

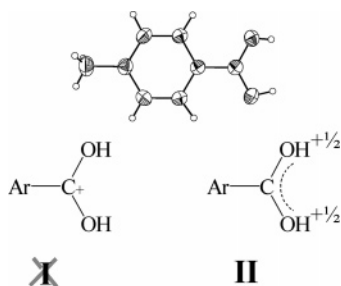
## Isolation and X-ray Structures of Labile Benzoic- and Acetic-Acidium Carbocations

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New carbocationic salts (via O-protonation of substituted benzoic acids) are prepared for the first time by controlled hydration of the corresponding benzylium salts and isolated in pure crystalline form. Precise X-ray structural analyses reveal the rather unexpected (electronic) structure of the carboxylic-acidium functionality.

Nonaqueous mixtures of acetic acid containing sulfuric (or perchloric) acid were initially proposed to be “superacid solutions” by Conant and co-workers starting in 1927 by their ability to protonate a variety of very weak organic bases.<sup>1</sup> Phase diagrams had earlier indicated the existence of the [1:1] addition compound  $\text{CH}_3\text{CO}_2\text{H}\cdot\text{H}_2\text{SO}_4$  (melting at  $-2.5\text{ }^\circ\text{C}$ );<sup>2</sup> and this was later structurally established to result from complete proton transfer, i.e.,  $\text{CH}_3\text{C}(\text{OH})_2^+ \text{HSO}_4^-$ .<sup>3,4</sup> Although the parent formic acidium salt  $\text{HC}(\text{OH})_2^+ \text{AsF}_6^-$ <sup>5-8</sup> was also isolated from the prototypical superacid system  $\text{HF}/\text{AsF}_5$ ,<sup>9</sup> there are no extant examples of such  $\alpha,\alpha$ -dihydroxycarbenium ions derived from aromatic carboxylic acids with which to establish substituent effects on acidium structures.<sup>10</sup>

(1) Hall, N. F.; Conant, J. B. *J. Am. Chem. Soc.* **1927**, *49*, 3047.

(2) Kendall, J.; Brakeley, E. *J. Am. Chem. Soc.* **1921**, *43*, 1826.

(3) Jönsson, P.-G., Olovsson, I. *Acta Crystallogr., Sect. B* **1968**, *24*, 559.

(4) Analogous acetic-acidium salts from other superacid solutions have been crystallographically confirmed as the fluorosulfate,<sup>5</sup> trifluoromethanesulfonate,<sup>6</sup> and hexafluoroantimonate salts.<sup>7</sup>

(5) Kvik, A., Jönsson, P.-G., Olovsson, I. *Inorg. Chem.* **1969**, *8*, 2775.

(6) Bartmann, K., Mootz, D. *Z. Anorg. Allg. Chem.* **1991**, *601*, 31.

(7) Minkwitz, R., Hertel, T. *Z. Naturforsch., B: Chem. Sci.* **1997**, *52*, 1283.

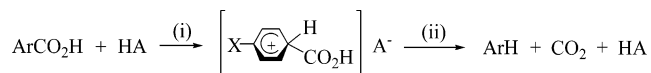
(8) Minkwitz, R.; Schneider, S.; Seifert, M.; Hartl, H. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1404.

(9) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1393.

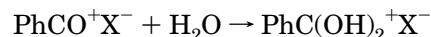
(10) However, crystalline salts of both acidium and diacidium cations of oxalic acid have been isolated by similar procedure: Minkwitz, R.; Hartfeld, N.; Hirsch, C. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1479.

Earlier attempts to prepare crystalline acidium salts of benzoic acid from superacid solutions suffered from competition via C-protonation and unavoidable protodecarboxylation as originally proposed by Schenkel et al. (Scheme 1).<sup>11,12</sup>

### SCHEME 1



Although protonation at the carbon center in step (i) may be slower than proton transfer to oxygen, irreversible loss of  $\text{CO}_2$  in step (ii) renders the isolation of the benzoic-acidium salt ineffective, and thus, any methodology based on proton transfer is basically flawed.<sup>13</sup> However, benzoic-acidium salts are addition complexes of benzoic acid with superacids (HX), and they can be alternatively viewed as [1:1] adducts of benzylium salts with water, i.e.



As such, we now report the successful isolation of crystalline acidium salts prepared via the controlled hydration of a series of pure benzylium salts under neutral (nonacidic) conditions as follows.

**Synthesis and Isolation of Dihydroxycarbenium Salts.** Two synthetic methodologies related to Friedel–Crafts acylation<sup>14</sup> were utilized in the preparation of crystalline dihydroxycarbenium salts suitable for X-ray crystallography. The more direct approach was based on the initial preparation of the acylium salt by treatment of carboxylic-acid chlorides with Lewis acids such as antimony pentachloride in dichloromethane solution, i.e.



to generate crystalline salts with the coordinatively saturated and low-nucleophilic counteranion  $\text{SbCl}_6^-$ . The second method was also found in Olah’s earlier studies and employed silver(I) salts, e.g.



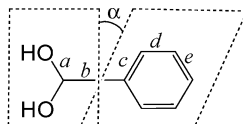
and this method depended on the careful separation of silver chloride which even as a minor contaminant could otherwise inhibit crystallization. Both methods were used interchangeably to prepare a series of substituted benzylium salts which were then recrystallized from dichloromethane containing traces of moisture. Alternatively, the two steps were combined into a single step without isolating the acylium intermediate. In both procedures, the rigorous control of water was critical for crystal preparation owing to the extreme hygroscopic nature of

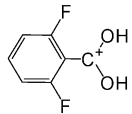
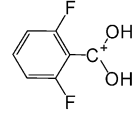
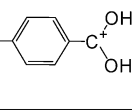
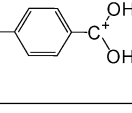
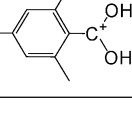
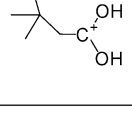
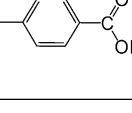
(11) Schenkel, H.; Schenkel, M. *Helv. Chim. Acta* **1948**, *31*, 514.

(12) See also: Olah, G. A.; Laali, K.; Mehrotra, A. K. *J. Org. Chem.* **1983**, *48*, 3360.

(13) Norman, R. O. C.; Taylor, R. *Electrophilic Substitution in Benzenoid Compounds*; Elsevier: New York, 1965; p 228.

(14) Olah, G. A.; Kuhn, S. J.; Tolgyesi, W. S.; Baker, E. B. *J. Am. Chem. Soc.* **1962**, *84*, 2733.

**TABLE 1. X-ray Structural Parameters of Substituted Benzoic and Acetic-Acidium Salts Relative to Those of Carboxylic Acids**

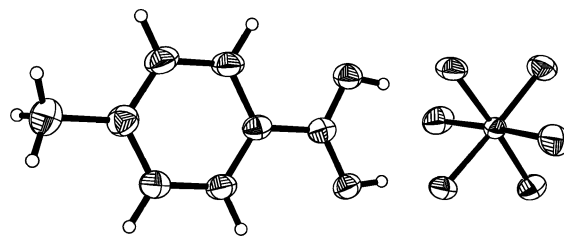
formula	$\alpha$	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
 SbF <sub>6</sub> <sup>-</sup>	6.3	1.270(3) 1.292(3)	1.448(4)	1.405(4) 1.406(4)	1.371(4) 1.389(4)	1.377(5) 1.386(5)
 AsF <sub>6</sub> <sup>-</sup>	3.2	1.279(2) 1.281(2)	1.445(2)	1.407(2) 1.397(2)	1.372(2) 1.368(2)	1.384(3) 1.391(3)
 SbF <sub>6</sub> <sup>-</sup>	5.4	1.276(2) 1.283(2)	1.446(3)	1.395(3) 1.407(3)	1.381(3) 1.374(3)	1.398(3) 1.396(3)
 AsF <sub>6</sub> <sup>-</sup> *	5.7	1.277(3) 1.282(3)	1.449(3)	1.386(3) 1.394(3)	1.379(3) 1.373(3)	1.393(3) 1.403(3)
 SbF <sub>6</sub> <sup>-</sup>	41.2	1.280(3) 1.288(3)	1.443(3)	1.419(3) 1.420(3)	1.385(4) 1.380(4)	1.383(4) 1.399(4)
 SbF <sub>6</sub> <sup>-</sup>	-	1.245(10) 1.276(8) 1.234(12) 1.315(9)	1.450(10) 1.451(11)	-	-	-
	6.9	1.232(3) 1.314(3)	1.470(3)	1.392(3) 1.393(3)	1.379(3) 1.381(3)	1.384(3) 1.399(3)

\* As a cocrystal with the parent *p*-toluic acid in entry 7.

acidium salts, especially those suited for X-ray analysis. The applicability of this procedure to acidium salts of fatty acids was also briefly examined by the isolation of the *tert*-butylacetic-acidium carbocation as the hexafluoroantimonate salt.

**X-ray Crystallography of Pure Dihydroxycarbenium Salts.** To quantitatively evaluate substituent effects on structure, the X-ray crystallographic analyses of the substituted benzoic-acidium salts were carried out at  $-150\text{ }^{\circ}\text{C}$  to a uniform precision of (esd) 0.003–0.005 Å. The low-temperature determination of the crystal structures of variously substituted benzoic-acidium salts consistently yielded the structural parameters with good precision as listed in Table 1. Typically, the ORTEP diagram of *p*-toluic-acidium hexafluoroantimonate in Figure 1 shows the symmetrical structure of the O-protonated carbocation closely paired to the counteranion at the dihydroxylated site.

In all derivatives, the trigonal carbocation center is planar; and it is generally coplanar with the benzenoid ring—the dihedral angle  $\alpha$  being merely  $\sim 5^{\circ}$ , except in



**FIGURE 1.** ORTEP diagram of *p*-toluic-acidium hexafluoroantimonate showing the  $\alpha,\alpha$ -dihydroxycarbenium moiety.

the case of mesitoic-acidium cation with  $\alpha = 41^{\circ}$  to minimize steric crowding from the pair of *o*-methyl groups.<sup>15</sup>

**Superacid Structures of Benzoic-Acidium Carbocations.** Most notable is the structure of the acidium

(15) We note that the two fluorines in the 2,6-difluoro derivative are inequivalent owing to differences in the hydrogen bonding to the counteranion, and the overall carbocation structure is asymmetric. Intramolecular hydrogen bonding is also responsible for the small dihedral angle of  $\alpha = 3\text{--}6^{\circ}$  despite the presence of two *o*-fluorines.

functionality, i.e., the cationic  $(\text{HO})_2\text{C}^+$  group, in which the carbon–oxygen bond length (identified as bond *a* in the figure for Table 1) of the two equivalent hydroxy groups lies between those of the carbonyl and the hydroxy groups of carboxylic acids in general.<sup>16</sup> It is thus instructive to consider their unique bond length ( $r_a$ ) in the context of  $\pi$ -bond order ( $n_a$ ) that is calculated according to Pauling<sup>17</sup> and listed in Table 2 (column 2).

**TABLE 2. Pauling Bond Orders for Benzoic-Acidium Carbocations**

	$n_a$	$n_b$	$\Sigma n$
2,6-difluorobenzoic-acidium/SbF <sub>6</sub> <sup>−</sup>	1.50(1)	1.01(2)	4.01(2)
2,6-difluorobenzoic-acidium/AsF <sub>6</sub> <sup>−</sup>	1.50(1)	1.02(1)	4.02(2)
4-methylbenzoic-acidium/SbF <sub>6</sub> <sup>−</sup>	1.50(1)	1.02(2)	4.02(2)
4-methylbenzoic-acidium/AsF <sub>6</sub> <sup>−</sup>	1.50(1)	1.00(2)	4.00(2)
2,4,6-trimethylbenzoic-acidium/SbF <sub>6</sub> <sup>−</sup>	1.49(1)	1.03(2)	4.00(2)

Viewed in this way, the bond order of  $n_a = 1.5$  is precisely intermediate between that of a single and double bond, and indicates that the acidium group is not to be considered a benzylic carbocation (structure **I**), but a resonance-stabilized cation (structure **II**) in which the



charge is equally delocalized between *gem*-dihydroxy groups in a manner somewhat reminiscent of  $\pi$ -electron delocalization in various allylic cations. [Based on such analysis, acidium is (strictly speaking) not a carbocation, but a quasi-oxonium cation.<sup>18</sup>] As such, there is a null in the (positive) charge density at carbon, and the electronic effects of the acidium group on the attached aromatic ring will therefore be largely inductive. In accord with this qualitative formalism, the nature of the slightly elongated C–C bond (labeled *b* in the Table 1) is expected to be relatively unaffected by changes in the substituents on the aromatic ring, as shown by the invariant values of  $n_b \sim 1.0$  in Table 2 (column 3).<sup>19</sup> Furthermore, the same applies to the rather minor quinonoidal distortion<sup>20</sup> experienced in the benzenoid ring despite strong pertur-

(16) For example, in the X-ray structure of *p*-toluic acid (present as a cocrystal with the *p*-toluic acidium hexafluoroarsenate)  $r_a = 1.31$  and  $1.23$  Å for the carbonyl and hydroxy groups. Search through the CSD database yields an average of  $1.30$  and  $1.23$  Å, respectively.

(17) Pauling, L. *Nature of Chemical Bond*; Cornell: Ithaca, NY, 1960; p 239. (b) According to Pauling, the bond order ( $n_i$ ) is related to the bond distance  $r_i$  by the relationship:  $n_i = \exp[2.303(r_1 - r_i)/K]$ , where  $r_1$  is the single-bond distance,  $r_i$  is the observed distance, and  $K$  is an empirical constant. For the hydroxy bond,  $r_1 = 1.43$  Å and  $K = 0.85$  Å. For the bond to alkyl  $r_1 = 1.48$  Å ( $K = 0.50$  Å) and to aryl  $r_1 = 1.45$  Å ( $K = 0.50$  Å), which includes the correction for the change in covalent radius with hybridization (see, e.g., Hubig, S. M.; Lindeman, S. V.; Kochi, J. K. *Coord. Chem. Rev.* **2000**, *200*, 831). The calculated bond orders are presented in the Table 2 with the esds in parentheses.

(18) It is noteworthy that the length of the C–O bond (*a*) in the acidium cation is essentially the same as those in dialkoxyphenylcarbenium cations (see: Childs, R. F.; Frampton, C. S.; Kang, G. J.; Wark, T. A. *J. Am. Chem. Soc.* **1994**, *116*, 8499).

(19) A wider range of substituents such as *p*-MeO with a more extended value of  $\sigma^+$  is desirable to establish this point. Unfortunately, we have been unable as yet to isolate these crystalline acidium salts (suitable for X-ray crystallography) due to the exceedingly delicate balance between hydration of the acylium cation and the further hydrolysis of the acidium salt.

bations arising from the presence of a powerful electro-positive (acidium) center.<sup>21</sup>

All of these factors lead to the conclusion that the superacid properties of various benzoic-acidium salts are expected to be minimally affected by aromatic substituents.<sup>22,23</sup>

## Experimental Section

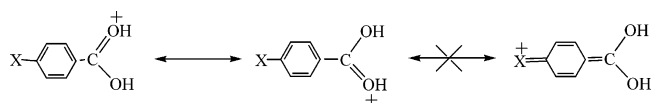
**Materials.** The acyl halides—acetyl chloride, acetyl fluoride, propionyl chloride, *p*-toluyl chloride, *p*-anisoyl chloride, and *p*-fluorobenzoyl chloride were commercial samples. 2,4,6-Mesityl chloride and pentamethylbenzoyl chloride were prepared from the corresponding carboxylic acids by the treatment with oxalyl chloride. SbCl<sub>5</sub>, SbF<sub>5</sub>, and AgSbF<sub>6</sub> were used without additional purification. Dichloromethane, benzene and hexane were purified according to published procedures. 1,1,2-Trifluoroethane (“Freon 113”) was used without additional purification. The oxocarbenium salts were prepared using literature method involving two general synthetic procedures described in eqs 1 and 2. The first method was used for acyl and aryl halides with either X = F and PF<sub>5</sub>, BF<sub>3</sub>, SbF<sub>5</sub>, AsF<sub>5</sub> or for X = Cl and AlCl<sub>3</sub>, GaCl<sub>3</sub>, SbCl<sub>5</sub>; and the second method was used for acyl and aryl chlorides and silver(I) PF<sub>6</sub><sup>−</sup>, BF<sub>4</sub><sup>−</sup>, SbF<sub>6</sub><sup>−</sup>, AsF<sub>6</sub><sup>−</sup>. It is important to emphasize that the target acylium salts are *extremely* sensitive to air. The acid halides were always freshly distilled, and anhydrous silver salts were carefully dried in vacuo (including cautious heating).

**X-ray Crystallography.** The intensity data for all the compounds were collected at  $-150$  °C on a X-ray diffractometer with a CCD detector using MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). In all cases, a semiempirical absorption correction was applied using SADABS program.<sup>24</sup> The structures were solved by direct

(20) (a) Such a minor quinonoidal distortion is shown by the shortening of the endocyclic *d* bond ( $1.378$  Å) as compared with the *c* bond ( $1.405$  Å) and the *e* bond ( $1.408$  Å) in Table 1. (b) For discussion of this type of quinonoidal distortion in other aromatic cations, see: Lindeman, S. V.; Rosokha, S. V.; Sun, D.; Kochi, J. K. *J. Am. Chem. Soc.* **2002**, *124*, 843. Rathore, R.; Lindeman, S. V.; Kumar, A. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 6012. Le Magueres, P.; Lindeman, S. V.; Kochi, J. K. *Organometallics* **2001**, *20*, 115. For the major quinonoidal distortions in benzylic cations, see: Laube, T.; Olah, G. A.; Bau, R. *J. Am. Chem. Soc.* **1997**, *119*, 3087.

(21) Electronic isolation between the acidium and aryl group is also indicated by the structural parameters in the skewed structure of mesitoic-acidium carbocation (which has dihedral angle of  $\alpha = 41^\circ$ ) relative to those in planar acidium structures with  $\alpha \sim 5^\circ$  in Table 2.

(22) This conclusion is contrary to that derived from the more conventional (physical-organic) analysis based on  $\sigma^+$  parameters. For example, the substituent effect on the carbocationic form of the acidium ion (structure **I**) is expected to be related to substituent effect on substituted cumyl cations, i.e., those used by Brown and co-workers to develop the  $\sigma^+$  substituent parameter (see: Lowry, T. H.; Richardson, K. S. *Mechanisms and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981; p 134.) However, our X-ray studies rule out this structure in favor of the dioxonium form (structure **II**) as the resonance hybrid



in which the cationic acidium functionality is largely *isolated* from the aromatic ring and thus insensitive to changes in substituents. By contrast, structure **I** is related to the cumyl cation and will be strongly affected by *p*-substituents, e.g.



Compare also: Kochi, J. K.; Hammond, G. S. *J. Am. Chem. Soc.* **1953**, *75*, 3445, 3452.

(23) Davlieva, M. G.; Lindeman, S. V.; Neretin, I. S.; Kochi, J. K. *New J. Chem.* **2004**, *28*, 1568.

methods and refined by full matrix least-squares procedure using SHELXTL suite of programs.<sup>25</sup> The details of the X-ray structure determination of the various acidium salts listed in Table 1 are on deposit (as CCDC 257622–257627) and can be obtained from the Cambridge Crystallographic Data Centre, Cambridge, U.K.

**Acknowledgment.** We thank Dr. G. K. Surya Prakash for helpful discussions on superacidity and the R. A. Welch Foundation for financial support.

**Supporting Information Available:** X-ray crystallographic data (CIF) for compounds in Table 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(24) Sheldrick, G. M. *SADABS v. 2.03, Bruker/Siemens Area Detector Absorption and Other Corrections*; Bruker Analytical X-ray Systems, Madison, WI, 2000.

(25) Sheldrick, G. M. *SHELXTL v. 6.12, Program Library for Structure Solution and Molecular Graphics*; Bruker Analytical X-ray Systems: Madison, WI, 2000.