First X-ray Crystallographic Study of a Benzyl Cation, Cumyl Hexafluoroantimonate(V), and Structural Implications

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Abstract: The crystal structure of the cumyl cation (**1**; 2-phenyl-2-propyl cation) has been determined at −124 °C (as hexafluoroantimonate, **1**·SbF$_6$; R_1 = 0.0502, wR_2 = 0.1054). The cation **1** is nearly planar and has a short C$^+$−C$_{ipso}$ bond (1.41(2) Å) and bond lengths in the phenyl ring which agree with strong benzylic delocalization. The weak but distinct shortening of the C$^+$−CH$_3$ bonds by 0.025(12) Å indicates weak C−H hyperconjugation. Nearly all H atoms are involved in H···F contacts to SbF$_6$ anions, and one close C$^+$···F contact (3.11(2) Å) is observed. The phenyl rings form infinite stacks and are shifted against each other in the stack.

The cumyl cation (2-phenyl-2-propyl cation, **1**; see Chart 1) is the simplest α,α-dialkylbenzyl cation and has been prepared in solution and investigated for the first time under superacidic conditions by Olah in 1964.[1]

Attempts to prepare methyl-substituted benzyl cations with aluminum chloride[2] were not successful, as has been shown by comparison with results from superacidic media.[3,4] The tertiary cation **1** is a benzylic cation related to the unsubstituted parent benzyl cation **2** which was, together with the isomeric tropylium cation **3**, the subject of intensive gas phase and theoretical studies.[5] Originally it was thought that the ion C$_7$H$_7{}^+$ obtained from toluene and other precursors is **3**. It is now known that both **2** and **3** are formed in the gas phase in a fairly complex isomerization/dissociation scheme.[5] Tropylium cations have so far not been observed as rearrangement products of benzyl cations in the condensed phase. Ab initio studies have shown that **3** lies 29 kJ mol^{-1} lower in energy than **2**.[6] The electronic properties of **1** are expected to be similar to those of **2** or ring-methylated primary benzyl cations, although C−H hyperconjugation should provide additional stabilization of **1**. The unsubstituted benzyl cation **2** is kinetically very unstable in condensed phases, as it can undergo ready head-to-tail condensation, and only its UV spectrum could be obtained by pulse radiolysis.[7] In contrast para (or other) substituted benzyl cations were obtained in superacid solutions. The benzylic delocalization in α,α-bis-(1-adamantyl)benzyl cations can be minimized by sterically forced twisting of the C$^+$−C$_{ipso}$ bond.[8,9] Cumyl cations have been used as polymerization initiators,[10,11] and their

Chart 1
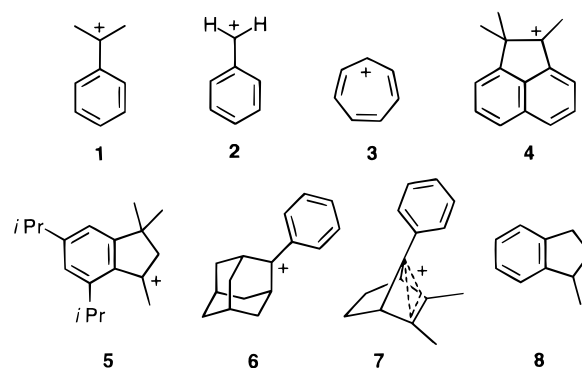
solvation[12] and reactions[12,13] have been studied recently. The polycyclic α,α-dialkylbenzyl cations **4**−**6** and the bridged ion **7** have been investigated by X-ray crystallography.[14−17] The indanyl cation **8** has been observed in 78% sulfuric acid, while **1** required 30% oleum;[18] i.e., **4** and **5** are probably more stable than **1**, and **4** could indeed be crystallized as an AlCl$_4{}^-$ salt. Also the larger π system of **4** and the higher degree of substitution of **5** should increase the stability of these ions with respect to **1**. According to a recent review article,[19] the Hammett acidity of **1** is even higher than that of the *tert*-butyl cation. However, it must be pointed out that simple comparison of observed ions in different acids does not give real stabilities. We report here the crystal structure of the tertiary cation **1** which is of substantial interest in our understanding of the structure of benzylic carbocations. Up to now, only solution data of **1**

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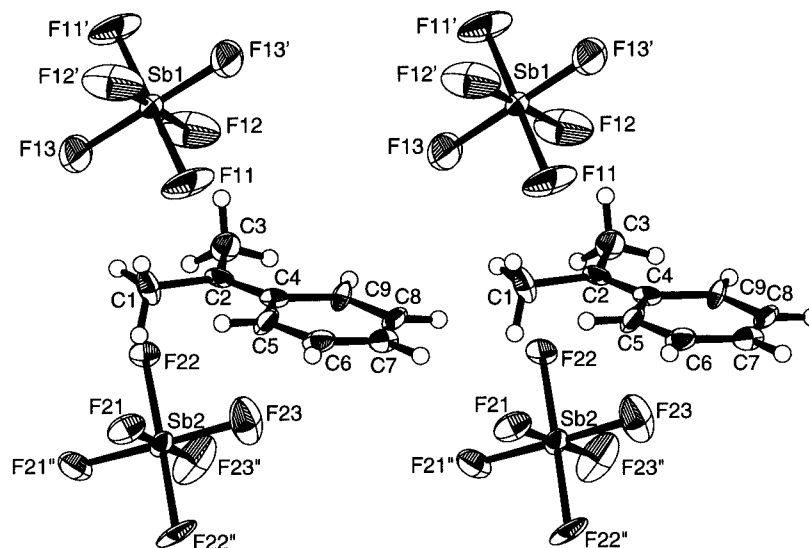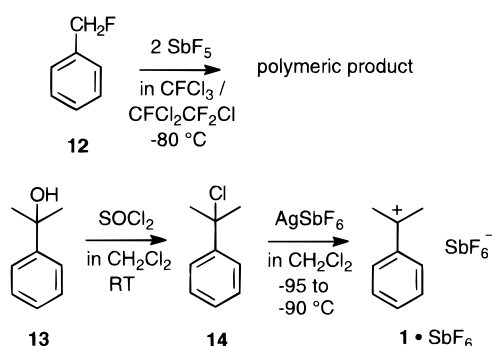
Figure 1. Stereo diagram (*Ortep*) of **1** and its two next counterions. The displacement ellipsoids are drawn at the 50% probability level, H atoms are represented by spheres with a radius of 0.1 Å. Symmetry operations: $' = -x, 2 - y, -z;$ $'' = 1 - x, y, {}^{3}/_{2} - z.$
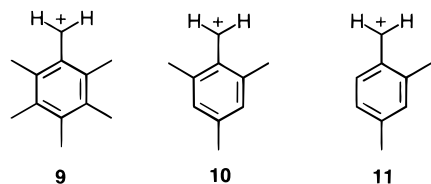
Scheme 1

were known, whereas our results are the first data about **1** in the crystalline state and thus of a benzyl cation.

Results

Crystal growth was attempted with several salts of ring-methylated benzyl cations **9**–**11** (counterions SbF_6^- or $SbCl_6^-$) at low temperatures, but the crystal quality was so far not sufficient for X-ray studies.

We also tried to obtain a crystalline salt of the parent ion **2** by reaction of **12** with 2 equiv of antimony pentafluoride (Scheme 1) at low temperatures, but only polymeric material was obtained.

Cumyl hexafluoroantimonate (**1**·SbF$_6$) was prepared by the reaction of α-chlorocumene (**14**) with silver hexafluoroantimonate from methylene chloride solution at −90 °C (see Experimental Section). Proper crystallization conditions for **1**·SbF$_6$ were found after a long optimization. Small but suitable single crystals were obtained by slow crystallization at dry ice temperature. Crystallization at higher or varying temperatures leads only to unsatisfactory crystals. The result of the crystal structure analysis is shown in Figures 1 and 2.
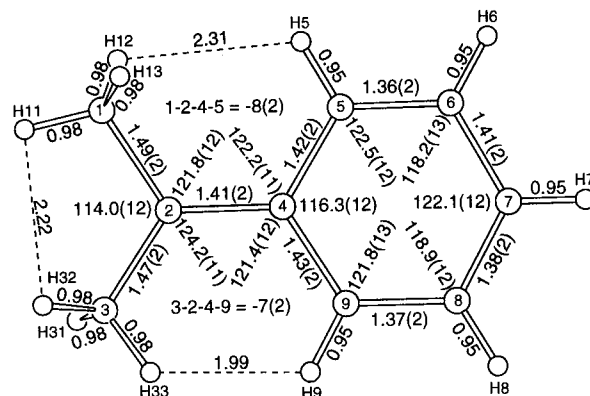

Figure 2. Bond lengths, angles, torsion angles, and contact distances of **1**. Lengths are given in angstroms, angles in degrees. The C atoms are labeled by their numbers.

The cationic C2 and the phenyl ring are each planar, but the isopropyl cation fragment and the phenyl ring are twisted around C2−C4 by 8(2)°; i.e., the C skeleton of **1** is nearly planar. The C2−C4 bond (1.41(2) Å) is shortened by 0.06(2) Å if compared with the reference value[20] C_{sp^2}–C_{ar} (conjugated) = 1.470(2) Å, and the average[21] C2−CH$_3$ bond of **1** (1.478(12) Å) is slightly shortened by 0.025(12) Å with regard to a normal C_{sp^2}–CH$_3$ bond[20] (1.503(1) Å). The bond lengths in the phenyl ring (see Table 1) are slightly but not significantly different on the 3σ level from those observed in trityl cation structures; see also the discussion below.
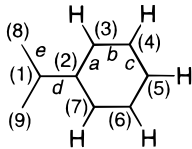
One very short nonbonding H···H contact is observed (H9··· H33 = 1.99 Å). Practically all H atoms are involved in H···F contacts shorter than the sum of the van der Waals radii, which can be interpreted as CH···F hydrogen bonds (see Figure 3).

A counterion is located on each side of the cationic C2, but a short C^+···F contact is found only on one side (C2···F12 = 3.11(2) Å). The anion on the other side of C2 is only involved in a H bond. The cations form infinite stacks in the [101] direction (see Figure 4).

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Table 1. Important Parameters[a] of Cationic and Neutral Benzylic Fragments in Crystal Structures

	1	**6**[c,d]	**7**[d,e]	trityl cations[d,f]	neutral fragments[d,g]
a/Å[b]	1.426(12)	1.42(1)	1.384(7)	1.415(4)	1.392(1)
b/Å	1.367(12)	1.36(1)	1.377(8)	1.382(5)	1.384(1)
c/Å	1.394(12)	1.37(1)	1.372(10)	1.392(7)	1.374(1)
d/Å	1.409(17)	1.41(2)	1.459(10)	1.444(2)	1.465(2)
e/Å	1.478(12)	1.45(1)	1.513(7)		
$|e-d-a|$[h]/deg	8(2)	18(1)	12(1)	27–40	0–20[i]
hybridization of $C^{(8)}$ and $C^{(9)j}$	sp^3	sp^3	sp^3	sp^2	not specified

[a] The atom numbering in the connectivity diagram is different from that of **1**. Bonds are designated by small letters. The letters are chosen for comparability with the results of other studies of the Ph ring geometry; see, for example: Domenicano, A. In *Stereochemical Applications of Gas-Phase Electron Diffraction*; Hargittai, I.; Hargittai, M., Eds.; VCH: Weinheim, 1988; Part B, pp 281–324. The usually assumed local C_{2v} symmetry of Ph rings is not applied here because of the twisting along the bond d. [b] Corresponding parameters have been averaged assuming local C_2 symmetry. For example, $a = (C^{(2)}-C^{(3)} + C^{(2)}-C^{(7)})/2$, etc. [c] Data from ref 16. [d] See Supporting Information. [e] Data from ref 17b. [f] Averages calculated from four structures in the Cambridge File. For the Cambridge File, see ref 22. [g] Averages calculated from 62 precise structures ($R \leq 0.05$, average $\sigma_{C-C} \leq 0.005$ Å) in the Cambridge File. [h] Smallest absolute value of the torsion angle. [i] This range was chosen for comparability with **1**, **6**, and **7**. [j] The atoms $C^{(1)}$ to $C^{(7)}$ in the connectivity diagram are sp^2 hybridized.
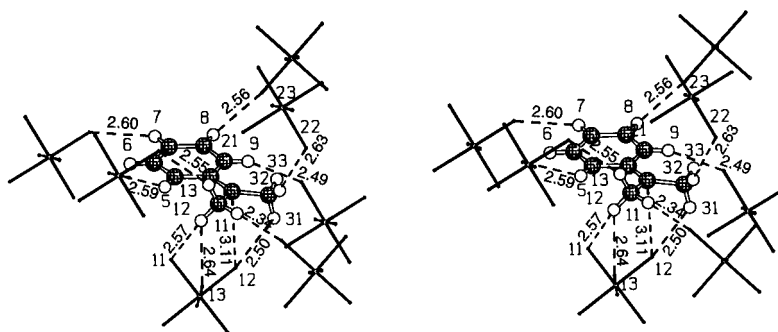

Figure 3. Stereodiagram of **1** with the seven counterions which are involved in H···F contacts less than 2.67 Å (= sum of the van der Waals radii of H and F) or in C···F contacts less than 3.17 Å (= sum of the van der Waals radii of C and F). These contacts are represented by dashed lines, and the distances are given in angstroms. The H atoms and the F atoms belonging to the asymmetric unit are labeled by their numbers.
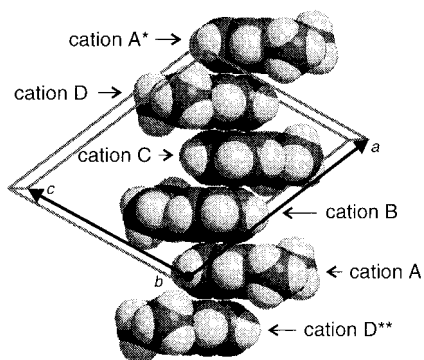

Figure 4. Space-filling diagram of a stack of six cations **1**. The cation stacks are infinitely extended in the [101] direction and consist of blocks of four symmetry-related cations (A–D). These blocks are related by lattice translations along [101]. The starred cations belong to neighboring blocks in a stack. The cation B was selected for the asymmetric unit.

The normal of the least-squares plane through the ring atoms C4 to C9 forms an angle of 3.4(2)° with the [101] direction; i.e. the phenyl rings are slightly tilted with regard to the stacking direction. There are two different cation···cation π contacts in the stacks (see Figure 5).

The cations A and B are related by a crystallographic inversion center and the cations B and C by a crystallographic C_2 axis. The smallest C···C distances are in both cases about 3.50 Å, i.e., 0.1 Å greater than the sum of the van der Waals

radii. The planes through the ring carbon atoms of cations A and B are parallel because of the inversion center, and those through cations B and C form an angle of 2.7(8)°. Projections (see Figure 6) show that the phenyl rings overlap only partially. The cationic isopropyl groups protrude from the stack, and therefore, they can interact with four anions (see Figure 3).

Discussion

Structural Aspects. Two electronic effects are expected to be mainly operative in the structure of **1**: benzylic delocalization and C–H hyperconjugation. In the VB description, the former is represented by the resonance formulae **Q1–Q3** and the latter by **HC1–HC4** (see Chart 2).

For simplicity, only one H atom of each Me group has been involved in **HC1–HC4**. The corresponding MO description is depicted in Chart 3.

To facilitate the analysis and interpretation of the observed bond lengths in **1**, we have calculated simple estimates of the bond orders and bond numbers according to Pauling[23,24] for the fragments listed in Table 1 (see Figure 7).

The similarity of the electronic effects in **1** and **6** is obvious from a comparison of parts a and b of Figure 7. The short

(23) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960; p. 239. Equation 7-5 is used with $D_1 = 1.54$ Å.

(24) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960; pp 235–236. Equation 7-3 is used with $D_1 = 1.504$ Å and $D_2 = 1.334$ Å.
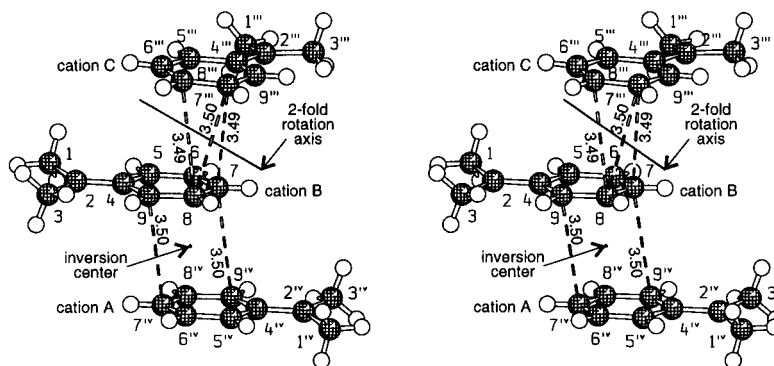
Figure 5. Stereodiagram with the nonbonding contact distances less than or equal to 3.50 Å between C atoms in the two different cation···cation contacts of the stacks. The C atoms are labeled by their numbers, and the cations are labeled as in Figure 4. Symmetry operations: $^{III} = 1 - x, y, ^{1}/_{2} - z$; $^{IV} = ^{1}/_{2} - x, ^{3}/_{2} - y, -z$.
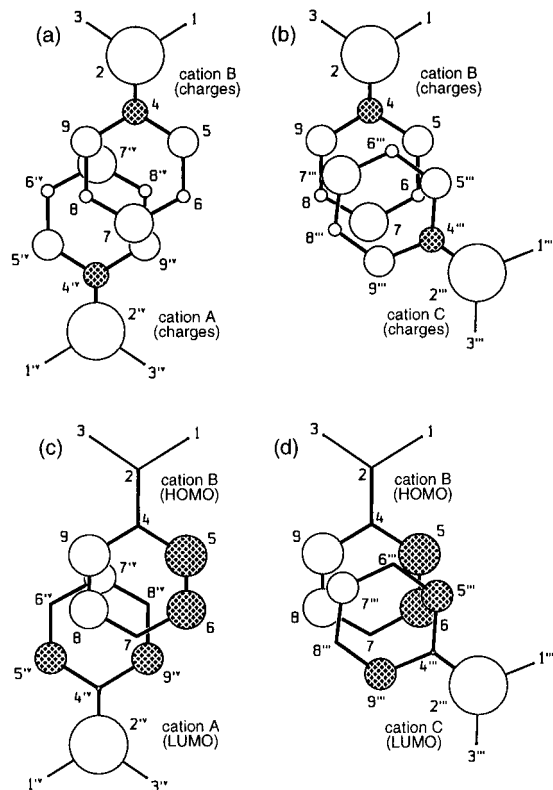

Figure 6. Approximate computed charges (a and b) and HOMO−LUMO AO coefficients (c and d) in the two different cation···cation pairs in the stacks of **1** (in all cases perpendicular view on the plane through C4 to C9 of cation B). The atoms C2 and C4 to C9 are represented by circles whose areas are proportional to the charges (a and b; empty circles = positive charge, rastered circles = negative charge) or to the squares of the AO coefficients (c and d; empty and rastered circles belong to coefficients with different signs) of the unsubstituted benzyl cation.[2] The atoms and the cations are labeled as in Figure 5.

$C^{+}-C_{ipso}$ bonds (bond *d* in Table 1; **4**, 1.40(2); **5**, 1.38 Å) and the pattern of the Ph ring bond lengths can be interpreted as the result of the influence of the resonance formulae of the types **Q1**−**Q3**. The benzylic resonance is somewhat weaker in trityl cations (Figure 7d); this can be explained by the delocalization of the positive charge into three rings and the stronger twisting of the Ph rings in trityl cations (see Table 1). The π bonding in the bridged benzylic cation **7** (Figure 7c) is quite different from that in **1** and **6**, but similar to that in neutral systems with benzylic delocalization (Figure 7e). Also the color of the crystals supports this classification (**1**·SbF₆ and **6**·Sb₂F₁₁, yellow; **7**·SbF₆, colorless[17a]); i.e. the benzylic resonance in **7** is

Chart 2. Resonance Formulae for the Description of **1** (AR, aromatic; Q, quinoid; HC, hyperconjugative)
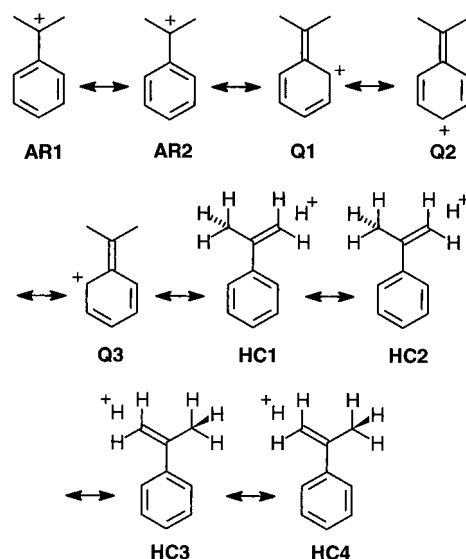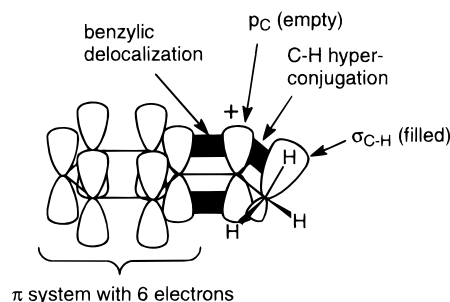

Chart 3. Qualitative MO Description of Benzylic Delocalization and C−H Hyperconjugation in **1**

unimportant because the three-center, two-electron bond emanating from the benzylic C atom yields an aromatic bishomocyclopropenylium ion with better delocalization.

Hyperconjugation should lead to a shortening of the C2−CH₃ bonds in **1** (see **HC1**−**HC4** in Chart 2) and an elongation of the C_{sp^3}−H bonds. The slight and only weakly significant average shortening of the C2−CH₃ bonds in **1** by 0.025(12) Å can thus be explained by weak C−H hyperconjugation. The corresponding shortening in the *tert*-butyl cation[25] is 0.061(5) Å, but of course this cation has no conjugative phenyl group. A C_{sp^3}−H lengthening cannot be detected because of the

(25) Hollenstein, S.; Laube, T. *J. Am. Chem. Soc.* **1993**, *115*, 7240−7245.
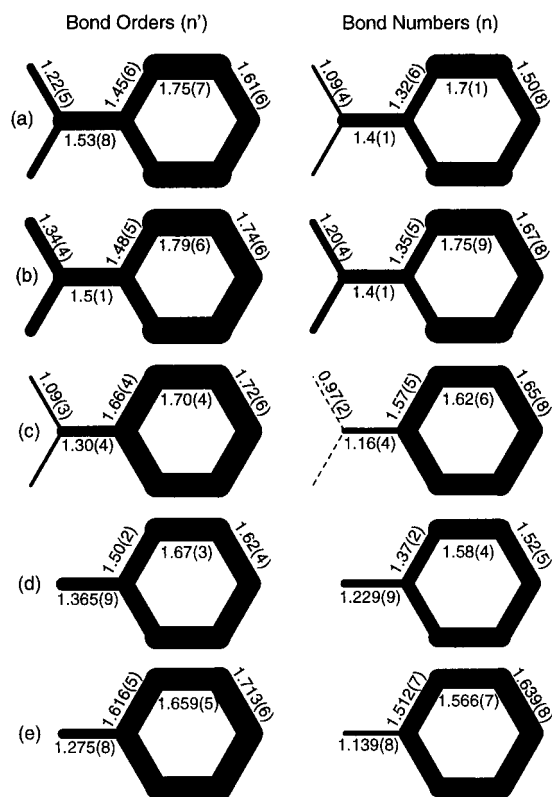
Figure 7. Bond orders[23] n' (left) and bond numbers[24] n (right) calculated from the experimentally determined bond lengths in the benzylic systems listed in Table 1 (esd's in parentheses). Local C_2 symmetry has been assumed in all cases. The thickness of the bonds in the diagrams is proportional to the π bond parameter estimates $n' - 1$ and $n - 1$, respectively. Negative values are indicated by dashed bonds. (a) **1**, (b) **6**, (c) **7**, (d) trityl cations, and (e) neutral systems.
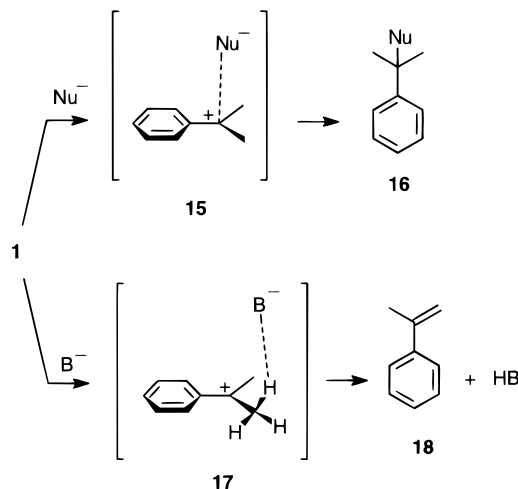
generally known difficulties in locating H positions reliably in X-ray crystal structures. On the basis of the C2—CH$_3$ bond lengths in **1**, one can conclude that the hyperconjugation in **1** is slightly weaker than in **6** (C—C hyperconjugation) but stronger than in **7** (practically no hyperconjugation). One would expect that the positive charge of the Me protons in **1** is increased by C—H hyperconjugation if compared with neutral molecules. The anions located in the nearest environment of the Me groups in the crystal (see Figure 3) can be interpreted as a hint to some positive charge on the Me hydrogens like in the *tert*-butyl cation structure[25] (see also below).

Crystal Packing. The C2···F and the C$_{methyl}$H···F contacts may be interpreted as initial stages of the nucleophilic attack[26,27] on C2 (**15**; Nu⁻ = nucleophile), leading to the addition product **16**, and of deprotonation (**17**; B⁻ = base), leading to α-methylstyrene (**18**), respectively (see Scheme 2).

Both reactions of **1** occur in solution;[12] i.e., the packing seems also in this structure to reflect the reactivity of the cation, because arrangements like in **15** and **17** can be found as sections of the packing (Figure 3).

The stacking of **1** is quite unusual because one would expect that electron-deficient phenyl rings of carbocations cannot as easily undergo charge transfer as alternating stacks consisting

(26) The interpretation of nonbonding contacts in crystals as initial stages of chemical reactions has been introduced by Dunitz and Bürgi. See, for example: Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153—161. Dunitz, J. D. *X-Ray Analysis and the Structure of Organic Molecules*; Cornell University Press: Ithaca, 1979; pp 366—384.

(27) General investigations of such contacts in carbocation crystal structures: Laube, T. In *Stable Carbocation Chemistry*; Prakash, G. K. S., Schleyer, P. v. R., Eds.; John Wiley & Sons: New York, 1997; pp 453—496.

Scheme 2

of electron-rich and electron-deficient π systems, for which stacking is well-known.[28] Cation **4** also forms stacks, but with overlap between the presumably more electron-rich non-benzylic 6-membered rings. Both the A···B and the B···C contact (Figure 6a,b) show electrostatically unfavorable interactions between ring atoms with significant positive charges (C7··· C9^{IV}, C7^{IV}···C9, C7···C9^{III}, C7···C7^{III}, C7^{III}···C9, C5···C5^{III}). On the other hand, binding HOMO—LUMO interactions seem to be possible in both contacts (Figure 6c,d). Probably most important are the facts that the highly charged C2 atoms are surrounded by anions and well-separated from each other in the stack. The distances between C2 atoms in different cations of the stack are (designation as in Figure 4) B—A = 7.82(2), B—C = 7.01(2), and B—D = B—D** = 8.02(2) Å. Also simple steric reasons may be responsible for the stacking.

Conclusions

The phenyl ring in the cumyl cation **1** is twisted by only 8(2)° around the C⁺—C$_{ipso}$ bond. The short C⁺—C$_{ipso}$ bond and the parameters of the phenyl ring agree with strong benzylic delocalization. The slightly shortened C⁺—CH$_3$ bond agrees with the assumption of weak C—H hyperconjugation. The presence of a C⁺···F and of C$_{methyl}$H···F contacts correlates with the known reactivity of **1** in solution. The stacking of the cations can be explained by HOMO—LUMO interactions or by steric reasons. The obtained data from the first crystallographic study of a benzyl cation provide significant structural data for this important class of carbocations. Both strong π-conjugative and weak σ-hyperconjugative effects are apparent in the structure. As still only very few X-ray structures of carbocations were possible to obtain, present work adds significantly to their understanding.

Experimental Section

α-Chlorocumene (**14**) has been prepared from **13** (Aldrich) in analogy to a procedure for substituted derivatives.[29] Dissolved gases, CH$_2$Cl$_2$, and SOCl$_2$ were distilled off from the reaction mixture below

(28) The crystal structures of many such complexes can be found in the Cambridge File (ref 22) in class 60. Several searches of the Cambridge File have shown that phenyl rings of neutral hydrocarbons (electron-rich aromatics) have a low tendency to form stacks; they prefer herringbone patterns. Nitro-substituted aromatics and annellated systems without other functional groups or complex partners have a high tendency to form stacks with tilted or slipped rings (see Supporting Information). This shows that stacking of electron-deficient aromatic rings occurs also for neutral molecules. Some recent reviews about crystal packing: Gavezzotti, A. *Acc. Chem. Res.* **1994**, *27*, 309—314. Brock, C. P.; Dunitz, J. D. *Chem. Mater.* **1994**, *6*, 1118—1127. Desiraju, G. R. *Angew. Chem.* **1995**, *107*, 2541—2558. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2311—2327.

room temperature (RT) in a high vacuum (HV) system, and the product was finally distilled at RT into a Schlenk tube and stored under Ar.

Preparation and Crystallization of Cumyl Hexafluoroanti-monate(V) (1·SbF₆). The reaction was carried out in the apparatus described in Figure 6 of ref 30; for more experimental details see the Experimental Part of ref 30. In part "A" of the reaction vessel, 45 mL of dry CH_2Cl_2 was cooled under Ar to −95 °C (bath temperature). A solution of 0.65 g of $AgSbF_6$ (1.89 mmol; Aldrich) in 5 mL of CH_2Cl_2 was added with a syringe through a septum on joint 3. To the resulting clear, colorless solution was added a solution of 0.28 g of **14** (1.81 mmol) in 5 mL of CH_2Cl_2 with a syringe within 10 min at a bath temperature of −95 to −90 °C. A yellow precipitate was obtained. After 35 min at −90 to −80 °C, the reaction mixture was filtered at −75 °C, the mother liquor was removed from the apparatus, and the filter cake on the frit in "A" was dried between −70 and −55 °C at 10^{-3} Torr for 90 min. The coarsely powdered dry filter cake was quickly transferred into part "C" of the filtration vessel, where 20 mL of dry CH_2Cl_2 was added slowly at −85 °C under Ar and stirring. The cooling bath was warmed up to −40 °C within about 10 min in order to increase the solubility of the organic salt, and the mixture was filtered into part "D" at this temperature. After the clear yellow solution was poured into a roughened 50 mL two-neck flask with a three-way stopcock adapter connected at joint 6, this flask was immediately cooled with a methanol/dry ice bath and connected to a HV system. The solvent was slowly distilled off at this temperature within 3 days. One obtains small yellow crystals (needles and prisms) with an average size of about 0.1 mm and a small amount of an oily product. A few needles have a length of up to 0.5 mm. The optical investigation and the mounting of the crystals were carried out at −70 °C using a microscope with the cryostage described in Figure 7 of ref 30.

X-ray Crystal Structure Analysis of 1·SbF₆. A crystal (approximate size in mm, 0.3 × 0.1 × 0.1) was mounted with a small drop of a perfluorinated polyether on a glass fiber and transferred at about −150 °C to the diffractometer (Siemens P4; Mo Kα radiation, sealed tube, graphite monochromator). Crystal data at −124 °C: monoclinic, $a = 13.751(2)$, $b = 16.241(2)$, $c = 11.200(1)$ Å, $\beta = 113.81(1)°$, $V = 2288.4(5)$ Å^3, space group $C2/c$ (No. 15), $Z = 8$, $Z' = 1$, sum formula $C_9H_{11}SbF_6$, formula weight 354.93, absorption coefficient $\mu = 2.461$ mm^{-1}, $\rho_X = 2.060$ g cm^{-3}, $F_{000} = 1360$. The data were collected at −124 °C (two quadrants, up to $\theta = 22.5°$, 2858 reflections collected, 1491 independent reflections). The data reduction was carried out with the Siemens *Xscans* software using the "learnt profile" option. The structure was solved with *Shelxs-86*[31] (Patterson method) and refined with *Shelxl-93*[32] (full-matrix least-squares on F^2). There are two crystallographically different positions for the eight anions

in the unit cell: four lie on inversion centers (Wyckoff position 4*a*; central atom: Sb1), four lie on two-fold rotation axes (Wyckoff position 4*e*; central atom: Sb2). The cation lies on a general position. All hydrogen atom positions were computed, but the methyl groups were allowed to rotate around their C−C bonds and refined each with a free common $U_{iso}(H)$; the aromatic hydrogens were computed with $U_{iso}(Hn) = 1.2 \times U_{eq}(Cn)$, $5 \leq n \leq 9$. The refinement of 151 parameters converged with the following final R indices for $I > 2 \sigma_I$: $R_1 = 0.0502$, $wR_2 = 0.1054$; for all data: $R_1 = 0.0977$, $wR_2 = 0.1164$; goodness-of-fit on F^2 0.799. The largest difference density peak and hole are 0.623 and −1.608 e Å^{-3}. The smallest eigenvalues of the displacement ellipsoids of all C atoms and of F11 and F22 are positive but not significantly different from zero (3σ criterion; computed with *Parst88*[33]). This is probably due to absorption because the refinement leads after an absorption correction with *Difabs*[34] to $R_1 = 0.0421$ for 847 data with $F_o > 4\sigma(F_o)$ and 0.0900 for all 1491 data and smaller ratios of largest to smallest U eigenvalues for most atoms; i.e., the U ellipsoids become more spherelike. Bond lengths and angles of the cation agree within 1 esd for the refinements with and without absorption correction. The average[21] shortening of the C2−CH₃ bonds is 0.026(10) Å with absorption correction. The absorption is mainly ascribed to the large amount of oil with regard to the mass of the crystal. The structure can be solved but not successfully refined in Cc, because this leads even with many restraints to nonpositive definite displacement ellipsoids. Figure 1 was produced with *Ortep*[35] and Figures 2−6 were produced with *Schakal92*.[36]

Supporting Information Available: Packing diagram, listing of crystal data, atomic coordinates and displacement parameters, bond lengths, angles, torsion angles, contact distances and H bond parameters for **1·SbF₆**, results of searches in the Cambridge File, geometrical data of **6** and **7** (63 pages). See any current masthead page for ordering and Internet access instructions.

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