

**Figure 4.** The low-energy structures of the *L,R* (A) and *L,S* (B) isomers as formulated by NMR studies and computer simulations.<sup>1</sup> There is close agreement between these structures and those from X-ray shown in Figure 1.

**Table IV.** Backbone Torsion Angles from X-ray Crystallographic Analysis and Conformation Studies<sup>a</sup>

torsion angle	crystal structure		structure in solution	
	<i>L,R</i>	<i>L,S</i>	<i>L,R</i>	<i>L,S</i>
$\psi$	172.0 (5)	166.4 (7)	118	123
$\omega$	-175.4 (5)	177.5 (6)	179	180
$\phi$	104.4 (5)	-99.7 (6)	8	21
$\phi'$	-97.3 (6)	104.8 (6)	88	81
$\omega$	166.8 (5)	-169.4 (5)	179	176
$\psi'$	-100.4 (6)	92.8 (6)	116	131

<sup>a</sup> Values in degrees. The estimated standard deviation of the least significant figure is given in parenthesis for the torsions of the X-ray structure.

The conformations of the *L,R* and *L,S* isomers determined from NMR and computer simulations are shown in Figure 4. A comparison of the torsions of the isomers in solution and in the solid state is given in Table IV. The differences observed in the torsions arise from the packing forces present within the crystal. A comparison of the isomers in Figures 1 and 4 indicates a dif-

ference in the orientation of the amide NH's; an anti array in solution and a syn array in the solid state. In the crystal structure the  $\phi$  and  $\phi'$  torsions arise from the complementarity of structures within the unit cell. In solution without the formation of the intermolecular hydrogen-bonding pattern this complementarity of conformations is not retained and the  $\phi$  and  $\phi'$  torsions are very similar for the two diastereomers.

Despite these minor differences in the conformations found in solution and solid state, largely derived from forces within the crystal, the overall topologies of the isomers are quite similar. The *L,R* diastereomer adopts the "L shape" both in the crystal structure and in solution. The "reverse L" found for the *L,S* diastereomer in the crystal can be converted to the "L shape" simply by a 180° rotation about  $\phi$  (Figure 1) which accounts for the preferred structure in solution.

The results found from the three techniques used in the conformational analysis of the two diastereomers, X-ray crystallography, NMR, and computer simulations, provide strong support for the value of the unified approach employed in the study of structure-taste relationships. The solid-state structures reported here only require facile rotations about one or two of the backbone torsions to obtain the structures found in solution which explains the fact that both diastereomers are sweet.

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**Supplementary Material Available:** Tables of positional parameters and their estimated standard deviations, refined displacement parameter expression, general displacement parameter expressions, root-mean-square amplitudes of thermal vibrations, bond distances and angles and torsion angles (12 pages); listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

## The Structure of Cyclopropylcarbinylium Cations: The Crystal Structures of Protonated Cyclopropyl Ketones<sup>1</sup>

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**Abstract:** The structures of 1-cyclopropyl-1-hydroxyethylium hexafluoroantimonate, **9**, 1-(1'-methylcyclopropyl)-1-hydroxyethylium hexafluoroantimonate, **10**, and 2-hydroxybicyclo[4.1.0]heptan-2-ylium hexachloroantimonate, **11**, have been determined by single-crystal X-ray diffraction methods. The structures of these cations show major differences in their bond distances as compared to those of the neutral cyclopropyl ketones with the distal bonds in the cyclopropyl ring being shortened, the vicinal bonds lengthened, and the C(=O)—C(apex) bonds shortened. The cations adopt a conformation which is either bisected (**9**) or close to this (**10**, **11**). The bond distances and conformation of these ions are fully consistent with those expected for a bisected cyclopropylcarbinylium cation. Comparison of the structures of these cations with those of other protonated cyclopropyl ketones reveals systematic changes in bond distances that can be related to the degree of charge delocalization into the cyclopropyl ring. Details of the structures of these cations and their crystal packing are discussed.

The cyclopropylcarbinylium cation is one of a series of closely related isomeric  $C_4H_7^+$  cations.<sup>2</sup> Entry into this series can be

(1) This work was supported by the Natural Science and Engineering Research Council of Canada and IBM Canada Ltd. under a cooperative agreement with McMaster University. Technical assistance of Mr. R. Fagiani is gratefully acknowledged.

(2) For reviews, see: Tidwell, T. *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley-Interscience: New York, 1987; Chapter 10. Friedrich, E. C. *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley-Interscience: New York, 1987; Chapter 11. Brown, H. C. (with comments by Schleyer, P. v. R.) *The Nonclassical Ion Problem*; Plenum: New York, 1977; Chapter 5. Richey, G. *Carbonium Ions* **1972**, *111*, 1201-1294. Wiberg, K. B.; Hess, B. A.; Ashe, A. J. *Carbonium Ions* **1972**, *3*, 1295-1345. Bartlett, P. D. *Nonclassical Ions*; W. A. Benjamin Inc.: New York, 1965.

achieved by ionization of cyclopropylcarbinylium, cyclobutyl, or homoallyl derivatives. In the parent system the product distributions arising from ionization of each of these different materials are remarkably similar suggesting the existence of common intermediates.

A long standing and continuing question is that pertaining to the structure of the  $C_4H_7^+$  cation(s). This has been investigated by a large variety of methods including isotopic tracer experiments,<sup>3</sup> solvolytic studies,<sup>4</sup> detailed NMR studies on solutions of

(3) Roberts, J. D.; Mazur, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 3542-3543. Mazur, R. H.; White, W. N.; Semenov, D. A.; Lee, C. C.; Silver, M. S.; Roberts, J. D. *J. Am. Chem. Soc.* **1959**, *81*, 4390-4398.

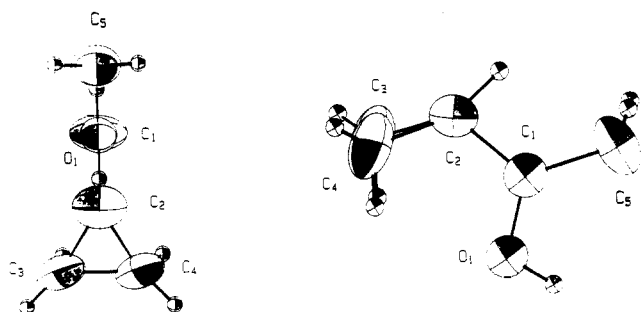
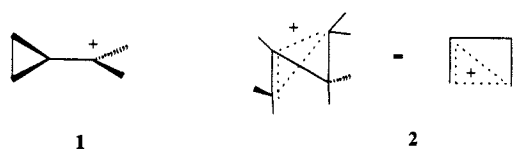


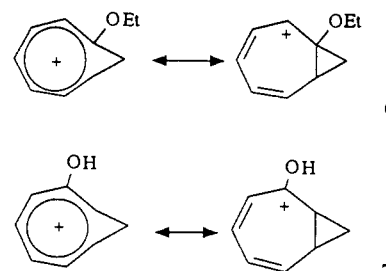
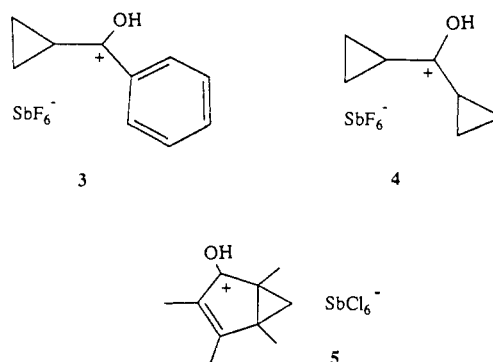
Figure 1. Structure of 9.

the stable ions,<sup>5</sup> and theoretical calculations.<sup>6</sup> The conclusions reached from this work are that the bisected cyclopropylcarbinyl ion **1** and the bicyclobutonium cation **2** are both energy minima on the potential energy surface, with the most recent calculations showing that **1** and **2** are almost isoenergetic.<sup>6a,b</sup> NMR studies of the ion in condensed phases indicate that **1** and **2** are in dynamic equilibrium, with the energy barrier to their interconversion being less than 2 kcal/mol.<sup>5</sup>

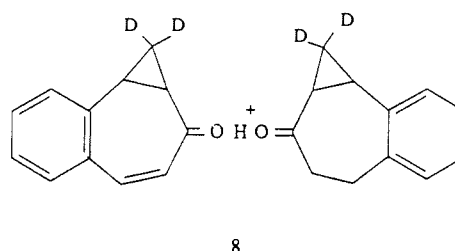


The relative stabilities of the various  $C_4H_7^+$  isomers can be changed by substitution. Thus the cyclopropylcarbinyl form can be stabilized by placing electron-donating substituents at the carbinyl carbon atom. For example, two methyl groups or a hydroxy substituent at this carbon atom is quite sufficient to make the cyclopropylcarbinyl form the only one which can be detected in solutions of the ion in superacid media.<sup>7</sup>

In order to provide direct structural information on the cyclopropylcarbinyl cations and related systems we have embarked on a program to determine the structures of these types of ions with the use of X-ray crystallography. We have already described the structures of **3** and **4**<sup>8</sup> and the related systems **5**,<sup>9</sup> **6**,<sup>10</sup> **7**,<sup>11</sup> and

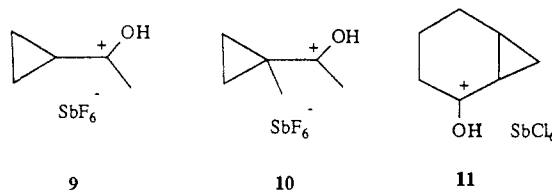


**8**,<sup>12</sup> While the last four ions represent special cases, in which the cyclopropylcarbinyl cation is incorporated into an unsaturated ring and questions of cyclic delocalization are raised, both **5** and **8** appear to have a cyclopropylcarbinyl-like structure. Each of the cations **3**–**8** is relatively stable with, apart from **6**, a hydroxy function and a second charge stabilizing substituent at the carbinyl carbon. The structures of two cyclopropyl-substituted cyclopropenium cations have also been reported.<sup>13</sup>



8

In this paper we describe the structure determination of three less stable, protonated cyclopropyl ketones, **9**, **10**, **11**, each of which has an alkyl substituent on the carbinyl carbon. Cations **10** and **11** were selected for study so that the structural effect of further alkyl substitution on the cyclopropane might be examined and compared to the established reactivity patterns exhibited in the solvolysis of cyclopropylcarbinyl derivatives.<sup>4b</sup> Salt **11** has the additional constraint of the six-membered ring which restricts the conformational mobility of the system and could prevent the adoption of a fully bisected conformation.<sup>14</sup>



9

10

11

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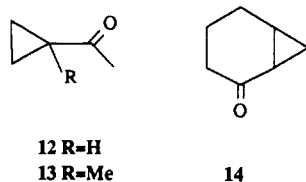
(14) The importance of a bisected conformation is well exemplified with the cyclopropyl-substituted adamantyl systems. Schleyer, P. v. R.; Buss, V. *J. Am. Chem. Soc.* **1969**, *91*, 5880–5882. Martin, J. C.; Ree, B. R. *J. Am. Chem. Soc.* **1969**, *91*, 5882–5883.

**Table I.** Selected Interatomic Distances (Å) and Angles (deg)

bond distance	compound			angle	compound		
	9	10	11		9	10	11
C(1)–O	1.256 (8)	1.268 (8)	1.293 (8)	C(2)–C(1)–C(5)	122.6 (6)	124.6 (6)	124.5 (7)
C(1)–C(2)	1.405 (10)	1.461 (9)	1.403 (10)	O–C(1)–C(2)	116.5 (6)	115.0 (6)	114.7 (7)
C(2)–C(3)	1.516 (8)	1.529 (9)	1.534 (11)	O–C(1)–C(5)	120.9 (7)	120.4 (7)	120.7 (6)
C(2)–C(4)	1.516 (8)	1.545 (8)	1.559 (12)	C(1)–C(2)–C(3)	118.8 (5)	116.0 (6)	116.4 (7)
C(3)–C(4)	1.418 (12)	1.448 (9)	1.433 (13)	C(1)–C(2)–C(4)	118.8 (5)	113.8 (6)	119.8 (7)
C(1)–C(5)	1.482 (9)	1.461 (10)	1.461 (19)	C(3)–C(2)–C(4)	55.8 (3)	56.2 (4)	55.2 (6)
C(2)–C(6)		1.491 (10)		C(2)–C(3)–C(4)	62.1 (4)	62.5 (4)	63.3 (6)
C(5)–C(6)			1.534 (11)	C(2)–C(4)–C(3)	62.1 (4)	61.3 (4)	61.6 (6)
C(6)–C(7)			1.540 (11)	C(2)–C(3)–C(7)			116.6 (7)
C(3)–C(7)			1.502 (11)	C(3)–C(7)–C(6)		117.7 (6)	112.7 (7)
				C(7)–C(6)–C(5)			112.0 (6)
				C(6)–C(5)–C(1)			116.0 (8)
				C(4)–C(3)–C(7)			120.5 (7)
				C(1)–C(2)–C(6)		119.7 (7)	
				C(3)–C(2)–C(6)		119.0 (6)	
				C(4)–C(2)–C(6)			
Anions (9 and 10, X = F; 11, X = Cl)							
Sb–X(1)	1.848 (4)	1.916 (4)	2.356 (2)	X(1)–Sb–X(2)	92.7 (2)	88.7 (2)	89.7 (1)
Sb–X(2)	1.841 (4)	1.858 (4)	2.402 (2)	X(1)–Sb–X(3)	88.9 (2)	84.4 (2)	177.9 (1)
Sb–X(3)	1.856 (5)	1.871 (4)	2.370 (2)	X(1)–Sb–X(4)	89.6 (2)	88.5 (2)	90.4 (1)
Sb–X(4)	1.837 (5)	1.872 (4)	2.351 (2)	X(1)–Sb–X(5)		179.6 (1)	90.1 (1)
Sb–X(5)		1.856 (4)	2.368 (2)	X(1)–Sb–X(6)		87.8 (2)	91.6 (1)
Sb–X(6)		1.861 (4)	2.341 (2)	X(2)–Sb–X(3)	90.5 (2)	89.7 (2)	88.3 (1)
				X(2)–Sb–X(4)	90.9 (2)	89.8 (2)	89.6 (1)
				X(2)–Sb–X(5)		91.0 (2)	88.0 (1)
				X(2)–Sb–X(6)		176.5 (2)	177.7 (1)
				X(3)–Sb–X(4)	178.0 (3)	90.1 (2)	90.2 (1)
				X(3)–Sb–X(5)		91.8 (2)	89.3 (1)
				X(3)–Sb–X(6)		89.9 (2)	90.4 (1)
				X(4)–Sb–X(5)		91.3 (2)	177.5 (1)
				X(4)–Sb–X(6)		90.5 (2)	92.3 (1)
				X(5)–Sb–X(6)		92.5 (3)	90.1 (1)

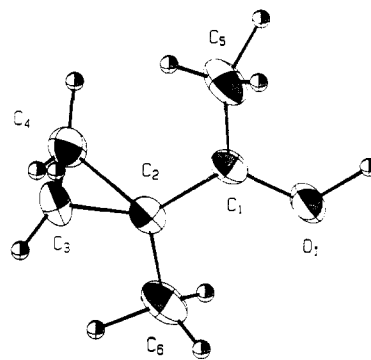
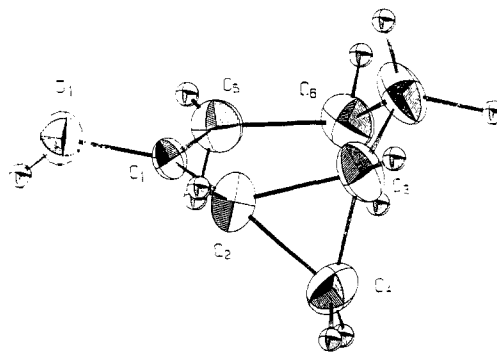
**Results**

The cations **9** and **10** were prepared as their hexafluoroantimonate salts by treatment of  $\text{CH}_2\text{Cl}_2$  solutions of the corresponding ketones, **12** and **13**, with  $\text{HF}/\text{SbF}_5$  at  $-78^\circ\text{C}$ . Reaction of **14** with  $\text{HCl}/\text{SbCl}_5$  in  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ\text{C}$  gave **11** as its hexachloroantimonate salt. The precipitated solids in these reactions were recrystallized from  $\text{CH}_2\text{Cl}_2$  to give single crystals suitable for X-ray crystallography. The salts were moisture sensitive and relatively thermally unstable undergoing facile isomerizations when kept at room or higher temperatures.<sup>15</sup> The occurrence of these facile rearrangements has thus far limited the extension of our studies to other related cyclopropylcarbinyl cations.



The crystalline salts were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. Solutions of **9** and **10** in  $\text{CD}_2\text{Cl}_2$  exhibited almost identical NMR spectra to those previously reported for the corresponding protonated ketones in strong acid media.<sup>7a,16,17</sup> The spectra of **11** were fully consistent with the assigned structure.

The structures of **9**, **10**, and **11** were determined by use of X-ray diffraction at low temperatures. The structures are shown in

**Figure 2.** Structure of **10**.**Figure 3.** Structure of **11**.

(15) These salts rearrange to give substituted 2*H*-3,4-dihydrofuranium cations: Burke, N. A. D.; Childs, R. F. Third North American Chemical Congress, Toronto, Canada, June 1988, Abstract No. ORGN-E-426. Pittman, C. U., Jr.; McManus, S. P. *J. Am. Chem. Soc.* **1969**, *91*, 5915–5918. Ward, H. R.; Sherman, P. D., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 3812–3817.

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Figures 1–3, selected interatomic distances and angles are given in Table I, and the crystal packing is shown in Figures 4–6. Full information is given in the tables in the supplementary material associated with this paper. In the case of **9** it was not possible to locate the third hydrogen atom of the methyl group, and the position of the hydrogen atom on C(2) is somewhat anomalous.

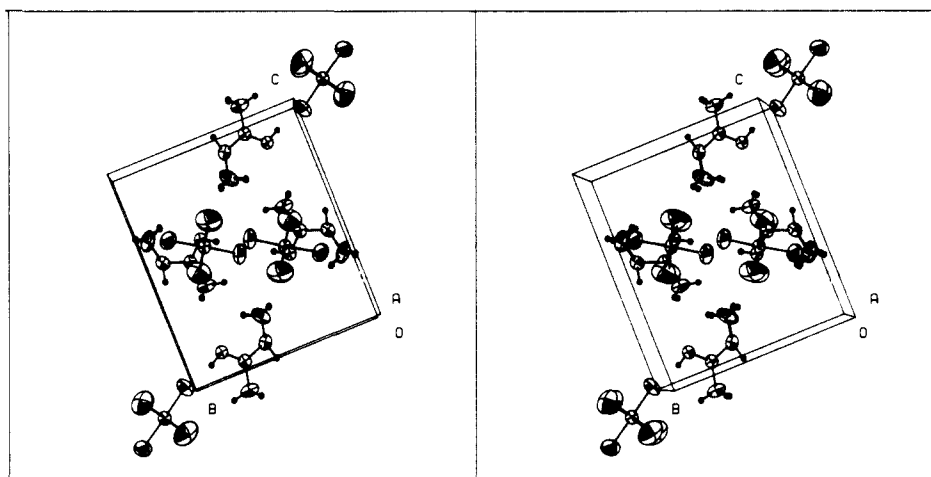


Figure 4. Crystal packing of 9.

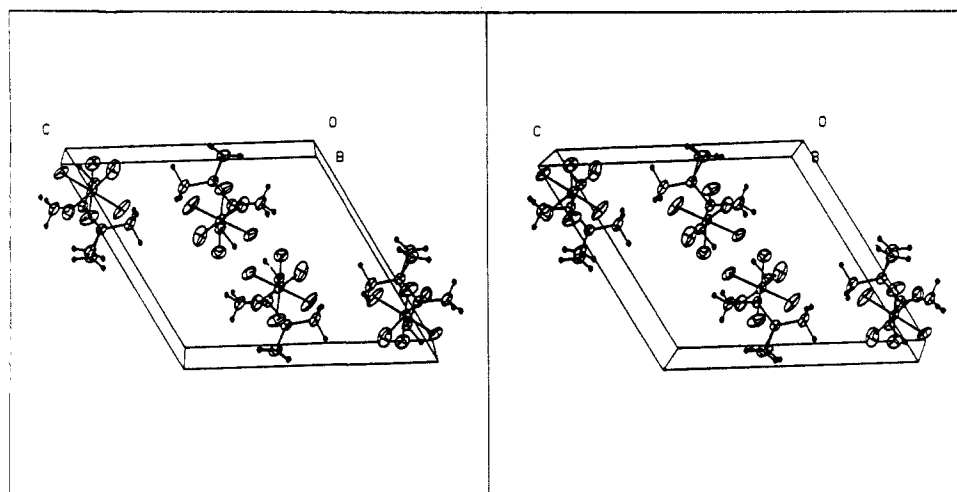


Figure 5. Crystal packing of 10.

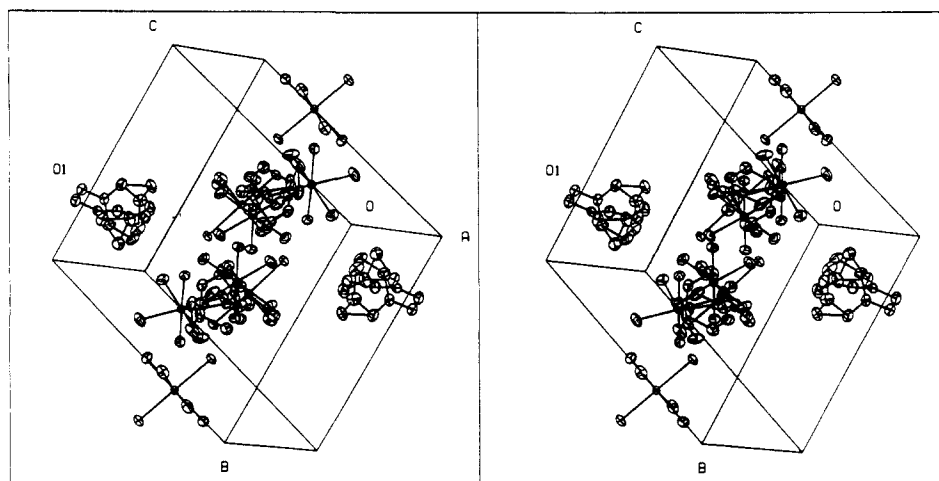


Figure 6. Crystal packing of 11.

All of the hydrogen atoms were found in 10 and 11.

#### Discussion

The structures of 9–11 are fully consistent with that expected for cyclopropylcarbiny! cations. Thus each of the cations has a conformation which is either bisected or close to bisected, bond distances which are far removed from those of a conventional cyclopropyl ketone, and a configuration about the carbonyl group that indicates the presence of an  $sp^2$  hybridized oxygen. While the structures obtained show similar trends to those previously described for 3 and 4, the structural changes described here resulting from oxygen protonation of the cyclopropyl ketones 12,

13, and 14 are much more pronounced.

**Cyclopropane Bond Distances.** The bond distances in the cyclopropane rings of 9 are remarkable in terms of the extent to which the ring is distorted from a symmetrical structure. Cation 9 exhibits the largest distortions of any of the cyclopropylcarbiny! cations or indeed, to the best of our knowledge, any cyclopropyl compound whose structure has yet been determined.<sup>18,19</sup> It is worth noting that the C(3)–C(4) (distal) bond length (1.418 (12)

(18) Allen, F. H. *Acta Crystallogr.* **1980**, *B36*, 81–96; **1981**, *B37*, 890–900.

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**Table II.** Summary of Bond Distances of Cations

compd	bond (Å)			torsion angle <sup>a</sup>
	av cyclopropyl	distal	C(1)-C(2)	
<b>9</b>	1.483	1.418 (12)	1.405 (10)	0.0
<b>10</b>	1.507	1.448 (9)	1.461 (9)	-173.5
<b>11</b>	1.509	1.433 (13)	1.403 (10)	176.3
<b>3</b>	1.506	1.448 (4)	1.417 (8)	-7.0
<b>4</b>	1.509	1.468 (3)	1.430 (2)	180.0
<b>5</b>	1.52	1.501 (8)	1.474 (7)	0.0
<b>8</b>	1.51	1.471 (9)	1.439 (10)	
neutral	1.504	1.478	1.474	

<sup>a</sup>Torsion angle O-C(1)-C(2)-(midpoint C(3)-C(4)).

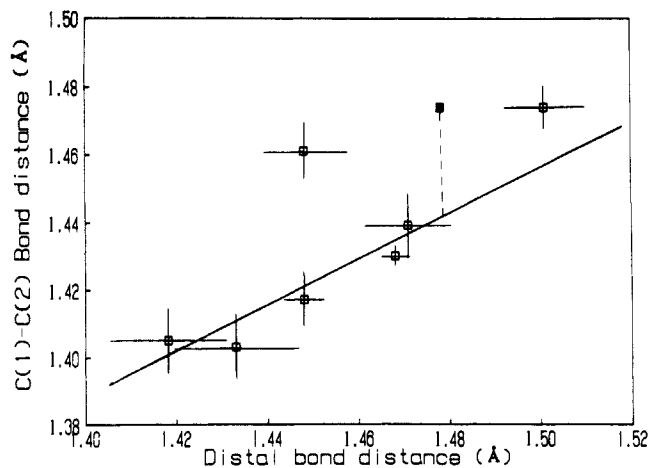
Å) is the same within experimental error as that of benzene. This means that the distal bond in **9** has an order which approaches 1.5!

One purpose in preparing this series of ions was to probe the effect of substituents on the cyclopropyl ring. An  $\alpha$ -methyl group has been shown to have a small stabilizing effect on a cyclopropylcarbiny cation,<sup>4b,20</sup> and, on the basis of NMR evidence, it would appear that charge delocalization into the three-membered ring is enhanced by the introduction of this group.<sup>17</sup> In terms of structure, as can be seen from the data in Table I, the introduction of a methyl group onto C(2), **10** as compared to **9**, makes no significant difference in the lengths of the C(2)-C(3) or C(2)-(4) bonds (differences 1.1 and 2.6 $\sigma$ , respectively, where  $\sigma = \sqrt{(\sigma_1^2 + \sigma_2^2)}$ ). On the other hand, the C(1)-C(2) bond in **10** is significantly lengthened as compared to the comparable bond in **9** (difference 4.2 $\sigma$ ). It is interesting that the calculations reported by Sorensen on methyl-substituted cyclopropylcarbiny cations suggest that the presence of an  $\alpha$ -methyl will cause an elongation of both the vicinal and C(1)-C(2) bonds of **10** as compared to **9**.<sup>6e,21</sup> It may well be that with further structures of cyclopropylcarbiny cations a difference in the vicinal bond lengths as a function of an  $\alpha$ -substituent may be observed; however, on the basis of this work the effect will likely be small.

The bicyclic cation **11** with an alkyl substituent at C(3), one of the  $\beta$ -ring carbons of the cyclopropane, would have been expected to show a marked elongation of the C(2)-(3) as compared to the C(2)-(4) vicinal bond.<sup>6e</sup> However, within the error limits of the structure determination there is no difference in the lengths of the two vicinal cyclopropane bonds (difference 1.5 $\sigma$ ). Overall, the cyclopropane bond distances in **11** are very similar to those of **9** with the short distal bond length (C(3)-C(4)) being particularly noticeable.

It is instructive to compare the cyclopropyl bond distances found here for **9-11** with those previously reported for **3-5** and **8**, Table II. As can be seen from these data, the degree of distortion of the three-membered ring in these cations away from a symmetrical structure varies considerably. However, in each case the average cyclopropyl bond distance in each of the cations **3-5** and **8-11** is approximately the same as is found for cyclopropane, Table II.<sup>18,19</sup> This means that the lengthening of the vicinal bonds is on average half the contraction of the distal bond. A similar coupling of the vicinal and distal bond distances has been noted for cyclopropylketones.<sup>18</sup> The average cyclopropyl carbon-carbon bond distances in the tricyclopropyl- and dicyclopropylphenyl-cyclopropenium cations were also found to be the same as that of a neutral cyclopropane.<sup>13</sup>

Associated with these changes in the cyclopropyl ring bond distances is a marked contraction of the C(1)-C(2) bond of all these protonated cyclopropyl ketones as compared to the neutral



**Figure 7.** Correlation between C(1)-C(2) and C(3)-C(4) bond distances. The position of a neutral cyclopropyl ketone is indicated by (■).

ketones, Table II. The average C(=O)-C(cyclopropane) bond distance of a cyclopropyl ketone in a bisected conformation is 1.474 (4) Å.<sup>18</sup> In **9** and **11** this distance is 1.405 (10) and 1.403 (10) Å, respectively, values which are significantly smaller than the corresponding bond of the neutral ketone (differences 6.3 and 6.5 $\sigma$ , respectively).

The bond distance changes observed in the cyclopropane rings of these cations are linked to the changes occurring in the C(1)-C(2) bond distance. This is shown in Figure 7 where the C(1)-C(2) and C(3)-C(4) bond distances for cyclopropylcarbiny cations **3-5** and **8-11** are correlated. It is clear that apart from two exceptions there is a good linear relationship between these two bond distances.

The two exceptions to the correlation shown in Figure 7 are **10** and **5**. These differ from the rest of the cations by having a methyl substituent at C(2) (or its equivalent position in **5**) and as such might not be expected to fall on the same line as the other systems which lack this methyl group.<sup>22</sup> It has been suggested that the unusually long C(1)-C(2) bond in **5** is caused by an unfavorable cyclic 4 $\pi$  electron configuration,<sup>9</sup> however, this looks unlikely given that a comparable elongation of the C(1)-C(2) bond also occurs in **10**.

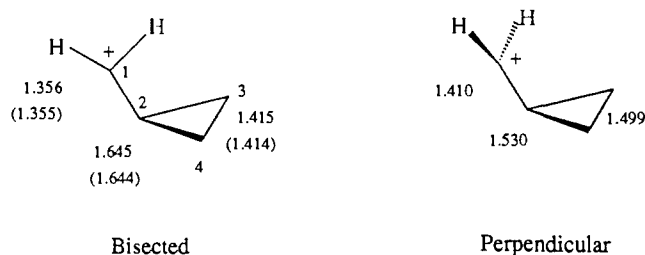
One way of viewing the correlation shown in Figure 7 is that the systematic geometry changes in the cyclopropane ring and the C(1)-C(2) bond reflect the degree of involvement of the cyclopropane in electron delocalization; the greater the degree of delocalization, the greater the distortion. The variable in these systems is the second substituent on the carbonyl carbon of the protonated ketone.<sup>23</sup> The better this group is at stabilizing a positive charge, the less the call on the cyclopropane to become involved and, consequently, the less the geometric distortion. Understood in these terms the correlation shown in Figure 7 represents a means whereby the charge stabilizing ability of the second substituent on the carbonyl group of these protonated cyclopropyl ketones can be gauged and related to other thermodynamic or kinetic measures of substituent effects. Because of the relatively large errors associated with the measurement of bond distances, the precision of this structural approach is lower than that normally associated with a linear free energy relationship generated under more conventional conditions. However, a qualitative examination of the order of the substituents shown in Figure 7 leads to the conclusion that methyl (**9**) is a poorer charge stabilizing group than phenyl (**3**) which is itself poorer than cyclopropyl (**4**). The relative order of these groups in terms of their charge stabilizing ability has been the subject of a consid-

(20) Kushner, A. S. Ph.D. Dissertation, The Pennsylvania State University, University Park, PA., 1966. Data quoted in ref 16.

(21) The structure of the  $\alpha$ -methylcyclopropylcarbiny cation has been the matter of some debate. See: Saunders, M.; Rosenfeld, J. *J. Am. Chem. Soc.* **1970**, *92*, 2548-2549. Olah, G. A.; Jeuell, C. L.; Kelly, D. P.; Porter, R. D. *J. Am. Chem. Soc.* **1972**, *94*, 146-156. Olah, G. A.; Prakash, G. K. S.; Donovan, D. J.; Yavari, I. *J. Am. Chem. Soc.* **1978**, *100*, 7085-7086. Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1977**, *99*, 6687-6693. Siehl, H.-U. *J. Am. Chem. Soc.* **1985**, *107*, 3390-3392, and ref 17.

(22) A similar effect elongation of a C-C bond is seen with both alkanes and alkenes, ref 19.

(23) A further variable in these structures is the extent to which H-bonding which occurs of the OH proton and the consequent variation in the amount of charge induced on the carbonyl carbon. This is particularly important in the case of **8** where the system exists as a dimeric cation. This point has been discussed in ref 24.



**Figure 8.** Calculated bond distances (Å) of bisected and perpendicular cyclopropylcarbiny cation: numbers without parentheses (ref 6a) and numbers in parentheses (ref 6b).

erable amount of controversy,<sup>16a,25</sup> and it would appear that no simple order exists.<sup>26</sup> The order found here is one that has commonly been found by other techniques including thermodynamic measurements in the gas phase.<sup>27</sup>

The important conclusion to be drawn from Figure 7 is the existence of a systematic change in the geometry of a cyclopropane conjugated to a positive center that depends on the electron demand of the cationic carbon. This result can be considered to be the structural counterpart to the concept of increasing neighboring group participation, advanced by Gassman and Fentiman and later formalized as the "tool of increasing electron demand".<sup>28</sup> It is interesting to note that the magnitude of the structural changes observed with these cations, as a function of substituent, are much larger than are normally encountered with neutral molecules. Indeed Topsom in a recent review has argued that substituent-induced structural changes in neutral molecules are generally very small and difficult to detect.<sup>29</sup>

There are two factors contributing to the contraction of the C(1)–C(2) bond in these cations; the enhanced conjugation between the cationic site and the cyclopropane discussed above and the shortening that will result from the presence of a positive charge on C(1). It would be attractive to be able to separate these two factors and determine their relative magnitudes. One way this could be done is by comparing the C(1)–C(2) distance of one of these bisected protonated cyclopropyl ketones with a similarly substituted system which is held in a perpendicular conformation. In the latter case conjugative effects would be eliminated, and the contraction observed would be caused solely by the charge effect. Allen has used a similar approach to analyze conjugative and hybridization effects in his comparison of the relative conjugative abilities of vinyl and cyclopropyl groups.<sup>30</sup>

No structures of perpendicular cyclopropylcarbiny cations with hydroxy substituents have yet been determined, and this approach cannot be used with the systems studied here. However, it can be used for the parent system by using the calculated structures of the cyclopropylcarbiny cation in bisected and perpendicular conformations, Figure 8, and comparing the C(1)–C(2) bond distances of these systems with that of the comparable bond in vinylcyclopropane (1.470 (6) Å).<sup>30</sup> As can be seen, the shortening of the C(1)–C(2) bond in the parent cation which can be attributed to charge effect is the dominant component.

In principle an alternative method for estimating the magnitude of the charge-induced contraction expected in the C(1)–C(2) bond in these systems is through the correlation shown in Figure 7 and placing on it a point corresponding to a neutral cyclopropyl ketone (marked as ■ in Figure 7). The charge effect will have its major

impact on the C(1)–C(2) bond but comparatively little effect on the more remote distal bond C(3)–C(4). Conjugation of the cyclopropyl group with the charged center on C(1) will affect both bonds. As such the vertical discrepancy between the position of the neutral cyclopropyl ketone and the line linking the cationic systems will largely reflect the charge-induced contraction of the C(1)–C(2) bond.

A similar charge-induced contraction of the C(1)–C(5) bonds would also be expected in these protonated systems when compared to those bonds in a neutral ketone (1.511 (15) Å).<sup>19</sup> However, the differences observed in these bonds in **9–11** and the model ketone are less than  $3\sigma$  in each case and are not significant. The C(1)–C(5) bond distances in **9** and **10** are the same within experimental error to that calculated for the C–C bond in O-protonated acetaldehyde (1.466 Å).<sup>31</sup>

It is informative to compare the structure of **9**, the simplest cyclopropylcarbiny cation described here, with the results of the best theoretical calculations on the parent system, Figure 8.<sup>6a,b</sup> It is immediately apparent that there are some considerable discrepancies between the two results. It is not unexpected that the replacement of the hydrogens at C(1) with a hydroxy and methyl substituents would result in an elongation of this bond. For example, this effect of methyl substituents on the C(1)–C(2) bond of the cyclopropylcarbiny cation has been seen in calculations on substituted systems.<sup>6c,d,20</sup> However, the lengths of the vicinal bonds in **9** are considerably shorter than those estimated for the parent cation despite there being a reasonable correspondence in the distal bond lengths. It is clear that the average cyclopropyl bond distance in the calculated structures of the parent cation is substantially different from the normal cyclopropane bond distance and that the type of correlation shown in Figure 7 would not seem to apply. Further structures of less highly substituted cyclopropylcarbiny cations are needed in order to link the structures of the hydroxy-substituted systems studied here with that of the parent cation.

**Conformation.** As is fully evident from inspection of the projection shown in Figure 1, **9** has adopted a fully bisected geometry. The angle between the plane defined by the cyclopropyl group and carbonyl plane is 90.0 (4)°. Compound **10** also has a 90° angle between the carbonyl and cyclopropyl planes (Table III), but this cation is not completely bisected. For **10** to be completely bisected the torsion angle  $\tau$ , defined as O–C(1)–C(2)–(midpoint of C(3)–C(4) bond), will be 0 or  $\pm 180^\circ$ . In **10** this angle is  $-173.5 (5)^\circ$  which means that this cation still has a conformation which is close to bisected. Both **9** and **10** have a planar configuration about the carbonyl carbon with C(1) lying in the plane defined by C(2)–C(5)–O, Table III.

In the case of **11**, the presence of the six-membered ring fused to the cyclopropane imposes some restraint on the conformational degrees of freedom. Even in this case, however, the angle between the cyclopropyl and carbonyl planes is 82.2 (6)°, Table III, and the torsion angle  $\tau$  is 176.3 (8)°. In order to achieve this relative arrangement the six-membered ring of **11** adopts a pseudoboat conformation. Kelly et al. have examined the conformation of bicyclo[4.1.0]heptan-2-yl cation and its 2-methyl derivative with the use of <sup>13</sup>C/<sup>1</sup>H coupling constants as a probe and concluded that these ions exist in either an anti pseudoboat or a pseudochair (twist) conformation.<sup>32</sup> A twist conformation would seem to be adopted by the parent ketone, bicyclo[4.1.0]heptan-2-one.<sup>33</sup> One interesting feature of the conformation of **11** is that the protonated carbonyl group is no longer planar as it is in the other structures determined here. The possible reasons for this nonplanarity are discussed below.

The torsion angles  $\tau$  for the cyclopropylcarbiny cations whose structures have been determined are given in Table II. It is clear in every case studied so far that the cations have either a bisected conformation or one which is very close to this. It is interesting

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(27) Aue, D. H.; Bower, M. T. *Gas Phase Ion Chemistry*; Academic Press: New York, 1979; Vol. II.

(28) Gassman, P. G.; Fentiman, A. F., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 1545–1546.

(29) Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 85–124. Cf.: Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146–153.

(30) Allen, F. H. *Acta Crystallogr.* **1981**, *B37*, 890–900.

(31) Nokes, R. H.; Radom, L. *Chem. Phys. Lett.* **1983**, *99*, 107–111.

(32) Kelly, D. P.; Leslie, D. R.; Smith, B. D. *J. Am. Chem. Soc.* **1984**, *106*, 687–694.

(33) Lightner, D. A.; Jackman, D. E. *Tetrahedron Lett.* **1975**, 3051–3054.

**Table III.** Least-Squares Planes for Compounds 9–11

compd	distance <sup>a</sup> of atoms from plane			dihedral angle <sup>b</sup> between planes A and B	distance from plane D <sup>f</sup> of nearest contacts to			
	A <sup>c</sup>	B <sup>d</sup>	C <sup>e</sup>		C(1)		H(0)	
<b>9</b>	O	0.00 (1)	2.26 (1)	90.0 (4)	F(1)	2.99 (1)	F(4)	0.00 (2)
	C(1)	0.00 (1)	1.18 (1)		F(1)'	-2.99 (1)		
	C(2)	0.00 (1)	0.00 (1)					
	C(3)	0.71 (1)	0.00 (1)					
	C(4)	-0.71 (1)	0.00 (1)					
<b>10</b>	O	0.00 (1)	1.20 (2)	90.3 (5)	F(4)	2.91 (1)	F(1)	-0.133 (9)
	C(1)	0.005 (9)	1.28 (3)		F(2)	-3.010 (9)		
	C(2)	0.00 (1)	0.00 (1)					
	C(3)	0.59 (1)	0.00 (1)					
	C(4)	-0.85 (1)	0.00 (1)					
	C(5)	0.00 (1)	2.59 (1)					
<b>11</b>	O	0.000 (8)	0.000 (8)	82.2 (6)	Cl(1)	-2.56 (3)	Cl(2)	-1.10 (5)
	C(1)	0.027 (9)	-1.18 (2)		Cl(4)	2.41 (3)		
	C(2)	0.00 (1)	0.00 (1)					
	C(3)	0.61 (2)	0.00 (1)					
	C(4)	-0.81 (2)	0.00 (2)					
	C(5)	0.00 (1)	-2.51 (1)					
	C(6)	0.31 (2)	-2.52 (1)					
	C(7)	1.17 (2)	-1.24 (2)		0.10 (1)			

<sup>a</sup>All distances in Å. <sup>b</sup>All angles in deg. <sup>c</sup>Plane of C(2)–C(5)–O. <sup>d</sup>Plane of C(2)–C(3)–C(4). <sup>e</sup>Plane of C(1)–C(2)–C(3)–C(7). <sup>f</sup>Plane of C(1)–O–H(O).

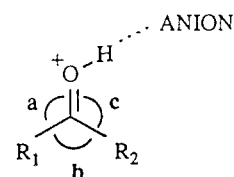
that while a bisected conformation is the preferred one for neutral cyclopropyl ketones, there is a broad energy minimum with the potential well corresponding to  $\tau$  ranges of  $\pm 30^\circ$ .<sup>18</sup> It is likely in the case of the cations that as more examples come available the potential well will be found to be narrower than that of the neutral ketones.

A further conformational aspect of these systems is the relative position of the cyclopropane with respect to the carbonyl oxygen. Allen has shown in his analysis of the structures of cyclopropyl systems that the ketones generally prefer to adopt a conformation that is close to bisected with the cyclopropane and carbonyl group in an *s-cis* configuration.<sup>18</sup> With those cations described in this and the earlier paper,<sup>8</sup> in which rotation about the C(1)–C(2) bond is possible, both *s-cis* and *s-trans* conformations are found. Thus **9**, **3**, and one of the cyclopropyl rings of **4** each has an *s-cis* arrangement of the cyclopropyl and carbonyl groups. It should be noted that in each of these cases the OH proton, with an attendant counterion hydrogen bonded to this proton, and the *s-cis* cyclopropyl ring have a *trans* configuration about the C(1)–O bond. The parent ketone **12** has been shown to prefer a bisected conformation with an *s-cis* configuration about the C(1)–C(2) bond.<sup>34</sup>

Olah and colleagues have examined the variable-temperature NMR spectra of **9** and **10** and shown that at  $-90^\circ\text{C}$  it is possible to slow down rotation about the C(1)–C(2) bond sufficiently so as to observe an equilibrium mixture of two conformations in ca. a 4:1 ratio.<sup>16a</sup> For each cation it was found that the major conformation present was one in which the OH group and cyclopropane have a *trans* configuration about the C(1)–C(2) bond. Thus it seems that the difference in conformation of **9** and **10** in the crystalline phase is attributable to crystal packing.

Cations **9**–**11** each have relatively large C(2)–C(1)–C(5) angles of 122.6 (6), 124.6 (6), and 124.5 (7) $^\circ$ , respectively. These are larger than the comparable angle in cyclopropyl ketones.<sup>35</sup> Similar large bond angles are found for **3** and **4** and in other protonated ketones such as substituted benzophenones,<sup>25</sup> and these have been attributed to the increased electronegativity of the O in a protonated ketone.

**Interactions within the Crystal Lattice.** The cations **9** and **10** each have a F atom and **11** a Cl atom in an anion which is situated close to the carbonyl plane (plane D, Table III) and arranged such

**Figure 9.** Bond angles around the protonated carbonyl group.**Table IV.** Bond Angles Around C(1) of Cations<sup>a</sup>

compd	angle (deg)			substituent	
	a	b	c	R1	R2
<b>9</b>	116.5 (6)	122.6 (6)	120.9 (7)	cpr	Me
<b>10</b>	115.0 (6)	124.6 (6)	120.4 (7)	cpr	Me
<b>11</b>	114.7 (7)	124.5 (7)	120.7 (6)	alkyl	cpr
<b>3</b>	116.1 (6)	123.8 (6)	120.1 (6)	cpr	phenyl
	117.2 (6)	122.1 (7)	120.7 (6)	cpr	phenyl
<b>4</b>	115.6 (4)	123.7 (6)	120.8 (6)	cpr	cpr
<b>8</b>	116.2 (7)	124.1 (5)	119.5 (7)	cpr	vinyl

<sup>a</sup>Cyclopropane is denoted as cpr.

that it forms a hydrogen bond with the OH proton. The O–F or O–Cl distances (**9**, O–F(4) 2.557 (6) Å; **10**, O–F(1) 2.601 (6) Å; and **11**, O–Cl(2) 3.286 (7) Å) are all shorter than the sum of the van der Waals radii of the respective atoms indicating the presence of strong hydrogen bonds. In the case of **11** the Sb–Cl(2) bond is significantly lengthened as compared to the other Sb–Cl bonds in the anion. The C(1)–O–F (or Cl) angles (**9**, C(1)–O–F(4) 115.3 (2) $^\circ$ ; **10**, C(1)–O–F(1) 119.6 (2) $^\circ$ ; **11**, C(1)–O–Cl(2) 112.9 (1) $^\circ$ ) and C(2)C(1)⋯OF (or Cl) torsion angles (**9**, C(2)–C(1)⋯OF(4) 180.0 (2) $^\circ$ ; **10**, C(2)C(1)⋯OF(1)  $-179.3$  (2) $^\circ$ ; **11**, C(2)C(1)⋯OC(2) 17.4 (1) $^\circ$ ) indicate the presence of an  $sp^2$  hybridized oxygen atom in these cations.

The presence of the anionic atom which is hydrogen bonded to the OH proton appears to effect distortion of the geometry about the carbonyl carbon atom. It has already been mentioned that the C(2)–C(1)–C(5) angle (designated “b” in Figure 9) in these cations is larger than would have been expected for a typical ketone. In addition there is a systematic distortion in the other two angles, “a” and “c”, Figure 9.

As can be seen from the data given in Table IV, angle a which is anti to the H⋯anion grouping, is significantly smaller than angle b. A survey of other reported cyclopropyl ketone structures shows that these two angles may vary significantly from the ideal 120 $^\circ$  but that this variation would seem to be random and not simply associated with the presence of the cyclopropane.<sup>35</sup> In this work

(34) Bartell, L. S.; Guillory, J. P.; Parks, A. T. *J. Phys. Chem.* **1965**, *69*, 3043–3048.

(35) A survey was made of all the cyclopropyl ketone structures retrieved by Allen, ref 18.

Table V. Crystal Data<sup>a</sup>

compd	9	10	11
fw	320.75	334.89	445.47
crystal size (mm)	0.30 × 0.25 × 0.35	0.20 × 0.20 × 0.10	0.30 × 0.20 × 0.35
systematic absences	rough cube	plate	rough cylinder
	$h0l, h + l = 2n$	$h0l, h + l = 2n$	$0kl, l = 2n$
space group	$hk0, k = 2n$	$0k0, k = 2n$	$hk0, k = 2n$
	$Pmnb$	$P2_1/c$	$Pc2_1b^c$
unit cell (Å and deg)	$a = 8.516 (2)$	$a = 11.569 (3)$	$a = 6.824 (1)$
	$b = 10.136 (2)$	$b = 8.209 (1)$	$b = 13.323 (2)$
	$c = 11.608 (1)$	$c = 12.621 (8)$	$c = 15.657 (2)$
		$\beta = 119.57 (2)$	
volume (Å <sup>3</sup> )	1002 (3)	1042.5 (4)	1423.6 (4)
Z	8	4	4
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	4.25	2.13	2.08
$\mu$ (cm <sup>-1</sup> )	56.82	26.79	28.76
max. $2\theta$ , reflcns meas	50°, $h, k, \pm l$	50°, $h, \pm k, \pm l$	50°, $h, k, \pm l$
std reflcns (csd)	(2, -2, 5) 1.66%	(-4, -4, 2) 1.27%	(0, 5, 8) 1.67%
	(1, 3, -6) 2.83%	(1, 3, -6) 1.40%	(1, 7, -8) 1.68%
temp (°C)	-65 ± 5	-65 ± 5	-65 ± 5
no. unique reflcns	1997	1965	2824
no. with $I > 0$	943	1827	1321
final $R_1, R_2$	0.0371, 0.0374	0.0618, 0.0678	0.0298, 0.0337
final shift/error max (av)	0.001 (0)	0.001 (0)	0.001 (0)
$\chi$ (secondary extinctn)	-0.0062	0.00655	0.00133
final difference map	0.553	2.304	1.351
max (e/Å <sup>-3</sup> ), location	(0.41, 0.66, 0.46)	(0.15, 0.79, -0.11)	(0.01, 0.50, 0.84)
min (e/Å <sup>-3</sup> )	-0.525	-1.499	-1.027
weighting	$(\sigma^2(F_o) + 0.00014F_o^2)^{-1}$	$(\sigma^2(F_o) + 0.0050F_o^2)^{-1}$	$(\sigma^2(F_o) + 0.0017F_o^2)^{-1}$
error in obs of unit wt	2.3372	1.0876	0.8653

<sup>a</sup>  $R_1 = \sum ||F_o - F_c| / \sum |F_o|$ ;  $R_2 = [\sum \omega(|F_o - F_c|)^2 / \sum \omega F_o^2]^{1/2}$ . <sup>b</sup> This cell may be transformed into the standard cell, space group  $Pmna$ ,  $a = 10.136 (2) \text{ \AA}$ ,  $b = 8.516 (2) \text{ \AA}$ ,  $c = 11.608 (1) \text{ \AA}$  by the matrix (0 1 0 / -1 0 0 / 0 0 1). <sup>c</sup> This cell may be transformed into the standard cell, space group  $Pca2_1$ ,  $a = 15.657 (2) \text{ \AA}$ ,  $b = 6.824 (1) \text{ \AA}$ ,  $c = 13.323 (2) \text{ \AA}$  by the matrix (0 0 1 / -1 0 0 / 0 0 1).

the distortion about the carbonyl carbon does not appear to be linked to the presence of either an *s*-cis conformation of the cyclopropyl/carbonyl functions in that the same phenomenon is found with **10** which has an *s*-trans configuration or the interchange of the cyclopropane between  $R_1$  and  $R_2$  in Figure 9. This distortion of the angles around the carbonyl carbon atoms seems to be a general property of protonated ketones.<sup>24</sup> It should be noted that a similar distortion is found in the results of high level calculations of the geometry of protonated formaldehyde in the gas phase.<sup>36</sup>

In the crystal lattices cations **9** and **10** have in addition to the fluorine atom of an  $\text{SbF}_6^-$  group hydrogen bonded to the OH proton, two further fluorines placed about 3 Å above and below the plane of the protonated carbonyl group, Table III.<sup>24,37</sup> In both cases the positioning of the fluorines is similar to that commonly found for protonated carbonyl compounds being placed over (under) the C(1)-O bond.

As was mentioned above, in the case of **11** C(1) is significantly displaced (0.027 (9) Å) from the carbonyl, C(2)C(5)O, plane. Examination of the crystal packing shows that in addition to Cl(2) which is hydrogen bonded to the OH proton, **11** is unique among the systems studied here in that it has only one further chlorine atom, Cl(1), in close proximity to the carbonyl carbon, C(1). The chlorine atom, Cl(1), is situated within the sum of the van der Waal's radii of C and Cl, 3.465 (7) Å from C(1) directly over the C(1)-O bond with a Cl(1)-C(1)-O angle of 84.6 (1)°. The carbonyl carbon atom, C(1), is displaced from the carbonyl plane toward Cl(1). A second chlorine (Cl(4)) on the opposite side of the carbonyl plane from Cl(1) is significantly further removed from C(1) (3.586 (7) Å). A similar specific interaction of a Lewis base with the carbonyl carbon of a protonated ketone has been observed in a protonated benzophenone.<sup>37</sup> Once more this interaction in this case leads to a nonplanar arrangement around the carbonyl carbon. This type of interaction can be considered

to represent a model for the attack of a nucleophile on a protonated carbonyl group.<sup>38</sup>

## Conclusion

With the results described in this work there is now a range of protonated cyclopropyl ketones whose structures have been determined. There is no question that these structures fully confirm the basic bonding picture for the cyclopropyl carbinyl cation. Further it is clear that there are systematic changes in the structures of these cations as a function of substituent, and these variations reflect the degree of involvement of the cyclopropane in charge delocalization. The challenge that remains is to determine the structures of cyclopropylcarbinyl cations which have groups on C(1) which are less charge stabilizing than the those used in this work and to relate the structures of these materials to those calculated for the parent cation. The propensity of cyclopropylcarbinyl cations to rearrange will make the extension of these studies to simpler systems a difficult challenge.

## Experimental Section

**General Methods.** Solution <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained by using Bruker AM500 and Varian EM390 spectrometers. Ketones **12** and **13** which are commercially available were dried over 4Å molecular sieves and distilled before use. The bicyclic material **14** was prepared from 2-cyclohexenone according to the procedure of Kuhn and Trischmann<sup>39</sup> and had identical spectroscopic properties to those previously reported.<sup>40</sup>

**Preparation of Cations.** The hexafluoroantimonate salts of **12** and **13** were prepared by slow addition of HF/SbF<sub>5</sub> (1:1, 0.5 equiv) to a cooled solution (-78 °C) of the corresponding ketone (~2 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (~15 mL) under an inert N<sub>2</sub> atmosphere as previously described.<sup>24</sup> The hexachloroantimonate salt of **14** was prepared by adding at -78 °C a CH<sub>2</sub>Cl<sub>2</sub> (~10 mL) solution of SbCl<sub>5</sub> (~1 mmol) which had been saturated with HCl gas to a CH<sub>2</sub>Cl<sub>2</sub> solution (~10 mL) of the corresponding ketone (~1 mmol). The salts were recrystallized from CH<sub>2</sub>Cl<sub>2</sub> at -20 °C. The crystals obtained were very sensitive to moisture and temperature, and all manipulations were carried out under a controlled atmosphere. The NMR spectra of CD<sub>2</sub>Cl<sub>2</sub> solutions of **9** and **10** were very

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similar to those previously reported.<sup>41</sup> The <sup>1</sup>H NMR spectrum of **11** (CD<sub>2</sub>Cl<sub>2</sub>) exhibited resonances at δ 1.78 (1 H, H<sub>7eq</sub>, m), 1.92 (2 H, protons on C<sub>6</sub>, m), 2.18 (1 H, H<sub>7ax</sub>, br d,  $J_{7,6\text{trans,aa}} \sim 15.4$  Hz), 2.33 (1 H, H<sub>4exo</sub>, dd,  $J_{4,3\text{cis}} \sim J_{4,2} \sim 15.5$  Hz), 2.60 (1 H, H<sub>4endo</sub>, m), 2.68 (1 H, H<sub>5,trans</sub>, m), 2.77 (1 H, H<sub>2</sub>, m), 2.98 (1 H, H<sub>3</sub>, dd), and 3.04 (1 H, H<sub>5,cis</sub>, br d). The corresponding spin-decoupled <sup>13</sup>C-NMR spectrum in CH<sub>2</sub>Cl<sub>2</sub> displayed resonances at δ 14.68 (C<sub>7</sub>), 19.09 (C<sub>6</sub>), 25.04 (C<sub>4</sub>), 25.04 (C<sub>4</sub>), 33.51 (C<sub>3</sub>), 34.48 (C<sub>2</sub>), and 234.01 (C<sub>1</sub>).

**Collection of Crystal Data.** Suitable single crystals were sealed in 0.3-mm diameter Lindemann capillary tubes with the aid of a drybox equipped with microscope and cold block at -40 °C. All crystallographic manipulations were carried out at low temperature (~-65 °C) on a Syntex P<sub>2</sub> diffractometer with use of graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å). The low-temperature crystal environment was maintained by passing a thin stream of cold N<sub>2</sub> gas along the  $\phi$  axis of the diffractometer. To prevent frosting of the Lindemann tube, a heater was used to warm the outer periphery of the cold stream. Because of thermal instability of these crystals, it was not possible to obtain Precession photographs. Alternatively axial photographs were taken. Unit cell parameters were obtained from a least-squares fit of  $\chi$ ,  $\phi$ , and  $2\theta$  for reflections of the crystal under investigation in the range  $19^\circ \leq 2\theta \leq 25^\circ$  for **9**,  $20^\circ \leq 2\theta \leq 30^\circ$  for **10**, and  $19^\circ \leq 2\theta \leq 38^\circ$  for **11**. All intensity data were collected at -65 °C with the use of a coupled  $\theta$ -(crystal)- $2\theta$ (counter) scan. Intensities were measured with an upper  $2\theta$  limit of 50°. Reflections having  $75^\circ \leq \chi \leq 90^\circ$  were converted into their Friedel equivalents with available software in order to avoid collision between the  $\chi$  circle and the low-temperature apparatus. For each crystal, two internal standard reflections were measured every 48 reflections to monitor crystal stability. Corrections were made for Lorentz-polarization factors but not for absorption. This will lead to a maximum error in  $F_o$  of 11.0%, 6.1%, and 10.5% for **1-3**, respectively. Scan rate selection and preliminary data treatment were as described previously.<sup>42,43</sup> Density measurements for the crystals were made under inert atmosphere by suspending crystals in a mixture of two solvents, one less and one more dense than the crystals themselves. Data relating to the crystals **9-11**, the collection of their intensity data, and their structure refinement are given in Table V.

**Structure Solutions. General Methods.** Computations were performed by using VAX 8600 and VAX 8650 mainframe computers. The XRAY76 package<sup>44</sup> and the XTAL program suite<sup>45</sup> were used for preliminary data treatment. Three-dimensional Patterson syntheses, electron difference syntheses, and full-matrix least-squares refinement cycles were performed with use of the SHELX<sup>46</sup> program. Least-squares refinements which

minimized  $\sum \omega(|F_o| - |F_c|)^2$  were terminated when the maximum shift/error was 0.001. X-ray scattering curves were taken from ref 46. Anomalous dispersion corrections from ref 47 were also applied to the scattering factors of the heavy atoms involved.

**1-Cyclopropyl-1-hydroxyethylum Hexafluoroantimonate (9).** The clear colorless crystal **9** was determined to be orthorhombic, and data were collected in the uniquely defined nonstandard space group *Pmnb*. The antimony atom was found by direct methods with the use of 943 reflections with  $|E| \geq 1.5$  and 20 sets of starting phases. All remaining atoms were found from subsequent electron difference maps. The coordinates of all atoms were refined by use of full matrix least-squares refinement cycles. Before locating the hydrogen atoms, the temperature factors of all non-hydrogen atoms were made anisotropic and refined.  $U_{12}$  and  $U_{13}$  were fixed at 0 Å<sup>2</sup> for those atoms occupying special positions. Hydrogen atoms were then located, and their positions and isotropic temperature factors were varied through three least-squares refinement cycles before being fixed. For final refinement a variable weighting scheme was imposed.

**1-(1'-Methylcyclopropyl)-1-hydroxyethylum Hexafluoroantimonate (10).** The clear colorless crystal **10** was found to be monoclinic having the uniquely defined space group *P2<sub>1</sub>/c*. The antimony atom in **10** was located by direct methods by using 1827 reflections with  $|E| \geq 1.5$  and 20 sets of starting phases. The positions of the remainder of the atoms were revealed from subsequent electron difference maps. All non-hydrogen atoms and their isotropic temperature factors were refined through a series of full-matrix least-squares refinement cycles before anisotropic refinement. Hydrogen atoms were then located; their coordinates and isotropic temperature factors were varied over three cycles of least-squares refinement before being fixed. Introduction of a variable weighting scheme did not improve the trial structure, hence a fixed weighting scheme was employed which led to a value closest to unity for the error in observation of unit weight, *S*.

**2-Hydroxybicyclo[4.1.0]heptan-2-ylum Hexachloroantimonate (11).** The clear colorless crystal **11** was determined to be orthorhombic, and data were collected in the uniquely defined nonstandard space group *Pc2<sub>1</sub>b*. A three-dimensional Patterson synthesis revealed the position of the antimony atom. The remaining atom positions were found and refined by using a series of full-matrix least-squares refinement cycles. All non-hydrogen atoms were refined anisotropically before the hydrogen atoms were located and isotropically refined before being fixed. In the final stage of the structure refinement a variable weighting scheme was imposed.

**Supplementary Material Available:** Tables of atomic positional parameters and equivalent temperature factors, anisotropic temperature factors, hydrogen atom positional parameters and isotropic temperature factors, and bond lengths and angles involving hydrogen atoms (10 pages); tables of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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