%, $wR2$ = 18.95%. For all data: $R1$ = 10.50%, $wR2$ = 23.67%. The highest difference density maximum in the cation region is 0.59 e $Å^{-3}$ and in the anion region 2.62 e $Å^{-3}$ near Sb1 (rms deviation from the mean: 0.22 e $Å^{-3}$).

Crystallographic Figures and Tables. Figures 1 and 4 were generated with ORTEP,[44] Figures 2, 3, 5, and 6 with SYBYL 6.0[19] (besides CorelDRAW 4.0[45] for Figures 2 and 6). Most geometry calculations and the preparation of most tables in the supplementary material were carried out with a modified version of PARST88.[46]

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Supplementary Material Available: Tables of positional and displacement parameters, bond distances, angles, torsion angles, interatomic distances for all four structures; photographs of crystals and packing diagrams for **1**·BCl_4, *endo*-**2**·CF_3SO_3, *endo*-**2**·CF_3SO_3–SbF_5; electron and difference density maps and NMR spectra of **1**·BCl_4 (82 pages); observed and calculates structure factors for all four structures (87 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(43) Trueblood, K. *THMA11*, version of Oct. 21, 1988, University of California, Los Angeles, CA 90024.

(44) Davenport, G.; Hall, S.; Dreissig, W. *ORTEP. Xtal 3.2 Reference Manual*; Hall, S. R., Flack, H. D., Stewart, J. M., Eds.; Universities of Western Australia, Geneva, and Maryland; Lamb: Perth, Australia, 1992; pp 219–224. Original version: Johnson, C. K. *ORTEP-II*; Oak Ridge National Laboratory, TN 37830, 1976.

(45) CorelDRAW Version 4.0, 1993. Corel Corporation, 1600 Carling Avenue, Ottawa, Ontario, Canada K1Z8R7.

(46) Nardelli, M. PARST88, Release April 1988, University of Parma, Italy. Nardelli, M. *Comput. Chem.* **1983**, *7*, 95–98.