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# Rotational Dynamics of Stable Carbocations in Superacids. Investigation of Carbocation–Medium Interactions

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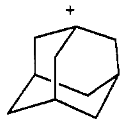
**Abstract:** The correlation times for rotational reorientation have been determined from the $^{13}$C dipole–dipole spin–lattice relaxation rates of 1-adamantyl (**1**), 2-methyl-2-norbornyl (**2**), 3-methyl-3-nortricyclyl (**3**), 2-phenyl-2-norbornyl (**4**), 1-methyl-1-phenylethyl (**5**), and 1-cyclopropyl-1-phenylethyl (**6**) cations in appropriate superacids. Measurement of the viscosity and temperature dependencies ($\eta/T$) of the rotational correlation times ($\tau$) of **1–5** have provided the data necessary for the calculation of their effective volumes by use of hydrodynamic relationships. For cations **2–5** these volumes were consistent with charge-induced interactions between the cations and the supporting media. However, rotational reorientation of the 1-adamantyl cation (**1**) does not conform to classical hydrodynamic theory despite a linear dependence of the correlation times upon $\eta/T$. The anisotropy of rotational reorientation as measured by the ratio of the diffusion coefficients ($\sigma = D_{\parallel}/D_{\perp}$) was consistent with restriction of rotation of cations **2** and **3** by interaction of the media, $FSO_3H/SO_2ClF$ and $SbF_5/FSO_3H/SO_2ClF$, respectively, at the cationic site. For the phenyl-substituted cations **4–6**, the interactions were not localized to specific sites. Application of two criteria, volumes calculated from hydrodynamic relationships and anisotropy of rotational reorientation of cations, showed that rotation of these cations **1–6** is restricted in superacids by electrostatic interactions with the supporting medium, but the cations do not rotate as ion pairs.

The constancy of $^{13}$C chemical shifts and coupling constants of carbocations generated in superacids has led to the use of spin–lattice relaxation times for the examination of interactions between the cations and their supporting media.[1-3] For the 1-adamantyl cation (**1**), the anisotropy of rotational reorientation ($\sigma$), defined as the ratio of the rotational diffusion coefficients ($D_{\parallel}/D_{\perp}$), was determined from the rotational correlation time ($\tau_c$), in turn determined from the dipole–dipole spin–lattice relaxation rates.[2] In $SO_2$ solution the 1-adamantyl cation reorients isotropically ($\sigma = 1$), but in $SO_2ClF$ it reorients anisotropically ($\sigma = 2.5$). This was interpreted as evidence for a weak electrostatic interaction between the cationic site of the carbocation and a diffuse anionic charge "cloud" in the $SO_2ClF$ medium, but not for formation of an ion pair.[2] In this work, we have applied the same procedure to extend the investigation of interactions between stable carbocations and their supporting media to include cations **2–6**.



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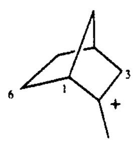

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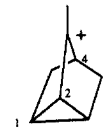

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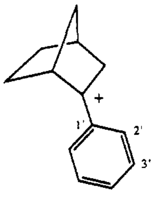

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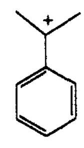

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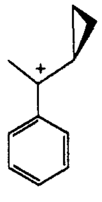
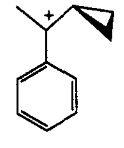
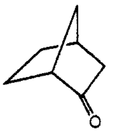


**6a**



**6b**

**7**



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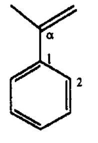

**9**

Investigation of such cation–medium interactions is also possible from consideration of the volume of the reorienting species $V$, available from $\tau_c$ via the familiar Stokes–Einstein–Debye equation or variants thereof, such as eq 1.[4,5] Use of this criterion requires

$$\tau = [V\eta/(kT)]fC + \tau^{\circ} \qquad (1)$$

the determination of the macroscopic solution viscosity ($\eta$) of superacid solutions at the (low) temperatures ($T$) required to observe the cations. The other terms include $f$, a dimensionless hydrodynamic frictional coefficient dependent on solute shape (1 for a sphere),[4] $C$, a dimensionless parameter, the value of which depends on whether the particle is best described as reorienting under "stick" ($C = 1$) or "slip" ($C = 0 \rightarrow 1$) boundary conditions, and $\tau^{\circ}$, an intercept time.[4] Interactions between the solute and the medium, such as specific solvation and ion pairing, that result in an increase in $V$ should increase $\tau$ and therefore be apparent from measured $T_1$ values. This approach has been used successfully to study the aggregation of lithium enolates[6] and ion pairing of cyclohexylammonium formate in nonaqueous solvent.[7]

Since we have previously developed procedures for the measurement of both viscosity and density of superacid solutions,[1] we are now able to report the results of solute–medium studies, using both hydrodynamic behavior and rotational reorientation criteria, for a range of typical carbocations.

## Experimental Section

The carbocations were prepared in the superacid in which they were most stable:[3] **1**, 0.69 M from 1-chloroadamantane in 5.2 M $SbF_5/SO_2ClF$; **2**, 0.50 M from 2-methyl-2-norbornanol in 7.5 M $FSO_3H/SO_2ClF$; **3**, 0.60 M from 3-methyl-3-nortricyclanol in 40% v/v $SbF_5/FSO_3H$ (1:1)/$SO_2ClF$; **4**, 0.50 M from 2-phenyl-2-norbornanol in 7.5 M $FSO_3H/SO_2ClF$; **5**, 0.46 M from 2-phenylpropan-2-ol in 25% v/v $SbF_5/FSO_3H$ (1:1)/$SO_2ClF$; and **6**, 0.46 M from 1-cyclopropyl-1-phenylethanol in 3.5 M $FSO_3H/SO_2ClF$. Details of the method of preparation, the NMR measurements, and the temperature calibrations have been given previously, together with the values of $T_1^{obs}$ and the nuclear Overhauser factors ($\eta$) for cations **2–6**.[3] Correlation times for

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rotational reorientation of the cations were calculated from dipole–dipole relaxation times as described previously.[2]

Viscosities were measured with a capillary flow viscometer of the Ubbelohde type. The densities ($d$) were measured in identical balanced U-tubes held in a refrigerated Dewar flask as described previously.[1] Calibration of the viscometer with 1-butanol at 253 K gave $\eta = 3.267 \times 10^{-5} dt$ P where $t$ was the flow time through the capillary. Calculated viscosities of 1-butanol from measurements of flow times at 222, 243, 273, and 303 K with use of reported values of $d$ reproduced literature values within 1%. The temperature dependencies of the viscosities of the solutions were determined from least-squares treatment of between 4 and 27 measurements at temperatures between 183 and 223 K. For $\ln \eta = a + b/T$, all correlation coefficients were ≥0.999. $a$, $b$: **1** (0.69 M from 1-chloroadamantane) −13.57, 2490; **1** (0.67 M from 2-adamantanol in 5.05 M $SbF_5/SO_2ClF$) −13.85, 2707; **1** (0.51 M from 2-adamantanol in 3.74 M $SbF_5/SO_2ClF$, 187–223 K) −11.59, 1927; **1** (0.25 M from 2-adamantanol in 1.87 M $SbF_5/SO_2ClF$, 186–223 K) −9.87, 1331; **2** (185–208 K) −13.96, 1886; **3** (193–213 K) −12.06, 1605; **4** (185–203 K) −14.59, 2206, **5** (187–213 K) −12.88, 1661; **6** (not measured).

## Results and Discussion

**Estimation of Structural Parameters.** The rotational diffusion coefficients were obtained by combining the experimental $T_1^{DD}$ data with the complete geometry of the reorienting species. In the case of **1**, the geometry was obtained from STO-3G calculations.[2,8] Complete structural details have not been reported previously for cations **2**–**6**; hence, estimates of relevant parameters were obtained as follows.

For the 2-methyl-2-norbornyl cation (**2**), the optimized 4-21G geometry of the classical 2-norbornyl cation reported by Goddard and co-workers was used with only slight modification.[9] The proton on C(2) (the cationic carbon) was replaced by a methyl group and C(1) was moved closer to C(6), resulting in an increase of the C(1)–C(2) bond length consistent with a reported partial structure of **2**.[10] Elaboration of the calculated 4-31G geometry of the classical cyclopropylcarbinyl cation in the bisected conformation provided the structure for **3**.[10] Estimates of the remaining structural elements of the tricyclic skeleton were obtained from the 4-21G geometry of edge-protonated nortricyclene.[11] In the case of the 2-phenyl-2-norbornyl cation (**4**), a phenyl group was substituted for the methyl group of **2**. The C(2)–C(1′) bond length is not important in the calculation of $D_\perp$ and $\sigma$ values and was arbitrarily set to $1.40 \times 10^{-10}$ m. Carbons 1, 2, and 3 of the norbornyl skeleton and the phenyl ring were assumed to be coplanar. The structure of the phenyl moiety was modeled on the 4-21G geometry of benzene.[12] The C–H bond lengths were adjusted to reflect the influence of a positive charge at the benzylic carbon.[13]

The structure of the cumyl cation (**5**) was calculated by combination of two methyl groups with the MINDO/3 structure of the benzyl cation,[13] such that all the carbon nuclei were coplanar. For the 1-cyclopropyl-1-phenylethyl cation (**6**), the 4-31G geometry of the classical bisected cyclopropylcarbinyl cation,[10] the phenyl group described for the 2-phenyl-2-norbornyl cation (**4**), and a methyl group were combined. The plane of the phenyl ring was assumed to be perpendicular to the vacant p-orbital of the cationic carbon, and the conformation of the ion was assumed to be **6a** rather than **6b**, in accordance with the work of Okazawa and Sorensen.[14] This is also the structure found in the solid state by X-ray crystal analysis of the hexafluoroantimonate salt.[15]

**Table I.** Relaxation and Rotational Diffusion Data for Carbocations **1**–**6** ($T_1^{DD}$(calcd) in Parentheses)

| cation | temp (K) | $T_1^{DD}$ (ms) C(1) | C(2) | C(3) | C(4) | C(5) | C(6) | C(7) | C(2′) | C(3′,5′) | C(4′) | diff coeff $D_\perp$ ($10^8$ s$^{-1}$) | $D_\parallel$ ($10^8$ s$^{-1}$) | $\sigma$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 178 | | 320 ± 1<br>(314) | 574 ± 30<br>(589) | 245 ± 10<br>(245) | | | | | | | 13 ± 0.4 | 35 ± 3 | 2.7 ± 0.2 |
| **2** | 193 | 645 ± 20<br>(663) | | 380 ± 20<br>(377) | 660 ± 50<br>(622) | 295 ± 10<br>(288) | 390 ± 30<br>(348) | 294 ± 20<br>(308) | | | | 15.8 ± 0.3 | 42 ± 3 | 2.7 ± 0.1 |
| **3** | 181 | 240 ± 10<br>(235) | 227 ± 20<br>(232) | | 230 ± 10<br>(234) | 107 ± 2<br>(107) | | | | | | 5.7 ± 0.1 | 14.2 ± 0.6 | 2.5 ± 0.1 |
| **4**[a] | 183 | 113 ± 10<br>(122) | | 61 ± 7<br>(70) | 101 ± 10<br>(114) | 55 ± 7<br>(58) | 62 ± 5<br>(64) | 65 ± 6<br>(61) | 125 ± 8<br>(125) | 123 ± 5<br>(119) | 91 ± 8<br>(94) | 3.4 ± 0.1 | 6.8 ± 0.4 | 2.0 ± 0.1 |
| **5** | 183 | | | | | | | | 244 ± 8<br>(246) | 243 ± 10<br>(237) | 185 ± 20<br>(185) | 6.9 ± 0.2 | 14 ± 1 | 2.0 ± 0.1 |
| **6**[b] | 183 | 187 ± 20<br>(198) | 102 ± 5<br>(103) | | | | | | 188 ± 10<br>(192) | 195 ± 10<br>(185) | 131 ± 10<br>(140) | 4.9 ± 0.1 | 11.7 ± 0.5 | 2.4 ± 0.1 |

[a] C(6′) 124 ± 6 (123). [b] Cyclopropyl carbons C(1″), C(2″) entered under C(1), C(2) for convenience.

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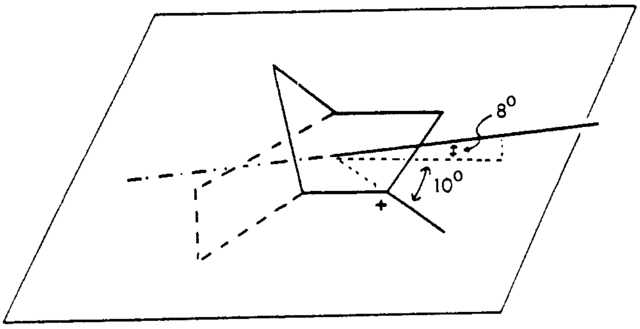
Since it has been shown that similar theoretical calculations for neutral molecules consistently either over- or underestimate C–H bond lengths ($r_{CH}$) with subsequent introduction of errors in $D_\perp$, the values of $D_\perp$ and $D_\parallel$ given in Table I have been corrected by the ratio of this systematic error, raised to the 6th power. The applied corrections were 0.897 for **1**,[2] 0.908 for **2**, **3**, **4**, and **6**,[12,16–19] and 1.106 for **5**.[16]

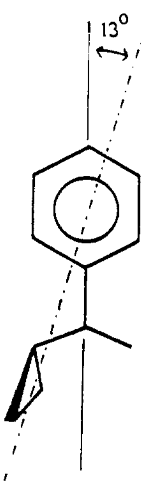
**Major Axes for Rotational Diffusion.** Extraction of $D_\perp$ and $\sigma$ for ions **2–6** from experimental $T_1^{DD}$ data required not only that their geometries be known but also that the major axes for rotational diffusion be identified. In the absence of specific interactions between the cations and surrounding media, the major axes may be chosen by inspection of their shape, in a similar fashion as has successfully been applied to neutral species.[20–23]

From symmetry considerations, the major axis for **1** is predicted to be coincident with the vacant p-orbital of the cationic carbon.[2] Cation **3** approximates a symmetric ellipsoid with the long axis coincident with the C(+)–CH$_3$ bond, which was therefore chosen as the major axis for rotational diffusion, while the C(+)–C(1′) bond serves this purpose for **5**, analogous with the finding that the corresponding bonds were the major axes of rotation in many monosubstituted benzenes.[24] Cations **2**, **4**, and **6** do not possess any obvious symmetry elements that would allow identification of their major axes of rotation by inspection. These axes were therefore assumed to be coincident with the major axes of the moment of inertia tensors.[23,25,26] Thus, for the 2-methyl-2-norbornyl cation, the major axis forms an angle of 8° with the plane defined by C(1), C(2), C(3), C(4) and the methyl carbon, and its projection onto this plane forms an angle of 10° with the direction of the C(2)–CH$_3$ bond. For **4** the corresponding angles are 3 and 4°; hence, the major axis is approximately collinear with the C(2)–C(1′) bond. The major axis of the moment of inertia tensor for the 1-cyclopropyl-1-phenylethyl cation (**6**) was calculated to be in the plane of the phenyl ring, forming an angle of 13° with the C(+)–C(1′) bond. The similarity of the calculated moments of inertia about the minor axes for ions **2**, **4**, and **6** suggests that these ions may reorient as axially symmetric ellipsoids.

**Calculation of Diffusion Coefficients.** By use of the structural parameters described above and the previously described methods,[2] the best fit values of $D_\perp$ and $\sigma$ were calculated for ions **1–6** from $T_1^{DD}$(exptl) data of their protonated skeletal carbons (Table I). The calculated relaxation times corresponding to these best fit values and experimental $T_1^{DD}$ data are included in this table. Good agreement of $T_1^{DD}$(exptl) with $T_1^{DD}$(calcd) was obtained for each cation, thereby rendering unnecessary the application of more complex models of rotational diffusion. Values of $D_\perp$ and $\sigma$ for cations **2–6** were calculated from $T_1^{DD}$ data obtained at two additional temperatures and for **1** at seven more temperatures to enable the determination of the temperature and viscosity dependence of $D_\perp$ and $D_\parallel$. The nuclear Overhauser enhancements ($n$) used to calculate the $T_1^{DD}$ values from $T_1^{obs}$ were measured at only one temperature and assumed not to vary over the temperature range studied. (This was necessitated by the very long time required for their measurement.) This assumption was validated in the case of **1**, where variation of $n$ with temperature for the resonances of the protonated carbons was no more significant than that observed for repeated measurements at a single temperature for the cation in a similar solution. (Average value of $n$ (178–213 K) = 1.9 ± 0.1.) The observed value confirms that the protonated carbons are relaxed exclusively by the dipole–dipole mechanism.



**2**



**6**

Implicit in the calculation of $D_\perp$ and $\sigma$ from experimental $T_1^{DD}$ data is the assumption that rotational reorientation of the cations is a diffusion-controlled process. Various criteria have been proposed to test the applicability of the rotational diffusion model, each involving comparison of the experimental correlation time ($\tau_c$(exptl)) with the theoretical value for the particle in the gas phase (i.e., the classical free-rotor correlation time ($\tau_f$)).[27–29] The ratio of these correlation times may be calculated according to

$$\chi = \tau_c(\text{exptl})/\tau_f = (\tfrac{5}{18}D^{-1})(kT\text{Im}^{-1})^{1/2} \qquad (2)$$

where Im is the moment of inertia and $D$ the diffusion coefficient about a given axis.[28] Gillen and Noggle have suggested that values of greater than 5 are indicative of a diffusion-controlled process.[29] For the cations **1–6**, the minimum value of $\chi$ obtained was approximately 50, thereby justifying the use of a diffusion model.

The good agreement of $T_1^{DD}$(exptl) and $T_1^{DD}$(calcd) values shown in Table I for all the cations was also observed at the other temperatures, except in the case of the 2-methyl-2-norbornyl cation (**2**), where significant differences occurred for C(1) and C(6) (Table II). It is considered that the exceptional behavior of **2** is a consequence of a degenerate rearrangement of this ion, although the rearrangement is not evident from the $^{13}$C chemical shifts. However, Sorensen and co-workers noted broadening of its proton resonances above 193 K, and, using the double-irra-

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**Table II.** Relaxation and Rotational Diffusion Data for the 2-Methyl-2-norbornyl Cation **2**[a] ($T_1^{DD}$(calcd) in Parentheses)

| | $T_1^{DD}$ (±10 ms) | | | | | | diff coeff | | |
|---|---|---|---|---|---|---|---|---|---|
| temp (K) | C(1) | C(3) | C(4) | C(5) | C(6) | C(7) | $D_\perp$ ($10^8$ s$^{-1}$) | $D_\parallel$ ($10^8$ s$^{-1}$) | $\sigma$ |
| 183 | 450[b] | 225 | 410 | 170 | 234 | 180 | | | |
| | (421) | (240) | (395) | (168) | (222) | (189) | 8.6 ± 0.2 | 32 ± 2 | 3.7 ± 0.2 |
| 193[c] | 645[b] | 380[b] | 660[d] | 295 | 390[e] | 294[b] | | | |
| | (663) | (377) | (622) | (288) | (348) | (308) | 15.8 ± 0.3 | 42 ± 3 | 2.7 ± 0.1 |
| 203 | 990[f] | 680[b] | 1220[g] | 546[b] | 840[h] | 540[e] | | | |
| | (1124) | (638) | (1079) | (539) | (594) | (554) | 32.4 ± 0.6 | 59 ± 3 | 1.8 ± 0.1 |
| | (1200) | (681) | (1132) | (540) | (629) | (567) | 30.5 ± 0.7[i] | 72 ± 5[i] | 2.3 ± 0.1[i] |

[a] Data from the same solution used to obtain data given in Table I. [b] ±20. [c] Reproduced from Table I. [d] ±50. [e] ±30. [f] ±40. [g] ±90. [h] ±60. [i] Calculated with only $T_1^{DD}$ for C(3), C(4), C(5), and C(7).

**Table III.** Hydrodynamic Data for Carbocations **1–5** in Superacid Media[a]

| | $f_\parallel$ | $f_\perp$ | $\rho_a$ | $G_\parallel$ ($10^{-8}$ sKP$^{-1}$) | $G_\perp$ ($10^{-8}$ sKP$^{-1}$) | $\tau^0_\parallel$ | $\tau^0_\perp$ ($10^{-12}$ s) | $\tau_\parallel^{max}$ | $\tau_\perp^{max}$ | $V_\parallel$ | $V_\perp$ ($10^{-30}$ m$^3$) | $V_{vdw}$[j] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 1.03 | 0.98 | 0.83 | 0.50[b] | 1.36[b] | 6.6[c] | 13.0[d] | 48 | 128 | 0.67[e] | 1.91[e] | 144 |
| **2** | 0.99 | 1.09 | 1.28 | 32 ± 3 | 148 ± 4 | 10 ± 3 | 14 ± 3 | 53 | 194 | 45[f] | 187[f] | 120 |
| **3** | 1.00 | 1.01 | 1.06 | 57 ± 3 | 126 ± 3 | −14 ± 3 | 2 ± 3 | 117 | 291 | 79[f] | 172[f] | 110 |
| **4** | 1.03 | 1.32 | 1.73 | 54 ± 12 | 85 ± 6 | 36 ± 18 | 100 ± 10 | 324 | 454 | 72[g] | 89[h] | 174 |
| **5** | 1.01 | 1.23 | 1.57 | 96 ± 8 | 219 ± 6 | −6 ± 3 | −12 ± 2 | 122 | 243 | 131[i] | 245[h] | 130 |

[a] Concentration and temperatures as given in Experimental Section. [b] ±0.03. [c] ±0.1. [d] ±0.5. [e] ±0.04. [f] ±4. [g] ±16. [h] ±6. [i] ±11. [j] Increments from ref 33.

diation spin saturation transfer technique, demonstrated that rearrangement proceeded via a pathway that results in C(1) and C(5) exchanging environments with C(6) and C(7), respectively.[30] Therefore, provided the lifetimes of the secondary cation intermediates were very short, the $T_1^{DD}$ values of the $^{13}$C nuclei that exchange environments would average if the lifetime in each environment was comparable to, or less than, these $T_1^{DD}$ values. This averaging should be most obvious for C(1) and C(6), as these carbons exchange between sites in which they have one or two directly bonded protons. Significantly, it is the $T_1^{DD}$(calcd) values for these carbons that do not agree with the experimental data. Furthermore, $T_1^{DD}$ for the C(1) (methine) resonance is shorter than and $T_1^{DD}$ for the C(6) (methylene) resonance is longer than the $T_1^{DD}$(calcd) values for C(1) and C(6), respectively, at 203 K. The good agreement of calculated and experimental values of $T_1^{DD}$ obtained at the lower temperatures (Table II) indicates that the exchange rate is slower than the relaxation rates of the $^{13}$C nuclei at these temperatures.

The reliability of $\sigma$ calculated from $T_1^{DD}$ data for the 2-methyl-2-norbornyl cation at 203 K is uncertain given that exchange at this temperature causes the $T_1^{D}$ values of C(1) and C(5) to average with C(6) and C(7), respectively. Calculation of $\sigma$ was therefore repeated, with use of only the $T_1^{DD}$ values of the C(3), C(4), C(5), and C(7) resonances. The degenerate exchange has little effect on these $T_1^{DD}$ values since C(2) and C(4) are not involved in the process, and although C(5) and C(7) do exchange environments and their $T_1^{DD}$ values should average, these $T_1^{DD}$ values are the same within experimental error even when exchange is slow (e.g., at 183 and 193 K, Table II). The value of $\sigma$ thus calculated is similar to that obtained when all the $T_1^{DD}$ data were used for the calculation. This may be fortuitous, as errors in $T_1^{DD}$ data are not necessarily transmitted equally into the different diffusion coefficients.[23] The values of $\sigma$ and the corresponding diffusion coefficients calculated for the 2-methyl-2-norbornyl cation at 203 K by use of only $T_1^{DD}$ data for the C(3), C(4), C(5), and C(7) resonances are the best estimates available and are therefore used in this study.

Calculation of $D_\perp$ and $\sigma$ for the 2-phenyl-2-norbornyl (**4**) and 1-cyclopropyl-1-phenylethyl (**6**) cations assumed that there were no internal reorientations in these cations. In **4** the phenyl group does not rotate freely, as evidenced by the observation of separate $^{13}$C resonances for C(2′) and C(6′) and a broadened resonance for C(3′) and C(5′). However, in cation **6** rotation of the phenyl group does occur, averaging the $^{13}$C resonances of C(2′) with C(6′) and also that of C(3′) with C(5′). The good agreement of experimental and calculated $T_1^{DD}$ values for **6** (Table I) indicates that internal reorientation of the phenyl group does not occur with a correlation time comparable to that of overall rotation and therefore does not affect the relaxation behavior. This is supported by the line-shape analysis of the proton spectrum that showed internal rotation to be slow compared to overall rotational diffusion.[14]

The smallest diffusion coefficient calculated for any of the ions was $3.4 \times 10^8$ s$^{-1}$ for $D_\perp$ of the 2-phenyl-2-norbornyl cation at 183 K. This value confirms adherence to the extreme narrowing condition necessary for calculation of rotational diffusion coefficients.

**Hydrodynamic Calculations.** The hydrodynamic coefficients $f_\parallel$ and $f_\perp$ were calculated according to the method of Perrin for symmetric ellipsoids, where the major axes of rotation of the cations **1–5** were taken as the major axes of the ellipsoids (Table III).[31] The values of $f$ depend only on the axial ratio ($\rho_a$) of the lengths of the major and minor axes of the ellipsoid, the alignments of which were taken as those of the moment of inertia tensors. The insensitivity of $f_\parallel$ to $\rho_a$ is characteristic of "stick" boundary hydrodynamic theory for prolate ellipsoids. The related parameter $f_\perp$ is more dependent on $\rho_a$, yet even for **4** with the largest axial ratio, $f_\perp$ varies only about 30% from that of a sphere. Consequently, the values of $f$ for ion pairs would not be very different from those of the free cations. Similarly, the $f$ values of approximately 1 for the 1-adamantyl cation (**1**), an oblate ellipsoid when free, would change only slightly with ion-pair formation, as this would alter the shape of the reorienting particle to that of a prolate ellipsoid. As shown above, $f$ values near unity are calculated for particles of this shape.

Rearrangement of eq 1 relates the volume of a particle ($V$) to the gradient ($G$) of the linear dependence of $\tau$ on $\eta/T$. Table III lists the least-squares estimates of the gradients $G_\parallel$ and $G_\perp$ and intercepts $\tau^\circ_\parallel$ and $\tau^\circ_\perp$ for plots of $\tau_\parallel$ and $\tau_\perp$ against $\eta/T$ for cations **1–5**. Typically, three pairs of relaxation and viscosity data were obtained in the range 183–204 K, which corresponded to a variation in $\eta/T$ by a factor of 4. However, for the cumyl cation (**5**) the temperature range was 183–233 K, while for the 1-adamantyl cation (**1**) measurements were taken at eight temperatures in the range 178–213 K. Generally, the linear correlation coefficients for the fits were good. The negative values of $\tau^\circ$ obtained for several ions were not anticipated since small positive

$$V = Gk(fC)^{-1} \quad (3)$$

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**Table IV.** Viscosity/Temperature Dependence of Rotational Correlation Times for the 1-Adamantyl Cation (**1**) in $SbF_5/SO_2ClF$ Solutions[a]

| soln | $[SbF_5]$ (M) | **1** (M) | $G_\parallel$[b] ($10^{-8}$ s$KP^{-1}$) | $G_\perp$[b] ($10^{-8}$ s$KP^{-1}$) |
|---|---|---|---|---|
| 1 | 5.05 | 0.67 | 0.38 ± 0.02 (0.999) | 0.87 ± 0.02 (0.995) |
| 2 | 3.74 | 0.51 | 1.9 ± 0.1 (0.997) | 3.7 ± 0.1 (0.998) |
| 3 | 1.87 | 0.25 | 6.6 ± 0.7 (0.988) | 10.4 ± 0.4 (0.994) |

[a] Correlation time ($= {}^1/_6D$) and viscosity data are given in the supplementary material. [b] Linear correlation coefficients of least-squares analyses in parentheses; minimum of four data pairs.

or zero values are usually observed for rigid molecular species such as these.[32] The negative values are thus probably indicative of the experimental error. However, since the magnitudes of these intercepts are small in comparison with the largest $\tau$ used ($\tau$(max)), the effect on the gradients of forcing a zero or small positive intercept would be slight.

The effective volumes of cations **1**–**5** were calculated from both $G_\parallel$ and $G_\perp$ with eq 3, values of $f$ were estimated for the free cations and the "stick" boundary values of 1 for $C$, and they are given in Table III, together with the volumes of the free cation estimated from van der Waals increments ($V_{vdw}$).[33] The extremely small value of $V$ calculated for the 1-adamantyl cation distinguishes it from all the other cations and necessitated additional experiments. An additional three solutions of **1** were prepared from 1-adamantanol in $SO_2ClF$ solutions of $SbF_5$ of varying composition but with a constant cation to $SbF_5$ ratio of 0.135. Experimental data were measured in the temperature range 183–226 K for each solution and the gradients $G_\parallel$ and $G_\perp$ calculated (Table IV).

**Carbocation–Medium Interactions.** It has been found that the "stick" boundary values of 1 for $C$, used to calculate the values of $V$ in Table III, are only appropriate for solutes that exhibit hydrogen bonding or other strong interactions with their surrounding media.[5,32] In nonassociating systems such as nonpolar liquids, a value between ${}^1/_6$ and ${}^1/_{12}$ is required to obtain agreement between the van der Waals and the calculated volumes.[34,35] For the neutral model compounds **7**–**9** used in this study, their volumes $V$, calculated according to eq 1 ($\tau^\circ = 0$, $C = 1$), are (14–16), (11–32), and (20–38) × $10^{-30}$ m$^3$, respectively. Their volumes estimated from van der Waals increments ($V$) are 118, 110, and 125 × $10^{-30}$ m$^3$, respectively. The calculated volumes of cations **2**–**5** are similar to the van der Waals volumes (Table III). This suggests that either the volume of the rotating cationic particle is larger than the free cation, i.e., an additional species such as a counterion reorients with the cations, or the cations are involved in some other charge-induced interactions with the supporting media. No independent measurement of $V$ or $C$ is possible to resolve this issue directly. In sharp contrast to cations **2**–**5**, the "stick" boundary estimate of $V$ for **1** is 2 orders of magnitude smaller than the volume of the free ion.

The detection of charge-induced interactions between cations **2**–**5** from their calculated volumes provides no information concerning the site of the interaction. This requires the investigation of the anisotropy of rotational reorientation.[2] To identify specific interactions between cations and other species from the rotational behavior of the cation, it is necessary that this behavior in the absence of any such interactions be known. For the 1-adamantyl cation, its approximate spherical symmetry suggested it would reorient isotropically when free of strongly interacting species and was subsequently shown to be so in $SbF_5/SO_2$ solution.[2]

Rotational reorientation of the cumyl cation (**5**) unhindered by localized, charge-induced interactions with its supporting media should be similar to that of neutral $\alpha$-methylstyrene (**9**). Relaxation data were thus obtained for the protonated aromatic carbons of **9** in $CDCl_3$ solution at 298 K, and $\sigma$ was calculated therefrom, assuming the symmetric top model for rotational reorientation with the major axis collinear with the C(1)–C($\alpha$) bond (Table V). The calculated anisotropy in the reorientation of the olefin suggested that the cumyl cation would reorient anisotropically in the absence of specific interactions. Strong interactions between this cation and some other species, which result in the pair reorienting as a unit, would have a major influence on the rotational behavior of the ion and should be reflected in the anisotropy of its reorientation.

The reorienting volumes calculated by application of eq 1 for **5** ((130–245) × $10^{-3}$ m$^3$) and its neutral model **9** ((20–38) × $10^{-30}$ m$^3$) demonstrate that interactions between the cumyl cation and its supporting medium ($SbF_5/FSO_3H/SO_2ClF$) were shown to be much greater than for a neutral solute particle of the same dimensions. However, the anisotropy in the reorientation of this cation ($\sigma = 2.0$) is similar to that of the olefin and is inconsistent with the cation reorienting predominantly as an ion pair. Thus, the restriction to rotation must be due to nonlocalized electrostatic interactions. Such interactions would not be localized at the cationic carbon in this charge-delocalized, aryl-substituted cation and would not therefore favor rotation about a particular axis when compared to a similarly shaped neutral compound.

The shape of the 2-methyl-2-norbornyl cation (**2**) indicates that it too may reorient anisotropically even if free of strongly interacting species. Although an empirical relationship between shape and rotational anisotropy has been demonstrated for several bicyclic hydrocarbons, it has not been successful in predicting the ratio of the diffusion coefficients of such species.[21,23] Thus, an a priori estimate of this ratio for the unencumbered 2-methyl-2-norbornyl cation was not available. Model compounds were therefore studied to obtain an estimate of this ratio.

The neutral compounds 2-methylenenorbornane (**7**) and 2-norbornanone (**8**) have the same gross shape as the cation. The alkene has no sites for localized, charge-induced interactions with solvent molecules and therefore provides a suitable model for the rotational behavior of the cation free of such interactions. In contrast, the carbonyl moiety of **8** may experience dipolar interactions with solvent, and this ketone provides a model for reorientation of a 2-substituted norbornane derivative that may experience specific interactions with the medium.

Rotational diffusion coefficients were calculated from relaxation-time data obtained at 298 K for **7** and **8** in $CDCl_3$ solutions assuming the symmetric top model for rotational reorientation with the major axes corresponding to those of the moment of inertia tensors (Table V). As geometries for these model compounds have not been reported, that of norbornane with the hydrogens at C(2) replaced with either a methylene moiety or a carbonyl oxygen was used in the calculation of the major axes and diffusion coefficients.[17] For these models and the 2-methyl-2-norbornyl cation, the alignments of their major axes with respect to the norbornyl skeleton are very similar. Included in Table V are the calculated $T_1^{DD}$ values corresponding to the best fit values of $D_\perp$ and $\sigma$. The calculated data are in good agreement with the experimental.

Reorientation of the alkene is isotropic ($\sigma = 1$). For the ketone, rotation about the major axis is unhindered by specific interactions between the carbonyl group and the solvent ($D_\parallel$ is similar for **7** and **8**). However, reorientation about the minor axes is severely restricted (compare $D_\perp$ for **7** and **8** in Table V). Thus, the rotational behavior of **8** ($\sigma = 3.2 \pm 0.1$) is consistent with "anchoring" of the carbonyl oxygen in solution, since rotation about the major axis, unlike rotation about the minor axis, does not alter greatly the orientation of the carbonyl dipole in solution. The rotational behavior of **7** and **8** reveals that the principal determinant of the alignment of the major axis of rotation is not the moment of inertia, but minimization of motion of the site involved in specific interactions with the solvent. For the ketone this site lies on the major axis of the moment of inertia tensor, which was used as the major axis of rotation in the calculation of $\sigma$ and $D_\perp$.

Reorientation of the 2-methyl-2-norbornyl cation is anisotropic ($\sigma$ = 1.8–3.7, Table II), with the cationic carbon close to the major axis. By analogy with the ketone, the rotational behavior of the

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**Table V.** Relaxation and Rotational Diffusion Data for Model Compounds **7–9** ($T_1^{DD}$(calcd) in Parentheses)

| | $T_1^{DD}$ (s) | | | | | | diff coeff | | |
|---|---|---|---|---|---|---|---|---|---|
| compd | C(1) | C(3) | C(4) | C(5) | C(6) | C(7) | $D_\perp$ ($10^{10}$ s$^{-1}$) | $D_\parallel$ ($10^{10}$ s$^{-1}$) | $\sigma$ |
| **7** | 21.1 ± 0.5 | 10.3 ± 0.2 | 18.5 ± 0.4 | 9.9 ± 0.2 | 10.8 ± 0.2 | 11.1 ± 0.2 | | | |
| | (20.0) | (10.6) | (19.0) | (10.5) | (10.5) | (10.6) | 8.0 ± 0.1 | 8.1 ± 0.2 | 1.01 ± 0.03 |
| **8** | 15.4 ± 0.3 | 8.3 ± 0.2 | 12.9 ± 0.2 | 6.0 ± 0.1 | 7.9 ± 0.2 | 7.0 ± 0.2 | | | |
| | (15.2) | (8.2) | (13.4) | (6.1) | (7.5) | (6.7) | 3.54 ± 0.03 | 11.3 ± 0.2 | 3.2 ± 0.1 |
| **9** | | 10.8 ± 0.3 | 7.8 ± 0.2 | | 11.3 ± 0.3 | | | | |
| | | (10.7) | (7.8) | | (11.2) | | 2.60 ± 0.03 | 6.2 ± 0.2 | 2.4 ± 0.1 |

**Table VI.** Rotational Correlation Time and Viscosity Parameters for the 1-Adamantyl Cation[a]

| soln | temp (K) | $\eta$ (P) | $\eta/T$ ($10^{-4}$ P K$^{-1}$) | $\tau_\parallel$ ($10^{-12}$ s) | $\chi_\parallel$ | $\tau_\perp$ ($10^{-12}$ s) | $\chi_\perp$[b] |
|---|---|---|---|---|---|---|---|
| 1 | 183 | 2.57 | 140 | 65 | 77 | 140 | 170 |
| 1 | 226 | 0.15 | 6.6 | 12 | 16 | 23 | 31 |
| 2 | 183 | 0.35 | 19 | 43 | 51 | 80 | 96 |
| 2 | 222 | 0.055 | 2.5 | 9.3 | 12 | 17 | 23 |
| 3 | 183 | 0.075 | 4.1 | 31 | 37 | 43 | 52 |
| 3 | 222 | 0.020 | 0.9 | 7.8 | 10 | 12 | 16 |

[a] Relaxation data are given in the supplementary material. [b] $\chi$ calculated from $\tau$ and Im according to eq 2.

cation is concluded to arise from polar interactions between the charged site and the weakly nucleophilic $FSO_3H/SO_2ClF$ solution, which restrict the mobility of the cationic carbon. Furthermore, the similarity in both the magnitude of the anisotropy and the alignments of the major axes for the cation and ketone suggests that these interactions do not result in a counterion reorienting with the cation (i.e., the cation does not reorient as an ion pair).

The 3-methyl-3-nortricyclyl cation (**3**) is approximately spherical ($\rho_a \sim 1$, Table III) yet reorients anisotropically ($\sigma$ = 2.5, Table I). Significantly, the major axis of this cation passes through its cationic carbon and is thus similar to the 2-methyl-2-norbornyl cation (**2**). Anisotropic reorientation of **3** is therefore consistent with interactions between its cationic carbon and the supporting medium ($SbF_5/FSO_3H/SO_2ClF$), which restricts the mobility of the cationic carbon, but not with ion-pair formation.

Delocalization of charge within the 2-phenyl-2-norbornyl (**4**) and 1-cyclopropyl-1-phenylethyl (**6**) cations revealed by $^{13}C$ shifts[36–38] of their cationic carbons and $^1J_{C\alpha H}$[39] suggested that, like the cumyl cation (**5**), the anisotropy of their rotational reorientation would not be greatly influenced by specific interactions with the supporting media localized at the cationic carbons. The rotational anisotropies observed for **4** ($\sigma$ = 2.0) and **6** ($\sigma$ = 2.4) are consistent with their nonspherical shapes, rotation being fastest about the axis that requires the least disturbance of the surrounding medium. However, hydrodynamic calculations revealed that reorientation of **4**, like **5**, was significantly slower than expected for a similarly shaped neutral compound.[40] Thus, for charge-delocalized cations, electrostatic interactions with the supporting media are readily detected by calculation of their volumes with use of eq 3. In contrast, the anisotropy in their rotational reorientation provides information about their ability to form ion pairs.

The rotational behavior of the 1-adamantyl cation (**1**) distinguishes it from each of the other cations studied. To obtain agreement of $V$ calculated from eq 3 with the van der Waals volume for this cation would require values of $C_\parallel$ and $C_\perp$ of approximately 0.005 and 0.013, respectively. Such low values for $C$ imply that rotational reorientation of the 1-adamantyl cation proceeds under "slip" boundary conditions.[41,42] Appropriate "slip" boundary friction coefficients for **1** were deduced by interpolation of tabulated values.[43] By use of the relationship between these coefficients and rotational correlation times,[44] values of $V_\parallel$ and $V_\perp$ were calculated to be 182 × $10^{-30}$ and 82 × $10^{-30}$ $m^3$, respectively. The agreement of these values with the volume of the free cation is remarkable given the approximations involved in estimating the length of the axes and the extreme sensitivity of the appropriate friction coefficients for near-spherical particles.[43,44]

Thus, it may appear that the rotational reorientation of the 1-adamantyl cation is adequately described by "slip" boundary hydrodynamic theory, which has been shown to be applicable to solutes devoid of strong interactions with the solvent.[41] In direct contrast to cations **2–5**, the existence of strong interactions between the 1-adamantyl cation and supporting media has therefore not been demonstrated from hydrodynamic considerations. Because of this, the dependence of the rotational behavior upon $\eta/T$ was determined for the cation in three additional solutions (Tables IV and VI). The increase in $G_\parallel$ and $G_\perp$ observed upon dilution of the cation would seem to indicate a corresponding increase in the coupling of the rotation reorientation of **1** with viscosity. However, inspection of the parameters from which the gradients were calculated reveals that the major factor governing the variation in $G_\parallel$ and $G_\perp$ is the temperature, rather than viscosity dependence of the correlation times $\tau_\parallel$ and $\tau_\perp$ (Table VI). For solution 1, $\eta/T$ at 183 K is only approximately 20 times that at 226 K, effecting a greater than 5-fold increase in $\tau_\parallel$ and $\tau_\perp$. The increases in $\eta/T$ for solutions 2 and 3 with decreasing temperature were smaller again (8 times and 5 times, respectively), yet resulted in 3.5–4-fold increases in the correlation times. In contrast, at constant temperature an increase in viscosity and therefore $\eta/T$ by a factor of 34 resulted in only an approximately 2-fold increase in $\tau_\parallel$ and a 3-fold increase in $\tau_\perp$. Thus, it is clear that the rotational behavior of the 1-adamantyl cation does not conform to classical hydrodynamic theory despite the apparent linear dependence of $\tau_\parallel$ and $\tau_\perp$ for this cation on $\eta/T$. A similar conclusion has been reached by others regarding the rotational reorientation of adamantane in *n*-alkanes.[45] Furthermore, linearity of rotational correlation items with $\eta/T$ does not necessarily imply a significant hydrodynamic component to rotational reorientation.[46]

Nevertheless, rotation about both the major and minor axes is restricted by interactions with the supporting medium. This is demonstrated by comparison of the observed correlation times with those calculated for the free cation in the inertial limit (i.e., $\chi$, eq 4). In each solution, $\chi_\parallel$ and $\chi_\perp$ are both significantly greater than unity (Table VI). The large values (10–170) show that

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rotational diffusion has a high coefficient of friction for **1**. The nature of the interactions with the medium has previously been delineated by measurement of the anisotropy of rotational reorientation ($\sigma$) and shown to involve weak electrostatic interaction between the cationic center and a diffuse negative charge "cloud" in the superacid medium.[2]

## Concluding Remarks

The rotational reorientation of the 1-adamantyl (**1**), 2-methyl-2-norbornyl (**2**), 3-methyl-3-nortricyclyl (**3**), 2-phenyl-2-norbornyl (**4**), cumyl (**5**), and 1-cyclopropyl-1-phenylethyl (**6**) cations is adequately described by the symmetric top model for rotational diffusion. Rotational diffusion coefficients calculated for this model of reorientation from $^{13}C-^{1}H$ dipole–dipole relaxation times indicate that the extreme narrowing condition is fulfilled for these cations in superacid media.

Temperature and viscosity dependencies of the rotational correlation times for these cations obey the general hydrodynamic relationship that was thus used to estimate effective volumes of the cations. Relatively strong charge-induced interactions between cations **2–5** and their supporting media (i.e., interactions greater than those anticipated for neutral molecules of similar dimensions) are evident from the volumes estimated assuming classical "stick" boundary conditions ($C = 1$) for rotation. However, application of eq 1 to the experimental data does not provide information regarding the nature of the interactions.

The 1-adamantyl cation is exceptional in that its effective volume, estimated in the same manner, is much smaller than the van der Waals volume of the free cation. It has been shown that although the rotational correlation times of this cation fit eq 1, its rotation does not conform to classical hydrodynamic theory. Therefore, there is a need for caution when hydrodynamic relationships are applied to experimental correlation times with the intention of calculating solute volumes or detecting the presence of solute–solvent interactions. This is particularly so for essentially spherical solute molecules studied in only one solution.[47]

The small values of the anisotropy in the rotational reorientation observed for the 1-adamantyl cation were not consistent with the cation reorienting predominantly as part of an ion pair. Examination of the cation-concentration and $SbF_5$-concentration dependence of $\sigma$ and the influence of solvent dielectric on this parameter has shown that the interactions responsible for the anisotropy in the reorientation of this cation involve antimony anions rather than solvent molecules.[2]

The alignment of the major axis of rotation of the 2-methyl-2-norbornyl cation (**2**) shows that this cation in $FSO_3H/SO_2ClF$ does not reorient as an ion pair. Nevertheless, localized interactions do restrict the reorientation of its cationic carbon. The rotational behavior of the 3-methyl-3-nortricyclyl cation (**3**) in $SbF_5/FSO_3H/SO_2ClF$ is similar to that described for cation **2** and provides no evidence for ion-pair formation. Examination of the anisotropic rotational reorientation of the aryl-substituted cations **4–6** in which the positive charge is delocalized has shown that the interactions between these cations and their supporting media are not localized at specific sites within the cations. Reorientation of these cations as ion pairs is therefore considered improbable.

The results of this study support the proposition that carbocations prepared as stable, long-lived species in the commonly utilized superacid media do not exist as ion pairs. However, the cations are influenced by charge-induced interactions with their supporting media. These interactions are localized at cationic carbons in cations that do not possess substitutents capable of extensively delocalizing the positive charge.

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**Supplementary Material Available:** Relaxation times, diffusion coefficients, and viscosity and temperature data for the three different solutions of **1** (3 pages). Ordering information is given on any current masthead page.

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(47) Study of a single solution of the 1-adamantyl cation (Table I) would have resulted in the conclusion that this cation reoriented with "slip" boundary conditions and that charge-induced interactions between it and the supporting media were not significant.