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$^{13}C–^{1}H$ Coupling Constants in Carbocations. 7.[1] Application of the ΔJ Equation to Polycyclic Systems Including Bicyclo[2.2.1]hept-2-yl Cations

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Abstract: One-bond $^{13}C–^{1}H$ coupling constants have been measured for the polycyclic carbocations 2-methylbicyclo[2.2.2]octyl (**10**), 2-arylbicyclo[2.2.2]octyl (**11**), 3-arylbicyclo[3.2.1]octyl (**15**), 8-methyltricyclo[5.2.1.0^{2,6}]decyl (**23**), 2-methyl-5,6-benzobicyclo[2.2.1]heptyl (**25**), 2-arylbicyclo[2.2.1]heptyl (**27**), 2-methyltricyclo[3.3.1.1^{3,7}]decyl (**17**), and 2-aryltricyclo[3.3.1.1^{3,7}]decyl (**18**). Comparisons with the corresponding ketones provided ΔJ values consistent with classical cations for **10**, **11**, **15**, **23**, and **25**. In the case of **17** and **18** the low ΔJ values suggest that 2-adamantyl cations are distorted significantly from sp^2 toward sp^3 hybridization. ΔJ_{C_1H} values for **27** give an excellent linear correlation with σ^+, with no deviation at high electron demand. For the parent 2-norbornyl cation (**28**), exceptionally high values for ΔJ are consistent with a nonclassical σ-bridged structure in superacid.

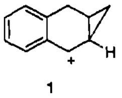
Introduction

The ΔJ equations (1) and (2), which relate the one-bond $^{13}C–^{1}H$ coupling constant of a group adjacent to a positive charge in a carbocation to the amount of charge and to the dihedral angle between the C–H orbital and the vacant p_π orbital,[2,3] have been used successfully to determine the structures of acyclic, cyclic, and bicyclic cations generated in superacids.[2–6]

$$\Delta J = 22.5 - 33.1 \cos^2 \theta \qquad (1)$$

$$\Delta J = (1 + 0.6\sigma^+)(10.9 - 14.3 \cos^2 \theta) \qquad (2)$$

In the case of internal cyclopropylcarbinyl cations, e.g. bicyclo[4.1.0]heptyl systems, it allowed the determination of the structure of the rearranged ion from 1,6-methano[10]annulene.[1,4] The value of 24 Hz for ΔJ_{C_2H} of this cation (**1**) is consistent with a 90° dihedral angle for C2–H and a static bisected, cyclopropylcarbinyl structure. In equilibrating classical systems, ΔJ for the group adjacent to the equilibrating center, e.g. C1 in **2**, is approximately half that predicted by eq 1 for static cations as a result of sharing of the positive charge between C2 and C3.



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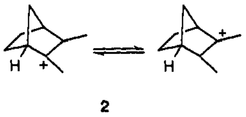

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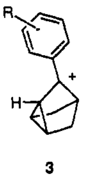

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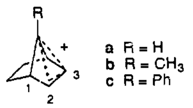
In dialkyl aryl cations, ΔJ is sensitive to the amount of charge at the adjacent carbon as measured by σ^+ in eq 2.[3] Replacing a methyl group by a phenyl group at the cationic center decreases the ΔJ value by approximately one half. In the case of the 3-aryl-3-nortricyclyl cations **3**, ΔJ for C$_2$H (θ = 90°) varies from 5 Hz for R = 4-OCH$_3$ to 16 Hz for R = 3,5-(CF$_3$)$_2$, compared to 22 Hz for the 3-methyl-3-nortricyclyl cation.[2]

Despite claims to the contrary,[7,8] the equation has been useful in distinguishing between classical and nonclassical cations, as has been demonstrated in the case of π- and $\pi\sigma$-bridged cations.[5] For the π-bridged 7-norbornenyl cations, e.g. **4**,[9] the J_{CH} values show large enhancements at both the bridging and bridgehead carbons over those for 7-norbornenone, e.g. **4a** $\Delta J_{(1,4)}$ = 20 Hz, $\Delta J_{(2,3)}$ = 19 Hz.[5] Classical, static or equilibrating structures for these cations can be excluded on both chemical shift and CH coupling grounds. A static structure is excluded by the observed symmetry (5 resonances for **4b**) and the δ values,[9] and equilibration between two tricyclic structures formed by C7–C2 or C7–C3 bonding would *reduce* the value of J_{CH}. Theoretically computed values for **4a** and **5** underestimate $J_{C_{1,4}H}$ by 4–10 Hz and overestimate J_{C_7H} by 6–10 Hz. Nevertheless, the theoretical values were considered to be an "attractive fit".[10] Additional evidence for the formation of the π-bridge in **4c** is provided by both X-ray[11] (which shows the C1–C7–C4 bridge canted toward C2–C3) and IGLO chemical shift calculations.[12]



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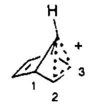

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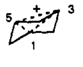

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For the $\pi\sigma$-bridged, trishomocyclopropenium systems of general structure **6**, ΔJ values range from 21 to 32 Hz at the bridge positions (C1,3,5) and from 18 to 27 Hz at the adjacent carbons (C2,4,6). These values are consistent neither with equilibrating classical nor static classical cations. The high values of ΔJ are,

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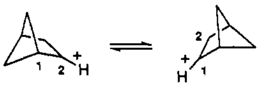
however, consistent with the proposition that π- and $\pi\sigma$-bridging result in increased internal strain and increased s-character of the involved C–H bonds.[5]

Bicyclo[2.1.1]hexyl cations are reported to have thermodynamic and spectroscopic properties intermediate between those of classical (cyclopentyl) and nonclassical (2-norbornyl) cations.[13] The J_{CH} values for the secondary (**7** and **8**) and tertiary (**9**) cations



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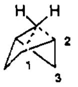

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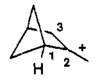

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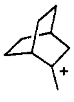
and the corresponding ketone[5] have been measured.[14] For the secondary cation, the ΔJ values obtained are 17 Hz for the averaged methylene carbons (C3,5,6) and 24 Hz at the bridging C1 and C2. These values are *greater* than those predicted for a classical equilibrating system (**7**), where the values should be *less* than those for a static, classical system. The tertiary cation **9**, with $\delta C^+ = 322$ and no J_{CH} value greater than 176 Hz, is such a cation. ΔJ for C3 is zero, consistent with $\theta = 30°$, but for C1 it is only 16 Hz, somewhat reduced from the expected value of 22 Hz for $\theta = 90°$.[15] Thus for the secondary cations **7**, equilibration would result in a value of 8–11 Hz for C1 of **8**, which is clearly not the case, the observed value of 24 Hz being similar to that observed in the parent trishomocyclopropenium cation.[5] Application of this ΔJ criterion to the bicyclo[2.1.1]-hexyl system lends support to a σ-bridged structure for the secondary cation as do the results of *ab initio* calculations and isotopic perturbation of resonance.[16] Equilibrating structures have also been ruled out as intermediates in the solvolysis of the secondary brosylate and diazonium ion by the ^{2}D, ^{13}C double-labeling experiments of Kirmse and co-workers.[17] However, the intermediate in the solvolysis of 1,2-dimethyl-2-bicyclo[2.1.1]-hexyl *p*-nitrobenzoate was shown to be a pair of equilibrating classical cations similar to **2**.[17] J_{CH} values for this cation are not available.[13]

We now report results of the application of the ΔJ equation to some other polycyclic systems, 2-bicyclo[2.2.1]heptyl (2-norbornyl), 2-bicyclo[2.2.2]octyl, 3-bicyclo[3.2.1]octyl, and 2-tricyclo[3.3.1.1^{3,7}]decyl (2-adamantyl) cations.

Results and Discussion

Bicyclo[2.2.2]octyl and Bicyclo[3.2.1]octyl Cations. Ionization of 2-methylbicyclo[3.2.1]octan-2-ol in superacid at −80 °C yields not the corresponding tertiary cation[18] but the rearranged 2-methylbicyclo[2.2.2]octyl cation (**10**).[19]

Comparison of $^1J_{CH}$ values (Table I) with those of bicyclo-[2.2.2]octan-2-one (**12**) yields ΔJ values of 16, −1, and 5 Hz for C1, C3, and CH_3 respectively.[5] The value of 16 Hz is approximately 5 Hz lower than that predicted by eq 1 ($\theta = 90°$) and is not a result of second-order effects, since $^1J_{C_1H}$ for **10** is



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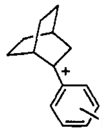

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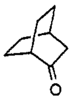

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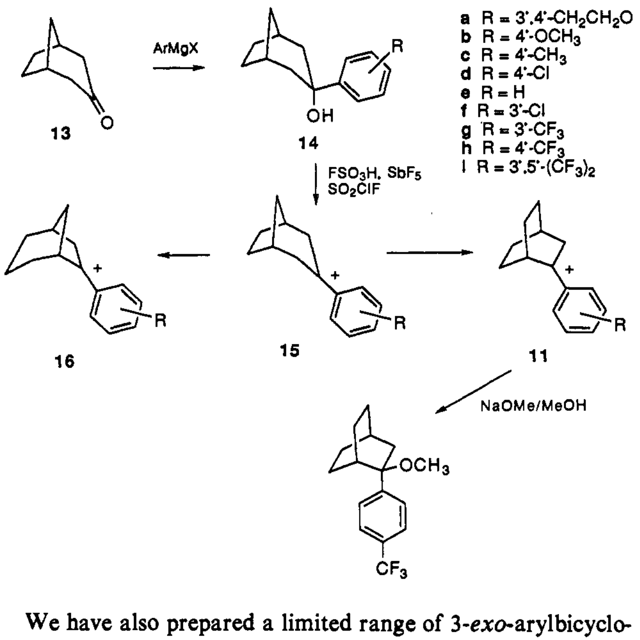
the same at different field strengths. The bicyclo[2.2.2]octyl skeleton should be relatively rigid;[19] nevertheless, the low value of ΔJ may reflect a distortion from the expected geometry ($\theta < 90°$) as proposed also for **9**. 2-Arylbicyclo[2.2.2]octyl cations[20] should show reduced values of ΔJ according to eq 2. For a limited range of these cations, this is indeed the case, J_{C_1H} increasing from 142 Hz for the coumaranyl cation (**11a**) to 145 Hz for the 3′-chloro derivative **11f** (Table I). Data for the cations with strongly withdrawing substituents (**11h** and **11i**) were unobtainable from the mixture of cations produced at *ca.* −80 °C. Previous ^{1}H and ^{19}F NMR studies of 2-arylbicyclo[2.2.2]octyl, 2-arylbicyclo[3.2.1]octyl, and 6-arylbicyclo[3.2.1]octyl cations bearing electron-withdrawing substituents have shown that equilibrium mixtures of cations are formed at −60 °C from any one of the precursors.[21]

Scheme I



We have also prepared a limited range of 3-*exo*-arylbicyclo-[3.2.1]octan-3-ols (**14**) from the corresponding ketone **13** by standard procedures[22] and ionized them in $FSO_3H/SbF_5/SO_2ClF$ solutions at −80 °C. For **14b,c,e**, the observed cations were **15b,c,e** identified by their ^{13}C spectra (Table I), the two α-methylene protons being nonequivalent. One of the couplings, $^1J_{C_{2,4}H}$, presumably that of the equatorial CH ($\theta = 90°$), shows the expected increase over that for the model ketone **13**, $\Delta J \sim 4$ Hz, the other (axial) remaining approximately the same (**14b**) or being reduced (**14c,e**) as expected for $\theta \leq 30°$.

However, ionization of **14h** and **14i** yielded a mixture of two cations, as indicated by additional cationic carbon peaks (from **14h**, δC^+ 281.8, 276.6 ppm; from **14i**, δC^+ 285.1, 279.3 ppm). These cations were identified as 2-arylbicyclo[2.2.2]octyl (**11h,i**)

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Table I. ^{13}C NMR Parameters for Carbocations and Model Ketones[a]

cation	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	aryl	CH$_3$
10	67.2[b] d, 156	322.1	59.0 t, 128	36.4 d, 143	23.9 t, 134	30.9 t, 142	23.9 t, 134	30.9 t, 142				39.5 q, 132
11a	40.0 d, 142	230.3	42.5 t, 128	28.9 d, 139	24.7 t, 131	26.5 t, 126					135.9 (C1′), 136.3 (166, C2′), 132.5 (C3′), 184.1 (C4′), 115.6 (176, C5′), 145.6 (167, C6′)	79.7, 27.4
11b (R = 4′-OCH$_3$)	40.7 d, 143	237.7	42.8 t, 128	28.9 d, 139	24.7 t, 133	26.8 t, 126					131.6 (C1′), 143.4, 143.7 (C2′,6′), 118.7, 120.3 (C3′,5′), 181.8 (C4′)	59.5 q, 150
11c (R = 4′-CH$_3$)	45.3 d, 144	262.0	46.5 t, 128	30.8 d, 137	25.3 t, 129	28.9 t, 125					136.0 (C1′), 139.6 (167, C2′,6′), 134.1 (170, C3′,5′), 172.4 (C4′)	25.3, q
11d (R = 4′-Cl)	47.8 d, 145	269.7	48.1 t, 128	31.4 d, 138	24.7 t, 133	28.9 t, 126					136.3 (C1′), 139.8 (169, C2′,6′), 133.5 (175, C3′,5′), 163.3 (C4′)	
11e (R = H)	47.5 d, 145	273.1	48.4 t, 128	31.1 d, 136	24.7 t, 130	28.9 t, 126					138.0 (C1′), 139.4 (168, C2′,6′), 132.9 (169, C3′,5′), 154.1 (171, C4′)	
11f (R = 3′-Cl)	50.7 d, 145	278.8	49.6 t, 128	32.3 d, 137	24.6 t, 131	29.8 t, 129					139.3 (C1′), 136.7 (169, C2′), 138.7 (C3′), 152.2 (171, C4′), 133.9 (170, C5′), 137.6 (169,C6′)	
11h[c] (R = 4′-CF$_3$)	52.3	285.1	51.5	33.4	24.8	30.8						
12	44.2 d, 141	218.0	44.8 t, 129	27.9 d, 136	23.3 t, 132	24.7 t, 132	23.3 t, 132	24.7 t, 132				
13	35.3 d, 135	50.4 d,d 129, 132	212.4			29.4 t, 132		37.8 t, 133				
15b (R = 4′-OCH$_3$)	40.1 d, 141	45.5 d,d 130, 134	226.0	45.5 d,d 130, 134	40.1 d, 141	29.9 t, 133	29.9 t, 133	39.0 t, 132			135.0 (C1′), 144.5, (C2′,6′), 118.6 (C3′,5′), 182.8 (C4′)	59.9 q, 151
15c (R = 4′-CH$_3$)	40.3 d, 141	49.3 d,d 125, 131	252.2	49.3 d,d 125, 131	40.3 d, 141	30.6 t, 132	30.6 t, 132	38.4 t, 131			139.5 (C1′), 140.5 (C2′,6′), 134.0 (C3′,5′), 174.5 (C4′)	25.0
15e (R = H)	39.6 d, 143	51.7 d,d 125, 136	265.4	51.7 d,d 125, 136	39.6 d, 143	31.1 t, 131	31.1 t, 131	37.9 t, 131			155.6 (C1′), 132.9 (C2′,6′), 140.2 (C3′,5′), 141.5 (C4′)	
17	66.5 d, 148	322.9	66.5 d, 148	52.8 t, 137	29.3 d, 137	36.7 t, 131						41.2 q, 132
18b[e] (R = 4′-OCH$_3$)	44.3 d, 141	237.5		45.6 t, 135	28.7 d, 138	36.4					*d*	59.2
18c (R = 4′-CH$_3$)	49.5 d, 140	260.4		48.1 t, 135	29.6 d, 136	36.6 t, 128						
18d (R = 4′-Cl)	51.8 d, 141	268.2		49.7 t, 135	30.0 d, 137	36.7 t, 129						
18e (R = H)	51.5 d, 142	271.6		49.5 t, 134	29.8 d, 135	36.5 t, 131						
18f (R = 3′-Cl)	54.2 d, 142	277.2		51.6 t, 135	30.2 d, 137	36.7 t, 133						
18i [R = 3′,5′-(CF$_3$)$_2$]	58.7 d, 145	286.2		54.3 t, 136	31.1 d, 136	37.1 t, 129						122.9 (q, 273)
19[f]	46.7 d, 137	218.4	46.7 d, 137	39.1 t, 129	27.4 d, 134	36.2 t, 129						
21[g]	80.7 d, 171	270.2	55.2 t, 133	42.8 d, 154	23.5 t, 137	35.5 d,d 145, 149	40.1 t, 141					27.9 q, 132
22[h]	49.8 d, 148	215.3	45.2 t, 133	35.4 d, 144	27.3 t, 132	24.2 t, 134	36.7 t, 135					
23	45.1 d, 148	45.1 d, 148	32.4 t, 133	29.4 t, 128	35.2 t, 133	55.8 d, 152	81.9 d, 168	298.6	61.1 dd, 133	36.7 t, 126		32.2 q, 132
24	39.7 d, 146	41.9 d, 137	31.4 t, 132	28.1 t, 131	31.6 t, 132	46.9 d, 137	54.3 d, 149	217.2	44.5 dd, 133	32.3 t, 129		
25	81.8 d, 178	200.3	57.9 dd, 137	42.4 d, 158					54.3 t, 140		132.7 (C5), 143.7 (C6), 125.3 (C7), 150.9 (C8), 177.9 (C10), 105.4 (C11)	26.7 q, 132
26	57.7 d, 154	213.0	50.6 dd, 138	40.1 d, 150					41.5 t, 138		126.4 (C5), 121.3 (C6), 123.3 (C7), 127.1 (C8), 139.5 (C10), 148.4 (C11)	
27a[i] (R = 3′,4′-CH$_2$CH$_2$O)	51.9 d, 152	227.2	45.7 t, 132	37.9 d, 148	26.6 t, 136	30.8 t, 136	40.8 t, 138				136.1 (C1′), 138.4 (C2′), 129.4 (C3′), 183.4 (C4′), 115.4 (C5′), 148.0 (C6′)	79.5 t, 158 27.0 t, 137
27b (R = 4′-F)	58.9 d, 157	255.9	50.4 t, 133	39.9 d, 153	25.8 t, 136	33.9 t, 140	41.8 t, 137				131.1 (C1′), 146.5[j] (16, C2′), 121.2 (23, C3′), 178.3 (288, C4′), 121.2 (23, C5′), 146.4 (16, C6′)	
27c (R = 3′-CH$_3$)	59.2 d, 157	259.7	50.6 t, 133	40.0 d, 152	25.9 t, 136	34.3 t, 140	41.8 t, 137				134.2 (C1′), 139.4[k] (C2′), 144.1 (C3′), 154.0 (C4′), 132.6 (C5′), 141.4[k] (C6′)	20.8 q, 129
27d (R = 3′-Cl)	62.1 d, 160	263.1	51.9 t, 132	40.8 d, 152	25.6 t, 137	36.0 t, 144	42.0 t, 140				138.8 (C1′), 139.6[k] (C2′), 134.5 (C3′), 150.4 (C4′), 133.7 (C5′), 139.9[k] (C6′)	

Table I. (Continued)

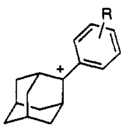
cation	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	aryl	CH_3
27e (R = H)	59.6 d, 158	260.6	50.8 t, 133	39.9 d, 153	25.7 t, 137	34.5 t, 142	41.7 t, 137				133.7 (C1′), 141.0^k (C2′), 132.6 (C3′), 152.4 (C4′), 132.6 (C5′), 141.8^k	
27f (R = 3′-CF_3)	63.3 d, 161	264.3	52.4 t, 133	41.1 d, 153	25.5 t, 136	36.6 t, 144	42.1 t, 140				133.0 (C1′), 143.2^k (C2′), 136.7 (23, C3′), 146.1 (C4′), 133.4 (C5′), 144.2^k (C6′)	123.4, (q, 273)

[a] Chemical shifts ±0.1 ppm from external (capillary) Me_4Si for cations and internal Me_4Si for neutral compounds; coupling constants ($^1J_{CH}$) ± 1 Hz. [b] From ref 5. [c] Complex spectra due to mixtures of cations, for both **11h** and **11i**. [d] A complete set of ^{13}C chemical shift data appears in ref 24. [e] J_{CH} values have been reported for other aryl cations in ref 3. [f] Chemical shifts for **19** have been reported previously, see: Hawkes, G. E.; Herwig, K.; Roberts, J. D. *J. Org. Chem.* **1974**, *39*, 1017. [g] From ref 2. [h] From ref 3. [i] Data for other cations in this series have been reported, see ref 3. Values reported here are for cations (0.3–0.5 M) at −40 °C in FSO_3H/SO_2ClF. [j] Couplings to ^{19}F in parentheses. [k] Assignments may be interchanged.

and 6-arylbicyclo[3.2.1]octyl cations (**16h**,**i**) by comparison of their ^{13}C shifts with literature values[20,23] and direct generation. In addition, quenching of the cation solution prepared from **14h** in methoxide/methanol yielded 2-methoxy-2-(4′-(trifluoromethyl)-phenyl)bicyclo[2.2.2]octane identical to authentic material (Scheme I). The methyl ether of **14h** was not detected (GLC) in the mixture.

2-Adamantyl Cations. Since both the tertiary 2-bicyclo[2.1.1]-hexyl and 2-bicyclo[2.2.2]octyl cations **9** and **10** are associated with the possibility of distorted geometry ($\theta < 90°$ for C_1H), we have examined data for the 2-adamantyl cations[23,24] in which steric strain/distortion should be minimized, if not absent. However, measurement of J_{C_1H} for **17** gave 148 Hz, only 11 Hz greater than that for the model ketone **19**. This is half that predicted for a rigid, strain-free adamantyl structure with θ = 90° (eq 1). Since J_{C_1H} of **19** (137 Hz) is similar to other α-CH couplings in bicyclic ketones, e.g. bicyclo[3.2.1]octan-2-one, 140 Hz,[25] the low ΔJ value of 11 Hz is due to an anomalously low value in the cation **17**. In the absence of significant delocalization of charge at C2 by equilibration or bridging (δ_{C2} = 323 ppm[26,27]), or of second-order effects in the proton spectrum,[28] the low value reflects a dihedral angle substantially less than 90°, i.e. *ca.* 54°. Such gross distortion from planarity at the cationic center to give essentially a pyramidal cation seems initially unlikely, but there is mounting, independent evidence to support this hypothesis.

17



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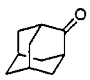

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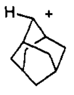

20

Firstly, from a ^{13}C study of unsymmetrically substituted 2-adamantyl cations, 2,5-dimethyl- and 2,2,4-trimethyladamantyl, Sorensen *et al.* argued for a rapidly equilibrating pair of nonplanar structures, on the bases of the temperature dependence of the (nonequivalent) β-carbons. They concluded, "distortions of up to ±20° do not seem unreasonable to us".[29]

Secondly, *ab initio* molecular orbital calculations support a C_s symmetric structure for the theoretical secondary 2-adamantyl cation (**20**), in which the C1–C2–C3 bridge is bent toward the β-carbons of one side by 17° and the C2–H bond by a further 11° toward the same side.[30]

Thirdly, from an X-ray study of the $SbCl_5$ complex of 5-phenyl-2-adamantanone, Laube concluded that distortion about the carbonyl bond was due to different electron distributions on the two sides as a result of C–C hyperconjugation.[31]

Fourthly, independent studies by le Noble[32] and Adcock[33] of reactions of 5-substituted-2-adamantyl derivatives, in which the ratio of *Z*/*E* products is influenced by the electron-donating ability of the 5-substituent (C < Si < Sn), support the capture of "pyramidal" 2-adamantyl cations.

Reduced values of ΔJ are also observed for the 2-aryl cations **18** where J_{C_1H} varies by only 4 Hz from 141 Hz for R = 4′-CH_3O to 145 Hz for R = 3′,5′-$(CF_3)_2$, which suggests nonplanarity in this series of cations as well (Table I). The low value of J_{C_1H} observed recently for the 2-vinyl adamantyl cation[34] is presumably due in part to charge delocalization (δC^+ 283.5, **18e** 271.6).

Bicyclo[2.2.1]heptyl Cations. The tertiary 2-methyl-2-norbornyl cation **21**, although claimed to be a partially σ-bridged species with an unsymmetrical three-center, two-electron bond,[35] appears to be a static, classical cation according to the ΔJ criterion. Thus $^1J_{C_1H}$ increases by 23 Hz over that of 2-norbornanone (**22**) ($\theta \sim 80°$) and $^1J_{C_3H}$ shows no enhancement as predicted for θ = 30°.[2]

In order to provide comparative data, we prepared the 5,6-disubstituted 2-norbornyl cations **23** and **25** from the corresponding tertiary alcohols. Comparison with the ketones **24** and **26** gives ΔJ values for all three cations consistent with our predictions of the stereochemistry of the cations (HC1–C$^+$ $\theta \sim$ 80°, HC3–C$^+$ $\theta \sim$ 30°), ΔJ_{C_1H} = 19–24 Hz, ΔJ_{C_3H} = 0–1 Hz. Thus these three tertiary norbornyl cations **21**, **23**, **25** are all nonbridged ions according to this criterion. In the series of 2-aryl-substituted norbornyl cations, J_{C_1H} of 2-phenylnorbornyl **27e** is reduced from that in **21** by 13 Hz to 158 Hz.[3] A plot of ΔJ_{C_1H}

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(25) Other examples include the following. (a) J_{C_5H} for bicyclo[3.2.1]octan-6-one δ (*J*) 18.8 (t, 129 Hz, C3), 30.5 [t, 130 Hz, C2 (C4)], 30.7 [t, 130 Hz, C4 (C2)], 32.2 (d, 138 Hz, C1), 37.2 (t, 133 Hz, C8), 43.6 (t, 128 Hz, C7), 46.2 (d, 136 Hz, C5), 222.3 (s, C6). Chemical shifts have been reported previously: Grover, S. H.; Marr, D. H.; Stothers, J. B.; Tan, C. T. *Can. J. Chem.* **1975**, *53*, 1351–1361. (b) J_{C_1H} for bicyclo[3.2.1]octan-2-one δ (*J*) 27.7 (t, 127 Hz, C6,7), 31.8 (t, 124 Hz, C4), 33.7 (d, 136 Hz, C5), 34.5 (t, 135 Hz, C3), 38.0 (t, 132 Hz, C8), 51.0 (d, 140 Hz, C1), 215.0 (s, C2). Chemical shifts have been reported previously: Lippmaa, E.; Pehk, T.; Belikova, N. A.; Bobyleva, A. N.; Kalinichenko, A. N.; Ordubadi, M. D.; Platé, A. F. *Org. Magn. Reson.* **1976**, *8*, 74–78. (c) J_{C_1H} for bicyclo[3.3.1]nonan-9-one δ (*J*) 20.5 (t, 128 Hz, C3,7), 34.2 (t, 130 Hz, C2,4,6,8), 46.5 (d, 135, C1,5), 221.9 (s, C9). Chemical shifts have been reported previously: Peters, J. A.; van der Toorn, J. M.; van Bakkum, H. *Tetrahedron* **1977**, *33*, 349–351. Schneider, H.-J.; Lonsdorfer, M.; Weigand, E. F. *Org. Magn. Reson.* **1976**, *8*, 363–367.

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(28) The possibility, that strong interproton coupling may give rise to second-order effects in the proton-coupled ^{13}C NMR spectrum, was checked by measurement of J_{CH} at a higher field strength. The ^{13}C–^1H spectrum of **17** gave J_{C_1H} = 148 Hz at 50 MHz and 147 Hz at 25 MHz.

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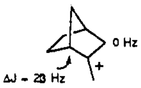

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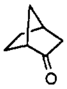

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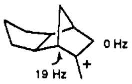

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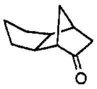

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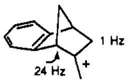

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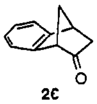

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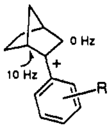

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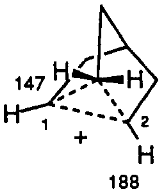
a R = 3′,4′-CH_2CH_2O-
b R = 4′-F
c R = 3′-CH_3
d R = 3′-Cl
e R = H
f R = 3′-CF_3

against σ^+ (or $\sigma^{\alpha C+}$) for a complete range of substituents,[36,37] 3,4-OCH_2CH_2 to 3,5-$(CF_3)_2$, gives an excellent linear correlation with no deviation at high electron demand, unlike the case for the cationic carbon shifts (Figure 1).[20,38] Thus no "onset" of bridging is detected with this probe.[38,39]

It is pertinent now to apply the ΔJ criterion to the parent secondary 2-norbornyl cation, the subject of intensive investigation and extensive review over many years.[40] Relatively recent studies both theoretical[41] and experimental[42] support a single, symmetrical minimum energy structure (**28**) for the cation in superacid media.



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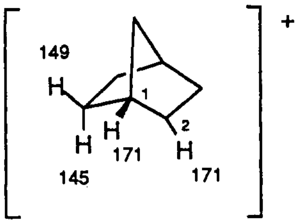

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At −80 °C, the ^{13}C signal attributed to C1,2,6 of **28** at δ 91.7 is a quintet with an unusually low J_{CH} value of 55.1 Hz.[43] This has been interpreted as being due to equilibration of the three carbons and four hydrogen atoms. At −159 °C the cation is essentially 'frozen out' with C1,2 appearing as a doublet at δ 124 with J_{CH} = 188 Hz and C6 as a triplet at δ 21.2 with J_{CH} = 147 Hz. Estimation of $J_{C_{1,2,6}H}$ at −80 °C [$(2 \times 188 + 2 \times 147)/12$] reproduces the equilibrium value of J_{CH} almost exactly (55.8 Hz).[43]

Estimation of the average value for an assumed classical cation yields a different value. Using values for a secondary C^+H (171 Hz) and for C1H and C6H from 2-methylnorbornyl (171, 145/149 Hz),[2] the J_{CH}(av) is 53.0 Hz. Although this value is only 2.1 Hz different from the experimental value at −80 °C, the difference is a result of averaging over four hydrogens and three carbons.

More convincing evidence for **28** may be elicited from consideration of $J_{C_{1,2}H}$ at −159 °C, 188 Hz.[43] This represents a massive increase over J_{C_1H} of 2-norbornanone (148 Hz), much greater than predicted by eq 1, greater than those observed in $\pi\sigma$-bridged cations, and consistent with the idea of increasing internal strain accompanying σ-bridge formation as originally proposed.[44] In fact $J_{C_{1,2}H}$ has the same value as that for C1,6 in the 3-methylnortricyclyl cation and is consistent with the formation of a three-membered ring bearing positive charge. Thus application of the ΔJ equation supports a σ-bridged nonclassical structure for the secondary 2-norbornyl cation.

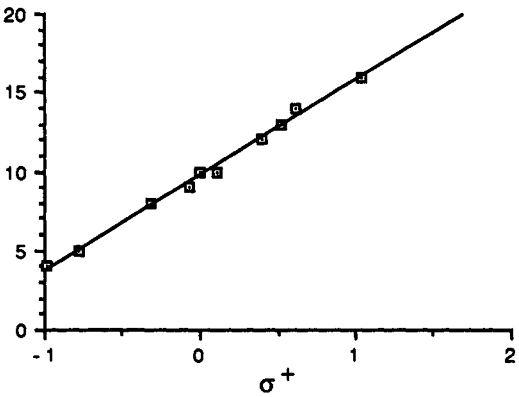

Figure 1. Correlation of ΔJ_{C_1H} with electron demand in 2-arylbicyclo[2.2.1]heptyl cations **27** (correlation coefficient 0.993; for $\sigma^{\alpha C+}$, $r = 0.988$).

The ΔJ equation is thus useful in determining the structure of carbocations in superacids. Low values of ΔJ result from equilibration as in the case of **2** or from distortion of the idealized geometry. In the case of **17** this provides additional evidence to support a hypothesis that these cations are distorted significantly from sp^2 toward sp^3(pyramidal) hybridization. Relatively high values of ΔJ are associated with the formation of nonclassical structures, as a result of π-bridging (**4**), πσ-bridging (**6**), or σ-bridging (**28**).

Experimental Section

NMR Spectra. The proton and carbon NMR spectra were recorded on a variety of instruments under conditions as described previously.[5] Chemical shifts of cationic solutions in superacids were measured from external (capillary) Me_4Si. Coupling constants (±1 Hz) were measured by hand from expanded plots. In some cases of complex spectra, selective excitation (DANTE) or editing (coupled DEPT) techniques were employed to obtain J_{CH} values from overlapping signals.

Synthesis. Bicyclo[3.2.1]octan-2-one, adamantanone (**19**), bicyclo[3.3.1]nonan-9-one, 2-norbornanone (**22**), and tricyclo[5.2.1.0^{2,6}]decan-8-one (**24**)[48] were commercially available (Aldrich). Bicyclo[2.2.2]octan-2-one (**12**),[45] bicyclo[3.2.1]octan-6-one,[46] bicyclo[3.2.1]octan-3-one (**13**),[47] and benzonorbornan-2-one (**26**)[49] were prepared according to literature procedures.

3-Arylbicyclo[3.2.1]octan-3-ols were prepared from **13** by reaction with the appropriate arylmagnesium bromide, the unreacted ketone was removed under vacuum, and the products were recrystallized from petroleum ether (60–80 °C). **14b**, white needles (43%), mp 84–85 °C, ν_{max} 3460 cm^{-1}; δ ^1H ($CDCl_3$) 7.2–7.5 (m, 4H), 3.8 (s, 3H, OCH_3), 1.5–2.8 (m, 12H); δ ^{13}C ($CDCl_3$) 35.0 (d, C1,5), 47.3 (t, C2,4), 74.2 (s, C3), 28.4 (C6,7), 143.4 (s, C1′), 125.6 (d, C2′,6′), 113.3 (d, C3′,5′), 157.9 (s, C4′), 55.1 (q, OCH_3); MS *m/z* (%) 232 ($M^{\cdot+}$, 40), 214 (37), 185 (63), 150 (100). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.6; H, 8.7. Found: C, 77.6; H, 8.8. **14c**, white plates (64%), mp 109–110 °C, ν_{max} 3460 cm^{-1}; δ ^1H ($CDCl_3$) 7.1–7.5 (m, 4H), 2.30 (s, 3H), 1.4–2.4 (m, 11H). δ ^{13}C ($CDCl_3$) 35.0 (d, C1,5), 47.4 (t, C2,4), 74.5 (s, C3), 28.5 (t, C6,7), 135.8 (s, C1′), 128.7 (d, C2′,6′), 124.4 (d, C3′,5′), 148.2 (s,

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[36] J_{CH} values for some of these cations have been reported previously.[3] Additional data are provided in Table I.

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Table II. ^{13}C NMR Chemical Shifts for 2-Arylbicyclo[2.2.2]octan-2-ols

aryl substituent	C1	C2	C3	C4	C5	C6	C7	C8	C1′	C2′	C3′	C4′	C5′	C6′	CX
3′,4′-CH_2CH_2O[a]	32.5	132.5	121.4	30.5	25.8	26.9	25.8	26.9	144.6	124.5	127.1	159.1	109.1	126.8	29.9 71.3
4′-OMe[a]	32.2	132.3	127.2	30.4	25.9	26.2	25.9	26.2	144.2	125.7	113.8	158.5	113.8	125.7	55.3
4′-Me	35.9	74.9	42.1	26.0	21.1	24.3	22.5	25.1	136.4	128.7	125.9	145.1	125.9	128.7	20.9
4′-Cl	35.9	74.7	42.0	25.7	20.9	24.0	22.2	24.9	132.4	127.9	127.5	146.4	127.5	127.4	
H	35.9	75.1	42.0	25.9	21.1	24.2	22.4	25.1	148.0	128.0	126.0	126.6	126.0	128.0	
3′-Cl	35.9	74.9	42.0	25.7	21.0	24.1	22.2	24.9	150.2	126.5[b]	134.0	129.2[b]	124.2	126.9[b]	
4′-CF_3	36.0	74.9	41.9	25.7	20.8	23.8	22.1	24.7	152.1	126.4	125.3	129.0	125.3	126.4	124.5

[a] Alkene. [b] Assignments may be interchanged.

C4′), 20.8 (q, CH_3). MS *m/z* (%) 216 ($M^{\cdot +}$, 34), 201 (42), 134 (100). Anal. Calcd for $C_{15}H_{20}O$: C, 83.3; H, 9.3. Found: C, 83.5, H 9.0. **14e**, white plates (77%), mp 80–81 °C, ν_{max} 3460, 3020 cm^{-1}; δ ^{1}H ($CDCl_3$) 7.2–7.5 (m, 5H), 1.5–2.8 (m, 12H). δ ^{13}C ($CDCl_3$) 35.0 (d, C1,5), 47.4 (t, C2,4), 74.6 (s, C3), 28.5 (t, C6,7), 38.6 (t, C8), 151.1 (s, C1′), 128.0 (d, C2′,6′), 123.5 (d, C3′,5′), 126.2 (d, C4′). MS *m/z* (%) 202 ($M^{\cdot +}$, 36), 173 (9), 159 (15), 145 (10), 120 (100). Anal. Calcd for $C_{14}H_{18}O$: C, 83.1; H, 9.0. Found: C, 83.7; H, 8.5. **14g**, white plates (35%), mp 67–68 °C, ν_{max} 3460, 3040 cm^{-1}; δ ^{1}H ($CDCl_3$) 7.3–7.8 (m, 4H), 1.5–2.5 (m, 12H). δ ^{13}C ($CDCl_3$) 35.0 (d, C1,5), 47.5 (t, C2,4), 74.5 (s, C3), 28.5 (t, C6,7), 38.5 (t, C8), 152.2 (s, C1′), 123.3 (q, C2′ or 4′), 129.5 (s, C3′), 121.6 (q, C4′ or 2′), 128.0 (d, C5′ or 6′), 128.6 (d, C6′ or 5′), 124.4 (q, CF_3). MS *m/z* (%) 270 ($M^{\cdot +}$, 32), 252 (15), 227 (12), 201 (10), 189 (31), 188 (100). Anal. Calcd for $C_{15}H_{17}OF_3$: C, 66.7; H, 6.3. Found: C, 67.3; H, 6.3. **14h**, pale-yellow needles (52%), mp 122 °C, ν_{max} 3460 cm^{-1}; δ ^{1}H ($CDCl_3$) 7.56 (s, 4H), 1.6–2.4 (m, 12H). δ ^{13}C ($CDCl_3$) 34.9 (d, C1,5), 47.5 (t, C2,4), 74.8 (s, C3), 28.5 (t, C6,7), 38.6 (t, C8), 155.0 (s, C1′), 125.1 (d, C2′,6′), 124.9 (d, C3′,5′), 129.3 (s, C4′), 124.3 (q, CF_3). MS *m/z* (%) 270 ($M^{\cdot +}$, 29), 201 (42), 187 (10), 173 (15), 169 (11), 134 (100). Anal. Calcd for $C_{15}H_{17}OF_3$: C, 66.7; H, 6.3. Found: C, 67.0; H, 6.4.

2-Arylbicyclo[2.2.2]octan-2-ols were prepared from **12** by reaction with the appropriate aryl magnesium bromide. Distillation and/or recrystallization gave the required alcohol. Some products were contaminated by the corresponding olefin, a result of dehydration during purification procedures. For the purposes of cation generation, however, the presence of alcohol/olefin mixtures can be tolerated, since both afford the same cation upon protonation in superacid media. The ^{13}C chemical shifts for the 2-arylbicyclo[2.2.2]octan-2-ols are presented in Table II. Apart from the 2-(3′,4′-ethyleneoxyphenyl) derivative, the 2-arylbicyclo[2.2.2]-octanols have been described previously.[21]

2-(3′,4′-(Ethyleneoxy)phenyl)bicyclo[2.2.2]oct-2-ene was prepared by reaction of **12** with 5-lithio-2,3-dihydrobenzofuran,[50] followed by workup and dehydration. Distillation afforded the title compound as a viscous yellow oil, bp 125–135 °C/0.3 mmHg, ν_{max} 2850, 1590, 1470, 1210 cm^{-1}; δ ^{1}H ($CDCl_3$) 7.1 (d, 2H), 6.7 (s, 1H), 6.3 (d, 1H), 4.5 (t, 2H), 3.1 (t, 2H), 1.2–1.9 (m, 10H).

2-(4′-Methoxyphenyl)bicyclo[2.2.2]octan-2-ol,[51,52] after distillation a yellow oil, bp 110–120 °C/0.2 mmHg, ν_{max} 3400 cm^{-1}. **2-(4′-Methylphenyl)bicyclo[2.2.2]octan-2-ol,**[51,52] after distillation an oil, bp 123–125 °C/0.5 mmHg, ν_{max} 3400, 2920 cm^{-1}; δ ^{1}H ($CDCl_3$) 6.9–7.4 (m, 4H), 2.3 (s, 3H), 1.0–1.9 (m, 12H). **2-(4′-Chlorophenyl)bicyclo[2.2.2]-octan-2-ol,**[52] after distillation a viscous oil, bp 125–135 °C/2 mmHg (lit.[52] 125–145 °C/3 mmHg), ν_{max} 3380, 2920 cm^{-1}; δ ^{1}H ($CDCl_3$) 7.1–7.4 (m, 4H), 1.3–2.5 (m, 12H). **2-Phenylbicyclo[2.2.2]octan-2-ol,**[51,52] after distillation a viscous oil, bp 95–100 °C/0.2 mmHg (lit.[52] 135–152 °C/15 mmHg), ν_{max} 3380, 2920 cm^{-1}; δ ^{1}H ($CDCl_3$) 7.1–7.5 (m, 5H), 1.3–2.5 (m, 12H). **2-(3′-Chlorophenyl)bicyclo[2.2.2]octan-2-ol,**[52] after distillation a viscous oil, bp 115–120 °C/0.5 mmHg (lit.[52] 60 °C/0.3 mmHg, molecular distillation), ν_{max} 3350, 2900 cm^{-1}; δ ^{1}H ($CDCl_3$) 7.0–7.5 (m, 4H), 1.2–2.5 (m, 12H). **2-(4′-(Trifluoromethyl)phenyl)bicyclo[2.2.2]octan-2-ol,**[51,53] after distillation a viscous oil, bp 110–120 °C/2 mmHg, ν_{max} 3300, 2950 cm^{-1}; δ ^{1}H ($CDCl_3$) 7.2–7.8 (m, 4H), 1.1–2.7 (m, 12H).

The syntheses of the **2-aryltricyclo[3.3.1.1^{3,7}]decan-2-ols,** precursors of cations **18**, have been reported in the literature.[24,37,54] Previously unreported ^{13}C NMR chemical shifts for these alcohols are tabulated in the supplementary material.

8-Methyl-2,6-*exo*-8-*endo*-tricyclo[5.2.1.0^{2,6}]decanol was prepared from ketone **24** by treatment with methylmagnesium iodide. Recrystallization (pentane) yielded the alcohol as white needles, mp 79–81 °C (lit.[48] 81.5–82 °C), δ ^{13}C ($CDCl_3$) 27.9 (C4), 30.3 (CH_3), 31.7 (C3), 32.4 (C10), 32.6 (C5), 39.2 (C2), 41.7 (C6), 46.5 (C9), 46.7 (C1), 52.7 (C7), 76.9 (C8).

The syntheses of the alcohol precursors to cations **27a–e** have been reported.[20,50,52] However, we now quote the previously unreported ^{13}C NMR spectral data for the following alcohols:

2-(3′,4′-(Ethyleneoxy)phenyl)-2-*endo*-bicyclo[2.2.1]heptanol, after distillation and recrystallization, a white solid, mp 71–74 °C (lit.[50] 75–76 °C); δ ^{13}C ($CDCl_3$) 22.2 (C5), 29.7 (C6), 37.6 (C4), 38.7 (C7), 46.7 (C3), 47.3 (C1), 80.6 (C2), 29.1 ($\mathit{C}H_2CH_2O$), 71.3 ($CH_2\mathit{C}H_2O$), 108.4 (C5′), 122.8 (C2′), 125.4 (C6′), 126.9 (C3′), 141.4 (C1′), 158.8 (C4′).

2-(4′-Fluorophenyl)-2-*endo*-bicyclo[2.2.1]heptanol as white crystals, mp 63–64 °C (lit.[52] 63–64 °C) δ ^{13}C ($CDCl_3$) 47.4 (C1), 80.4 (C2), 46.9 (C3), 37.6 (C4), 22.3 (C5), 29.0 (C6), 38.7 (C7), 144.9 (C1′), 127.6 (C2′,6′), 114.9 (C3′,5′), 161.6 (C4′).

2-(3′-Methylphenyl)-2-*endo*-bicyclo[2.2.1]heptanol as white crystals, mp 57–58 °C; δ ^{13}C ($CDCl_3$) 47.2 (C1), 80.7 (C2), 46.5 (C3), 37.5 (C4), 22.2 (C5), 29.1 (C6), 38.7 (C7), 137.8 (C1′), 126.7 (C2′), 149.0 (C3′), 128.1 (C4′), 122.7 (C5′), 127.5 (C6′), 21.6 (CH_3). Anal. Calcd for $C_{14}H_{18}O$: C, 83.1; H, 9.0. Found: C, 83.5; H, 9.1.

2-(3′-Chlorophenyl)-2-*endo*-bicyclo[2.2.1]heptanol as white crystals, mp 39–41 °C (lit[52] 42–44 °C); δ ^{13}C ($CDCl_3$) 47.3 (C1), 80.5 (C2), 46.8 (C3), 37.6 (C4), 22.3 (C5), 28.9 (C6), 38.8 (C7), 158.2 (C1′), 126.4 (C2′), 134.1 (C3′), 129.5 (C4′), 124.1 (C5′), 126.9 (C6′).

2-Phenyl-2-*endo*-bicyclo[2.2.1]heptanol as white crystals, mp 40–42 °C (lit.[52] 41–42 °C); δ ^{13}C ($CDCl_3$) 47.3 (C1), 80.8 (C2), 46.7 (C3), 37.7 (C4), 22.5 (C5), 29.3 (C6), 39.0 (C7), 149.2 (C1′), 128.4 (C2′,6′), 126.1 (C3′,5′), 126.9 (C4′).

2-(3′-(Trifluoromethyl)phenyl)-2-*endo*-bicyclo[2.2.1]heptanol as white crystals, mp 47–48 °C; δ ^{13}C ($CDCl_3$) 47.4 (C1), 80.6 (C2), 46.9 (C3), 37.6 (C4), 22.2 (C5), 28.9 (C6), 38.8 (C7), 150.0 (C1′), 122.8 (q, 3, C2′), 130.5 (q, 32, C3′), 123.6 (q, 4.4, C4′), 128.7 (C5′), 129.5 (C6′), 124.4 (q, 273, CF_3). Anal. Calcd for $C_{14}H_{15}OF_3$: C, 65.6; H, 5.9; F, 22.2. Found: C, 65.9; H, 6.1; F, 22.4.

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Supplementary Material Available: Table of ^{13}C chemical shifts of 2-aryltricyclo[3.3.1.1^{3,7}]decan-2-ols (2 pages). Ordering information is given on any current masthead page.

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