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Cubyl Onium Ions: Cubylcarboxonium, Cubylacylium, and Dimethyl Cubyl-1,4-dihalonium Ions[1]

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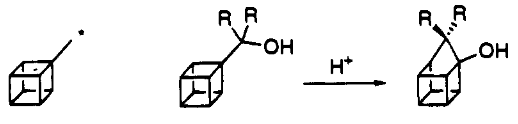
Abstract: The first onium ions of cubane: cubylcarboxonium, cubylacylium, and cubylhalonium ions were prepared and characterized by ^{13}C NMR spectroscopy. Treatment of mono-, di-, or tetracubanecarboxylic acids (or esters) with FSO_3H in either SO_2ClF or SO_2 gave the respective cubylcarboxonium ions. Reaction of mono- or dicubanecarbonyl chlorides with SbF_5 gave rise to the corresponding mono- and diacylium ions. These ions were also subjected to theoretical investigation at the DFT B3LYP/6-31G* and IGLO II′ levels. The NMR experimental data were well reproduced by the IGLO calculations with similar accuracy seen in earlier onium ion studies. The calculated charge density distributions indicate that the cubyl system by virtue of its strained C−C bonds is able to engage in hyperconjugative stabilization of the adjacent charge to a greater extent than unstrained systems such as adamantyl. Treatment of 1,4-dihalocubanes with CH_3F-SbF_5 complex in SO_2 afforded the first stable bridgehead halonium ions, namely the dimethyl cubyl-1,4-dihalonium ions. These halonium ions were found to possess typical halonium ion structures in most respects although hyperconjugative delocalization of the positive charge also appears to be important for these species. The corresponding cubylmonohalonium ions could not be prepared as stable species.

Introduction

Due[1] to the high degree of strain present in the cubyl framework, cubylmethyl species **1** undergo remarkably rapid rearrangements. The cubylmethyl radical, **1a**, has been shown to undergo a multiple ring opening process,[2] the initial β-scission being amongst the fastest known.[3] However, substitution at the radical center in **1a** by a hydroxyl group reduces the rate of rearrangement by three orders of magnitude and stabilizes the radical sufficiently that it may be characterized by ESR.[4] Cubylmethyl cations (**1b**), on the other hand, undergo Wagner−Meerwein ring expansion to the corresponding homocubyl systems. For example treatment of cubylcarbinol (**2a**) with neat 70% pyridine poly(hydrogen fluoride) (PPHF)[5] results in rearrangement to homocuban-1-ol (**3b**) without interception by fluoride.[6] Eaton has reported[2] that the even diphenylcubylcarbinol (**2b**), the carbocation of which should be highly stabilized by the two phenyl groups, undergoes complete ring expansion on solvolysis.



1a: • = •
1b: • = +

2a: R = H
2b: R = Ph

3a: R = H
3b: R = Ph

Carboxonium and acylium ions play important roles as intermediates in many acid catalyzed reactions.[7] Considerable interest therefore centers on the elucidation of the structure of carboxonium and acylium ions.[8] In our most recent work[9] on this subject, we measured ^{13}C NMR data and performed *ab initio* calculations for a series of cycloalkyl, including adamantyl and 2-norbornyl (*exo* and *endo*), carboxonium and acylium ions. It was observed[9] that the nature of the alkyl substituent had little effect on the carbocationic ^{13}C NMR shifts in these ions. Chemical shifts for C^+ in both cycloalkyl carboxonium and acylium ions were found to span only 4.1 ppm each. Consequently it must be concluded that as stabilization by the oxygen atom(s) is very effective, charge transfer from the carbocationic center into the alkyl rings does not take place to further enhance stabilization.

As stabilization of carbocationic centers by oxygen is so effective we thought that cubylmethyl cations stabilized at the carbinyl carbon by neighboring oxygen atoms, i.e. cubylcarboxonium and cubylacylium ions, might prove to be long lived stable species observable under superacidic stable ion conditions.[8b]

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(1) Part 44 of the series *Onium Ions.* For part 43 see: Olah, G. A.; Wang, Q.; Li, X.-Y.; Rasul, G.; Prakash, G. K. S. *Macromolecules*, submitted.

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Furthermore, cubyl is an unusual cycloalkyl group, again due to its highly strained bonding, and the possibility that it would have an unusual influence on the structure of its carboxonium and acylium ions was also of interest.

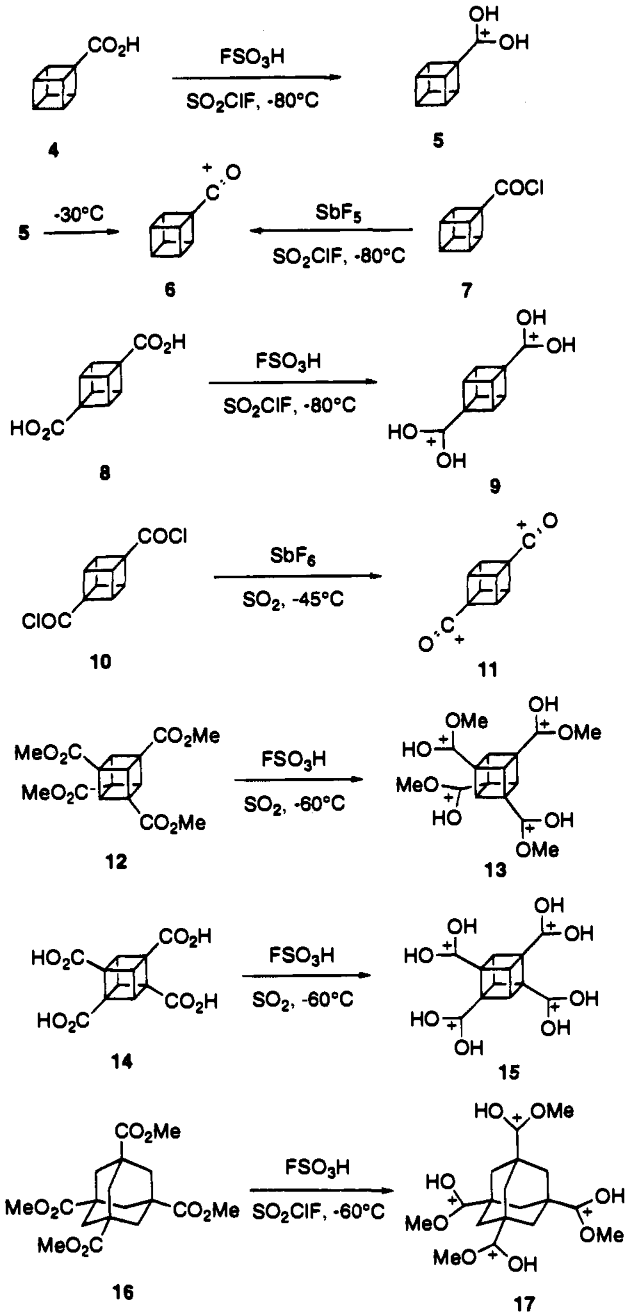
Closely related to cubylmethyl cations would be cubyl halonium ions[10] in which the cationic carbinyl carbon is replaced by a halogen atom. However, to date no acyclic tertiary, or bridgehead, halonium ions have been reported. Presumably this is because tertiary halonium ions are more prone to cleave[11] to their corresponding tertiary cations than are primary, as well as secondary alkyl or aryl, halonium ions. However, the cubyl cation,[12] by virtue of its constrained pyramidal structure, is a relatively high energy cation and therefore cleavage of the corresponding halonium ions should be far less likely than for other comparatively less strained systems.

Herein, we report our findings on the first examples of stable cubylmethyl cation derivatives (cubylcarboxonium and cubylacylium ions) and on the first stable bridgehead halonium ions, the dimethyl cubyl-1,4-dihalonium ions. These positively charged ions are stable under superacid conditions and represent the first cubyl derivatives stable in such media.[13]

Results and Discussion

Cubylcarboxonium and Acylium Ions. Treatment of cubanecarboxylic acid (**4**) in SO_2ClF with FSO_3H at −78 °C gave rise to a clear colorless solution whose ^{13}C NMR spectrum indicated the formation of the protonated species **5**. Although stable at −80 °C, on standing at −15 °C (ice/salt mixture) for 2 h considerable decomposition took place to give a complex ^{13}C NMR spectrum. When **5** (prepared at −78 °C) was allowed to stand for a few hours at −30 °C, two new peaks at δ 53.4, 49.4 were observed. These new peaks correspond with the two sets of three methine carbons in the cubylacylium cation **6** (*vide infra*) formed from **5** by further protonation and dehydration.[14] Similarly treatment of cubane-1,4-dicarboxylic acid (**8**) with FSO_3H (SO_2ClF, −78 °C) gave diprotonated species **9**. In contrast to **5**, **9** was found to be highly stable remaining unchanged for 24 h at −20 °C. Acylium ion **6** was also directly prepared via ionization of cubylcarbonyl chloride (**7**) with SbF_5 (SO_2ClF, −78 °C). Although stable at low temperature, **6**, like **5**, decomposed at −15 °C with loss of CO. Attempts to prepare the diacylium ion **11** in SbF_5/SO_2ClF from the diacid dichloride **10** were unsuccessful. When more stabilizing SO_2 was employed as the solvent, **11** could be observed after warming the sample above −45 °C. As with the diprotonated species **9** the diacylium ion **11** was found to be stable remaining unchanged for 24 h at −20 °C. Even the tetrasubstituted cubyl derivatives **12** and **14**[15] were completely protonated with FSO_3H (SO_2, −60 °C) to their corresponding tetracations **13** and **15**. The ^{13}C chemical shifts for the observed cubylcarboxonium and cubylacylium ions are presented in Tables 1 and 2.

Scheme 1



At first sight the data indicate that the cubyl carboxonium and acylium ions observed are essentially typical examples of these classes of ions. The ^{13}C chemical shifts for the carbocationic carbons in the cubylcarboxonium (**5**, **9**) and cubylacylium

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(10) Olah, G. A. *Halonium Ions*; Wiley: New York, 1975.

(11) Our attempts to prepare a series of methyl adamantylhalonium ions have not yet proved successful. Treatment of either 1-bromoadamantane or 1,3-dibromoadamantane with $CH_3F\text{-}SbF_5$ (SO_2, −60 °C) gave rise to a mixture of the adamantyl cation and the dimethyl bromonium ion as the major identifiable species. Treatment of 1,3,5,7-tetrabromoadamantane under the same conditions gave only a complex mixture. Curiously, the formation of the adamantyl cation from 1,3-dibromoadamantane seems to imlpy the formation of the adamantane-1,3-diyl dication as an intermediate. Head, N. J.; Mitra, A.; Prakash, G. K. S.; Olah, G. A. Unpublished results. The adamantyl cation: Olah, G. A.; Prakash, G. K. S.; Shih, J. G.; Krishnamurthy, V. V.; Mateescu, G. D.; Liang, G.; Sipos, G.; Buss, V.; Gund, T. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, *107*, 2764.

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(13) (a) Our attempts to observe the cubyl cation under superacidic stable ion conditions were not successful. We believe this to be due, in part, to reaction of the strained, electron rich C−C bonds of the framework with the strongly acidic medium. Olah, G. A.; Prakash, G. K. S. Unpublished results. See also: Prakash, G. K. S.; Krishnamurthy, V. V.; Herges, R.; Bau, R.; Yuan, H.; Olah, G. A; Fessner, W.-D.; Prinzbach, H. *J. Am. Chem. Soc.* **1988**, *110*, 7764. (b) Eaton has also mentioned that the cubyl system is reactive toward strong acids (ref 2). (c) Our attempts to prepare the $\alpha,\alpha,\alpha',\alpha'$-tetramethylcubane-1,4-dicarbinyl dication and $\alpha,\alpha,\alpha',\alpha'$-tetraphenylcubane-1,4-dicarbinyl dication under a variety of superacidic conditions were also unsuccessful. Head, N. J.; Prakash, G. K. S.; Olah, G. A. Unpublished results.

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(15) (a) Bashir-Hashemi, A.; Li, J.; Gelber, N.; Ammon, H. *J. Org. Chem.* **1995**, *60*, 698. (b) We were unable to prepare the corresponding tetraacylium ions as stable species under the conditions described for the preparation of **11**.

Table 1. Experimental and Calculated (in parentheses) ^{13}C NMR Chemical Shifts for **5**, **6**, **9**, **11**, **23**, **24**, **31**, **33-36**, **38a−c**[a−c]

	C^+	C1	C2	C3	C4	Me
5	190.6 (208.4)	53.0 (43.2)	51.1 (50.0)[d]	45.6 (45.3)[e]	47.0 (47.2)	
9	189.2 (204.8)	52.5 (46.8)	49.0 (48.9)[f]	49.0 (48.9)[f]	52.5 (46.8)	
23	199.9 (218.2)	42.8 (38.8)	37.3 (35.4)[g]	27.7 (26.3)[h]	35.6 (33.0)[i]	
6	151.4 (173.0)	27.5 (12.5)	53.4 (53.1)	49.4 (49.7)	47.6 (48.3)	
11	148.1 (165.0)	34.7 (25.0)	54.2 (54.9)	54.2 (54.9)	34.7 (25.0)	
24	151.6 (177.9)	32.8 (23.8)	35.4 (36.0)	25.4 (25.1)	33.7 (32.4)	
31	189.3	52.4	49.2	49.2	52.4	
33	187.6	52.9	48.9	48.9	52.9	62.1
34	185.3	54.5	49.6	49.6	54.5	61.5
35	187.5	52.6	48.7	48.7	52.6	62.8
36	184.9[j]	54.6	49.6	48.7	52.8	61.5[j]
	187.2[k]					62.8[k]
38a		61.0	60.1	60.1	61.0	9.5
38b		86.9	58.5	58.5	86.9	37.2
38c		91.0	61.2	61.2	91.0	50.5

[a] Relative to external acetone-d_6 (CD_3: 29.8 ppm). [b] In SO_2ClF or SO_2 (see text). [c] IGLO II′//B3LYP/6-31G*. [d] Average of C2, C6, C8. [e] Average of C3, C5, C7. [f] Average of C2, C3, C5, C6, C7, C8. [g] Average of C2, C8, C9. [h] Average of C3, C5, C7. [i] Average of C4, C6, C10. [j] *syn-anti*. [k] *anti-syn*.

Table 2. Experimental ^{13}C Chemical Shifts for **13**, **15**, and **17**[a,b]

	C^+	C_b	C_{CH}	Me
13	182.1	49.9	55.8	64.5
15	182.3	53.4	53.6	
17	187.6	42.3	33.4	63.5

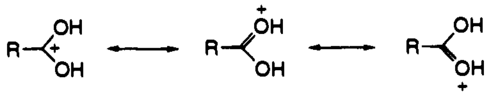
[a] Relative to external acetone-d_6 (CD_3: 29.8 ppm). [b] In SO_2.

Table 3. Shielding/Deshielding of **5**, **6**, **9**, **11**, **23**, **24**, and **38a−c** Relative to Their Respective Hydrocarbons[a−c]

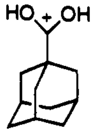
	C1	C2	C3	C4
5	5.3	3.4	−2.2	−0.7
9	4.7	1.3	1.3	4.7
23	14.5	-0.5	−0.7	−2.2
6	−20.2	5.6	1.7	0.1
11	−13.1	6.5	6.5	−13.1
24	4.4	−2.4	−3.0	−4.1
38a	13.3	12.4	12.4	13.3
38b	39.2	10.7	10.7	39.2
38c	43.3	13.5	13.5	43.3

[a] Cubane: ^{13}C NMR δ 47.73 (ref 18a). [b] Adamantane: ^{13}C NMR δ 37.82, 28.43 (ref 18b). [c] A positive sign implies deshielding.

ions (**6**, **11**) are close to those observed for other carboxonium and acyl ions substituted with other alkyl (cycloalkyl) groups.[9] Closer examination, however, especially of the substituent effects (Table 3) of both the carboxonium and acyl groups on the ^{13}C NMR shifts of the cubane framework as well as the effect of the cubyl moiety on the carbocationic centers of the aforementioned groups when compared with known cycloalkyl carboxonium and acyl ions, reveals some interesting differences. NMR spectroscopic studies (^{1}H, ^{13}C, ^{17}O)[9,14b,16] and X-ray crystallography[7d,17] along with theoretical investigations[14,18] have shown that of the possible resonance contributors, **18−20** and **21−22**, those localizing positive charge at the oxygen atoms dominate.


18 **19** **20**


21 **22**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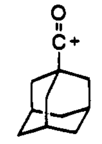
24

Even so the deshielding experienced at the formal cationic carbon (C^+) in **5** appears anomalously small. At 190.6 ppm it is somewhat less deshielded than that of other alkyl carboxonium ions considering the narrow range of variations previously observed (195.8−199.9 ppm).[9] This is also reflected in the deshielding experienced by C1 in **5** which is deshielded by only 5.2 ppm, relative to cubane,[19a] compared to 14.1−17.7 ppm reported for other cycloalkyl carboxonium ions, again relative to their respective hydrocarbons.[19b] Compared to their precursor acids[19] the C1 carbon in **5** is actually shielded by 2.51 ppm while the same carbon in the adamantyl carboxonium ion **23** is deshielded by 2.21 ppm, and in other cycloalkyl carboxonium ions there is almost no change (0.05−0.68 ppm). The anisotropic effect in acylium ions[16a] due to the C−O triple bond in the dominating contributor **22** results in the ^{13}C NMR shift for the carbocationic carbon being shielded relative to those in the corresponding carboxonium ions despite their being one less neighboring oxygen atom in the former to effect stabilization. Although C^+ in the cubylacylium ion **6** appears quite typical,[9] C1 in **6** is influenced by an unusually strong anisotropic effect. With the exception of the cyclopropylacylium ion[9,20] the effect of the acyl group on the C1 carbon of cycloalkylacylium ions (relative to their corresponding hydrocarbons) is minor and ranges from shielding of 3.9 ppm to deshielding of 4.4 ppm. As can be seen in Table 3 the cubylacylium ion is a notable exception exhibiting a strong 20.2 ppm shielding for C1 (relative to cubane).

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(20) (a) The C1 carbon in the cyclopropylacylium ion is deshielded (22.5 ppm relative to cyclopropane) by the well known ability of the cyclopropyl group to delocalize positive charge: Olah, G. A.; Reddy, V. P.; Prakash, G. K. S. *Chem. Rev.* **1992**, *92*, 69. (b) There exists a resonance contributor to the overall structure of the cyclopropylcarbinyl cations which localizes positive charge at C1: Olah, G. A.; Head, N. J.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 875 and references therein.

Table 4. Calculated (B3LYP/6-31G*) Charge Densities (charge of the hydrogens summed into the charge of heavy atoms) for **5**, **6**, **9**, **11**, **23**, and **24**

	C^+	C1	C2	C3	C4
5	0.573	−0.070	0.079[a]	0.067[b]	0.073
9	0.609	−0.066	0.126[a]	0.126[b]	−0.066
23	0.660	−0.041	0.024[c]	0.062	0.041
6	0.489	−0.098	0.157	0.084	0.090
11	0.561	−0.097	0.217	0.217	0.097
24	0.608	−0.108	0.101	0.070	0.056

[a] Average of C2, C6, C8. [b] Average of C3, C5, C7. [c] Average of C2, C8, C9.

Table 5. Optimized (B3LYP/6-31G*) Geometries of **5**, **6**, **9**, **11**, **23**, and **24**[a,b]

	C^+-C1	C1−C2	C2−C3	C3−C4
5	1.431	1.581[c]	1.565[d]	1.527
9	1.459	1.591[c]	1.562[d]	1.591[e]
23	1.484	1.564[f]	1.545[g]	1.542
6	1.371	1.618	1.561	1.571
11	1.400	1.608	1.558	1.608
24	1.419	1.581	1.545	1.542

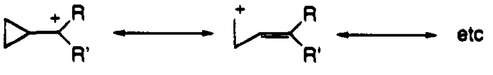
[a] Cubane C−C bond length (MP2/6-31G**): 1.565 Å (ref 12c). [b] Adamantane C−C bond length (B3LYP/6-31G*): 1.544 Å. [c] Average of C1−C2, C1−C6, C1−C8 bonds. [d] Average of C2−C5, C2−C3, C6−C7, C8−C3, C8−C7 bonds. [e] Average of C4−C4, C4−C5, C4−C7 bonds. [f] Average of C1−C2, C1−C8, C1−C9 bonds. [g] Average of C2−C3, C7−C8, C5−C9 bonds.

Ordinarily such variations would be assessed in terms of the usual chemical shift−charge density relationship.[21,22] However, in carboxonium and acyl ions anisotropic changes due to possible variations in the C−O bond[16d] order renders such comparisons invalid. Furthermore, such relationships can only be made between carbon centers of similar hybridization.[21,22] Due to its strain the carbon atoms of the cubyl system possess unusual hybridization which more closely resembles sp^2 [23a] rather than the essentially sp^3 carbons found in other known cycloalkyl carboxonium and acyl ions.[9] As an alternative we have calculated the Mulliken charge densities[23b] along with the geometries and chemical shifts of **5**, **6**, **9**, and **11** at the density functional theory (DFT) B3LYP/6-31G* level. To enable comparisons we have also calculated the same data for the adamantylcarboxonium ion **23** and adamantylacylium ion **24**.[9] We have found the DFT method[24] to be a reliable alternative to MP2 calculations for larger molecules. The DFT method, for example, reproduces the geometry and charge distributions recently calculated for the cubyl cation at the MP2/6-31G** level.[12c,25]

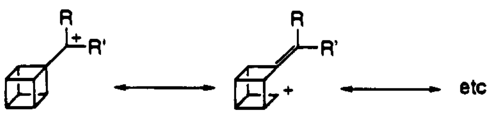
The calculated chemical shifts, determined by the IGLO II′ method with the B3LYP/6-31G* optimized geometry, reproduced the experimental values with generally good accuracy for both the mono- and dicarboxonium ions and mono- and diacylium ions (Table 1). The main discrepancy is that the formal carbocationic sites are calculated to be 15−25 ppm more deshielded than observed. This was also seen to be the case for other cycloalkylcarboxonium and acyl ions.[9] The deviations appears to be systematic in nature. Most importantly the deviation is the same in both the cubyl and adamantyl systems allowing at least qualitative, if not exact quantitative, comparisons between these two systems. As all other carbons are calculated with good accuracy (0−10 ppm) the systematic deviation of the cationic center chemical shifts seems to reflect an underestimation of the charge delocalization to the oxygen atoms.

Comparison of the calculated charge densities of the carboxonium ions **5** and **23** and of the acylium ions **6** and **24** also reveals some differences between the interaction of the cubyl and adamantyl systems with their carbocationic substituents. Firstly, it can be seen that the formal cationic centers in **5** and **6** bear considerably less charge than do those in **23** and **24**. Secondly, summation of the charge for the remaining carbons (and hydrogens) in each case reveals that the cubyl system is able to accommodate more charge than the adamantyl system. Whereas the cage carbons of **5** accommodate 44% of the charge, **23** accepts only 36%. More significantly while the cubyl framework of **6** accepts 71% of its charge **24** accepts only 57%. That delocalization into the cage framework of either system is greater for the acylium ions than for the carboxonium ions is consistent with the greater electronic demand due to their being only one neighboring oxygen atom in the former to effect stabilization of **6** and **24**. Even if only qualitative in nature these figures suggest that some of the spectroscopic differences detailed above may have their origin in the greater ability of the cubyl system to delocalize positive charge relative to the adamantyl system.

The superior delocalizing ability of the cubyl system is undoubtedly due to its strain. One of the consequences of strain is, as eluded to above, a high degree of s-character in the exocyclic orbitals of the carbon atoms.[26a] This is compensated for by high p-character in the endocyclic C−C bonds, i.e. strained C−C bonds are richer in electron density than unstrained C−C bonds. Such electron rich bonds are particularly suited to hyperconjugative stabilization of adjacent positive charge. It is precisely for these reasons that the strained cyclopropyl group is so effective at stabilizing carbocationic centers as shown in Figure 1.[26b]



25 **26**



27 **28**

It would appear, based on the calculated charge densities discussed above, that the cubyl system also responds in a similar fashion[27] (depicted in general terms by resonance contributor **28**) and more so than the adamantyl system. In both **5** and **6** the positive charge is greatest at the three equivalent C2 carbons

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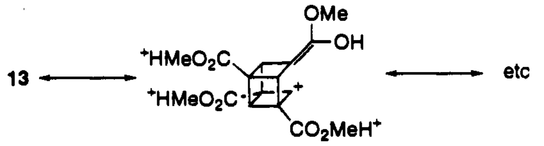
(25) The geometry and charge distributions and ^{13}C chemical shifts for the cubyl cation determined by the DFT method at the B3LYP/6-31G* level were calculated to be the following: bond lengths (Å): $C1^+-C2$ 1.501, C2−C3 1.582, C3−C4 1.568; charge Distributions: $C1^+$ 0.117, C2 0.191, C3 0.057, C4 0.140. IGLO II′//B3LYP/6-31G* chemical Shifts (ppm): C1 345.5, C2 124.8, C3 43.0, C4 40.1.

(26) (a) Della, E. W.; Hine, P. T.; Patney, H. K. *J. Org. Chem.* **1977**, *42*, 2940. (b) Olah, G. A.; Reddy, V. P.; Prakash, G. K. S. *Chem. Rev.* **1992**, *92*, 69.

and greater than that at the three equivalent C2 carbons in **23** and **24**. The calculated charges are also consistent with the experimentally observed deshielding and shielding seen in **5**, **6**, **23**, and **24** (Table 3). As could be expected on the basis of contributors such as **28** the C2 carbons in **5** and **6** are deshielded and, in agreement with the calculations, those of **6** more so than **5**. In contrast, the C2 carbons in **23** and **24**, in which it is suggested that hyperconjugative interactions such as those illustrated above are minor, are actually slightly shielded.[28] It should be pointed out that the charge in **28** may also be further distributed amongst the other carbons of the framework by additional hyperconjugative interactions from the other strained C−C bonds.

Based on comparison of the experimental data there appears to be little, and no systematic, effect by the second carboxonium or acyl group on the other carbon atoms in **9** or **11**. Relative to the monocarboxonium ion **5**, C^+, C1, and C2 of **9** are shielded by 1.4, 0.5, and 2.1 ppm, respectively. The same carbons in **11**, relative to **6**, are shielded by 3.3, −7.2, and −0.8 ppm. The effect of the second positively charged substituent may be better assessed through theoretical means. The ^{13}C chemical shifts of **9** and **11** are both reproduced by the IGLO II′ method with the same accuracy observed for the monosubstituted cases. Relative to their corresponding monosubstituted analogs the charges on both the cationic sites and the cage carbons (except C1 and C4) in both **9** and **11** are greater. However, while more charge overall is delocalized into the frameworks of **9** and **11**, the degree of delocalized charge per unit of overall charge is less in both cases. The cages of the disubstituted systems **9** and **11** bear 13% and 16% less charge, respectively, compared to their corresponding monosubstituted cases. The calculations also predict a lengthening (0.03 Å) of the C^+−C1 bonds in both **9** and **11** due to the second charged substituent. All of these predictions are consistent, not only between **9** and **11** but with the expected electrostatic repulsion between the two charged groups.



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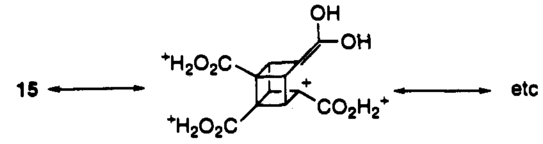

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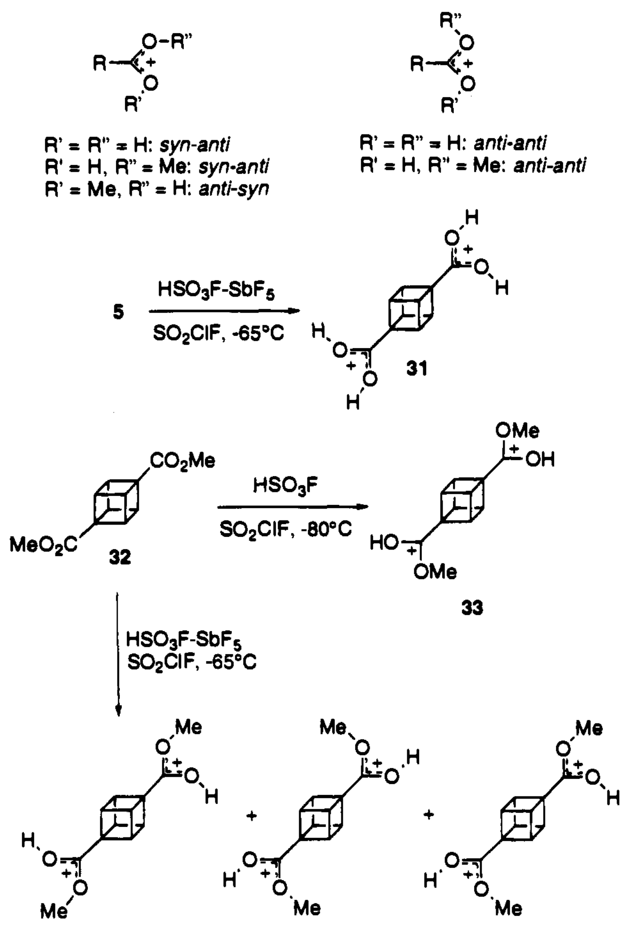
Scheme 2



The experimental data for the tetracations **13** and **15** are also of some interest and offer the best experimental evidence for strong hyperconjugation in the cubyl system. Of principal interest are the chemical shifts for the bridgehead (C_b) and methine (C_{CH}) carbons in the two systems. Considering firstly the methine carbons it is seen that those of **13** are further deshielded than those of **15** (Table 2). Due to its *pseudo*-tetrahedral symmetry, each of the methines in **13** are located between three carboxonium bearing carbons and thus should receive some positive charge, through hyperconjugation, from all three carboxonium groups. The methines of **15** can only be influenced hyperconjugatively by two carboxonium groups and thus would be expected to be less deshielded than those of **13** as seen. The bridgehead carbons of **13**, on the other hand, are more deshielded than those of **15**. This is due to the hyperconjugative delocalization of C_b−C_b bonds in **13** to stabilize the adjacent carboxonium group, as shown for one such contributor (**30**), which results in further charge being delocalized to the bridgehead carbons. As each bridgehead carbon in **13** is surrounded only by methines, hyperconjugative delocalization of charge directly to any of the other bridgehead carbons is not possible. Consequently the bridgehead carbons in **15** should be deshielded by hyperconjugative interactions while those in **13** should not, as observed. Because of their size, we were not able to calculate ions **13** and **15** at the B3LYP/6-31G* level.

NMR studies of carboxylic acids in HF−SbF$_5$ or HSO$_3$F−SbF$_5$ (Magic Acid) have shown that protonated acids (i.e. carboxonium ions) may exist in two different conformers (*syn-anti* and *anti-anti*) and that these conformers can be frozen out at low temperatures.[7e] Of the two possible isomers, in carboxylic acids except formic and acetic acid, only the *syn-anti* isomer is observed. Similarly only the *syn-anti* and *anti-syn* isomers have been detected in protonated esters, with the exception of formates.[7e] In agreement with this, diprotonated **9** shows only one resonance for C^+ in its ^{13}C NMR for the

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[27] Unfortunately the greater strain of the cubyl system and other geometrical factors result in Wagner−Meerwein rearrangement of most cubylmethyl cations rather than cationic charge stabilization as is often, but not always, the case with cyclopropylmethyl cations. Wiberg, K. B.; Hess, B. A., Jr.; Ashe, A. J., III. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, Chapter 26, and references therein.

[28] Such small differences may be due to solvent effects. However, shielding of the C2 carbons in **23** and **24** may result from the decrease (**23**) or increase (**24**) in C−O bond order, and hence anisotropic shielding, on protonation of the carbonyl group in adamantanecarboxylic acid or ionization of the adamantanecarbonyl chloride.

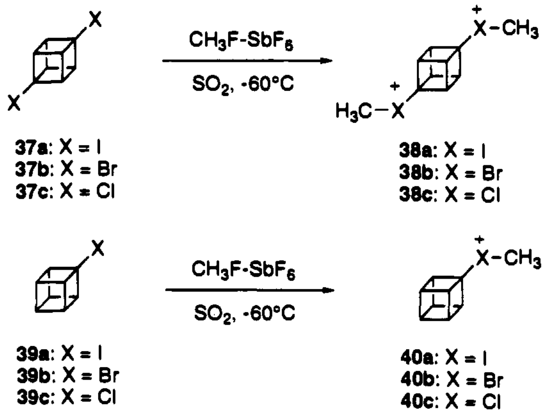
syn-anti isomer **31** in magic acid at −65 °C. However diester **32** in the same medium displays four resonances in the same region of the ^{13}C NMR spectrum. Two of these peaks can be assigned to the identical cationic carbons in the *syn-anti,syn-anti* isomer **34** and in the *anti-syn,anti-syn* isomer **35**. In the *syn-anti,anti-syn* isomer (**36**) the nonequivalence of each protonated ester group effects the other via a remarkable long range interaction the result of which is that each carbocationic center in **36** is slightly different to that seen for the equivalent conformation in **34** or **35**. Similarly the bridgehead resonances in **36** are nonequivalent to those in **34** or **35**. The methyl and methine groups were not affected in the same way; however, two resonances were seen for each as might be expected. The assignments made in Table 1 are based on the ^{13}C NMR peak areas and the known preference for protonated esters to adopt the *syn-anti* configuration.[7e] The observed substituent effect over such a distance (five carbons) through an aliphatic system involving substituent groups that differ only in configuration is remarkable and reflects the unusual transmission properties of the cubane framework.[29]

As mentioned earlier for both carboxonium and acylium ions spectral evidence clearly shows that, in general, the majority of the charge is located on the oxygen atoms. Therefore the cubylmethyl nature of these ions is limited and delocalization of charge to the oxygen atoms explains their stability toward ring expansion. The stability of **9** and **11**, relative to **5** and **6**, is most likely due to a variety of factors including electronic stabilization of the framework toward the superacid medium by the additional electron-withdrawing group.[13]

Cubyl Halonium Ions. Halonium ions are known to localize most of their charge on the halogen atoms.[10] Therefore it is not surprising that attempts to prepare the series of halonium ions **38a−c** and **40a−c** were only partly successful. Addition of a solution of CH_3F-SbF_5 complex in SO_2[30,31] at −70 °C to the dihalides **37a−c** gave rise to clear, near colorless solutions. Examination of the NMR spectra at −40 °C indicated that **38a** and **38b** had been cleanly prepared as evidenced from the strong deshielding of the bridgehead carbons and the appearance of appropriately deshielded methyl peaks.[31] Although these dihalonium ions (**38a**, **38b**) were stable up to at least −20 °C **38c** was accompanied by other unidentified products which complicated its ^{13}C NMR spectrum. Warming above −50 °C resulted in decomposition. Consequently the assignments for **38c** at this time are tentative. Our attempts to prepare the corresponding monosubstituted analogs **40a−c** were uniformly unsuccessful. The ^{13}C NMR spectrum observed on treatment of iodocubane **39a** with $CH_3F-SbF_5-SO_2$ (−70 °C) displayed seven methine (^{13}C NMR δ 62.91, 61.85, 61.16, 51,27, 50.27, 50.43, 47.99, 47.55) and two methyl (^{13}C NMR δ 9.33, 7.20) peaks. We are unable to attribute any of these to the methylcubyliodonium ion with any certainty. At −30 °C only the dimethyliodonium ion[31] could be detected.

As can be seen from Tables 1 and 3, a positively charged halogen directly bonded to the cubane cage effects the cubyl ^{13}C NMR chemical shifts in far more dramatic a way than either the carboxonium or acylium groups. The reason is that the majority of the charge now lies on the atom directly attached to the cubyl framework. As with other halonium ions[10] there is a considerable deshielding trend for C1 (C4) going from diiodonium to dichloronium ions, consistent with the inductive effect of the halogen atoms and their relative sizes (the smaller the halogen atom, the less positive charge it can accommodate). Relative to the deshielding observed for the cyclopropyl ring carbons in cyclopropyl methyl halonium ions[32] the deshielding effect of the methylhalonium substituents on the cubyl carbons (relative to cubane) seem to be fairly typical.[33] The deshielding of C1 in the cyclopropyl methyl halonium ion series is somewhat greater than that seen for **38a−c** which may be due to either a greater ability of the cyclopropyl group to delocalize charge[26b] or a greater localization of charge on the halogen atoms in **38a−c** by electrostatic repulsion. The deshielding of the C2 carbons in **38a−c** is fairly uniform, a trend that has been previously observed in other alicyclic halonium ions.[10] The chemical shifts of the methyl groups themselves in **38a−c** are also very typical being within 3 ppm of values reported for other systems.[31,32] The deshielding of the C1 carbons in **38a−c** relative to their respective precursors **37a−c**[34] (25.38, 23.39, and 18.20 for **38a−c**, respectively) is more uniform and similar to that observed in dialkyl halonium ions, which also show the α-effect is greatest in the order iodonium > bromonium > chloronium. This again illustrates that the majority of the charge lies on the halogen atoms. In contrast, whereas the β-effect in dialkyl halonium ions relative to alkyl halides results in slight shielding of the C2 carbons,[10] in **38a-c** they are all deshielded relative to **37a−c**. That the deshielding is also greatest for **38c** which is least able to support its charge on the halogen atoms, suggests this may have its origin in the same hyperconjugative charge delocalizing ability of the cubyl system outlined above. Conformation of this suggestion by comparison of **38a−c** with **40a−c** or by comparison of the charge-delocalizing ability of the cubyl framework for the halonium ions **38a−c** with a suitable unstrained analog such as adamantyl is not currently possible.

Scheme 3



37a: X = I
37b: X = Br
37c: X = Cl

38a: X = I
38b: X = Br
38c: X = Cl

39a: X = I
39b: X = Br
39c: X = Cl

40a: X = I
40b: X = Br
40c: X = Cl

The inability to prepare the monohalonium cubyl ions serves to reiterate the stabilizing effect that an additional electron-withdrawing group (at C4) exerts upon the cubyl framework toward both superacidic media and ring-opening processes and illustrates the overall greater stability of carboxonium and acylium ions over halonium ions.

Conclusions

It was shown that "cubylmethyl cations" stabilized by one (cubylacylium ions) or two (cubylcarboxonium ions) oxygen atoms are long-lived species stable under superacidic conditions.

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While the NMR data indicate that the cubylcarboxonium and acylium ions observed possess essentially typical structures for these classes of ions, the experimental evidence and the theoretical data indicate that the strained cubane C−C bonds interact with the electron deficient center(s) to a greater extent than in the comparatively unstrained adamantyl systems **23** and **24**. This interaction is clearly the onset of the Wagner−Meerwein ring expansion seen in less stabilized systems.[6,13c,27] Furthermore it was seen that the degree of hyperconjugative interaction was greatest for the cubylacylium ions (**6**, **11**) and was diminished in the 1,4-disubstituted cases, **9** and **11**, relative to the monosubstituted analogs.

Dimethyl-1,4-cubyl dihalonium ions, the first stable acylic tertiary halonium ions, were also prepared as stable species under superacidic methylating conditions. The stability of these ions relative to other unstrained systems[11] can be attributed to their resistance to undergo cleavage to high energy cubyl cation derivatives. In most regards, comparison of the experimental data with those of previously investigated systems indicated that the dimethyl-1,4-cubyldihalonium ions possess typical halonium ion structures. In contrast the monocubylhalonium ions could not be prepared as stable species. The reported data are significant in the definition of limits for polycations based on carbocyclic systems. It was demonstrated for the cubyl system that while up to four carboxonium groups may be attached to the cage framework, while maintaining its integrity, only two acylium groups or methylhalonium groups (but no diphenylmethenium or dimethylmethenium groups[13]) may be borne. For the adamantyl system it was previously shown[34] that two diphenylmethenium, dimethylmethenium, or acylium groups may be accommodated at two of its bridgehead carbons. We are now continuing exploration of possible tetrahedral tetracations of the adamantyl system.

Experimental Section

Dimethyl cubane-1,4-dicarboxylate (**32**) was purchased from the Aldrich Chemical Co. and used as received. Saponification to the diacid **8** was effected according to the reported half-hydrolysis procedure[35] with an excess (4 equiv) of base. Cubanecarboxylic acid (**4**) was prepared by reduction[36] of 4-iodocubanecarboxylic acid which in turn was obtained by hydrolysis of the corresponding ester.[37] Both cubanecarbonyl chloride (**7**) and cubane-1,4-dicarbonyl chloride (**10**) were prepared with freshly distilled thionyl chloride as reported.[38] The halocubanes **35a**−**c**[33] and **39a**−**c**[39] were prepared from their respective acid chlorides (**7** or **10**) via the Barton PTOC ester route.[40] The procedure employed was essentially that reported recently by Eaton[38] with the minor modification that 2-mercaptopyridine *N*-oxide (Aldrich, used as received) was employed for the *in situ* generation of the Barton ester rather than *N*-hydroxypyridine-2-thione sodium salt which requires extensive desiccation[38] before use. Doubly distilled FSO_3H, SbF_5, and SO_2ClF were used for the preparation of the ions. ^{13}C and ^{1}H NMR spectra were obtained on a Varian Unity-300 instrument equipped with a variable temperature probe.

Carbocation Preparation. To a slurry of the appropriate precursor (ca. 30 mg) in SO_2ClF (ca. 0.5 mL) in a 5 mm NMR tube and cooled to −78 °C (dry ice/acetone slurry) was added a small quantity of neat FSO_3H, magic acid, or a 50% v/v solution of SbF_5 in SO_2ClF, as required (see text). The ensuing mixture was vigorously stirred (Vortex agitator) with periodic cooling prior to transfer to a precooled NMR instrument.

Halonium Ion Preparation. To a slurry of the dihalide (ca. 15−20 mg) in a small quantity of SO_2 (ca. 0.2 mL) was added at −75 °C a solution of CH_3F-SbF_5 in SO_2, itself prepared by bubbling CH_3F through SbF_5-SO_2 (ca 1:5 by volume) complex for approximately 1−2 min at −78 °C. The mixture was vigorously stirred until clear, with periodic cooling, and then transferred to a precooled NMR instrument.

Method, Basis Set, and Geometry. Geometries and charge distributions were determined by DFT[24] methods (at the B3LYP/6-31G* level) using the GAUSSIAN94[41] program on an IBM RISC/6000 Model 560 computer. IGLO calculations were performed according to the reported method.[42] Huizinaga[43] Gaussian lobes for the II′ basis set are as follows: C and O 9s 5p 1d contracted to [51111, 2111, 1], d exponent = 1.0; H, 3s contracted to [21].

Acknowledgment. Partial support of our work by the National Science Foundation is gratefully acknowledged.

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