Rapidly Equilibrating Unsymmetrically Bridged 1,3,5,7-Tetramethyl- and Rapidly Equilibrating Trivalent 1,2,3,5,7-Pentamethyl-2-adamantyl Cations. Additivity of ^{13}C NMR Chemical Shifts Relating the Classical vs. Nonclassical Nature of Carbocations[1]

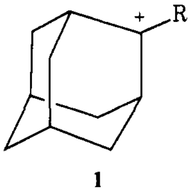
Paul v. R. Schleyer,*[2a] Dieter Lenoir,*[2b] Pierre Mison,[2c] Gao Liang,[2d]
G. K. Surya Prakash,[2e] and George A. Olah*[2e]

Contribution from the Institut für Organische Chemie der Universität Erlangen-Nürnberg, 8520 Erlangen, West Germany, the Organisch-Chemisches Institut der Technischen Universität München, 8046 Garching, West Germany, the Laboratorie de Chimie Organique III, Université Claude Bernard, 69621 Villeurbanne, France, and the Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90007. *Received March 27, 1979*

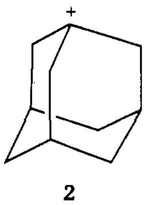
Abstract: The stable secondary 1,3,5,7-tetramethyl-2-adamantyl cation (**3**, R = H), studied by ^{13}C NMR spectroscopy in SbF_5-SO_2ClF solution, was found to be described best as a rapidly equilibrating set of degenerate unsymmetrically bridged ions (**5a–d**). The corresponding tertiary 1,2,3,5,7-pentamethyl-2-adamantyl cation (**3**, R = CH_3), in contrast, is a static trivalent carbocation at low temperatures (below −80 °C). At higher temperatures, **3** (R = CH_3) undergoes degenerate equilibration involving skeletal rearrangement via the corresponding protoadamantyl cations. At higher temperatures, **3** (R = H) isomerizes to the 1,2,5,7-tetramethyl-2-adamantyl cation (**6**, R = H) by a similar mechanism. The differing structures and nature of the secondary and tertiary 2-adamantyl cations (**3**, R = H vs. CH_3) are assigned by means of the ^{13}C chemical shift additivity criterion. The conclusion that deviations from such additivity are due to a higher coordination at carbon (bridged or nonclassical structures) is supported, e.g., by comparisons with known nonclassical and trivalent (classical) ions and by comparisons with related boron compounds. The total ^{13}C chemical shift difference between a carbocation and the corresponding neutral hydrocarbon also provides a rough, but useful, structural index. Classical carbocations show large chemical-shift differences, typically 350 ppm or more, whereas related nonclassical cations display differences often hundreds of parts per million less. There is no sharp distinction between these categories; some cations are indicated to be intermediate in character (e.g., they may be unsymmetrically bridged).

Introduction

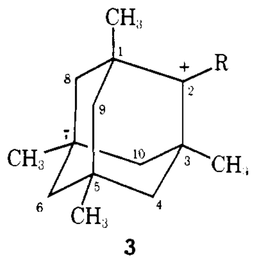
In contrast to the corresponding tertiary species, relatively few secondary carbocations are directly observable in superacid media.[3] For example, both the 2-methyl-2-adamantyl (**1**, R = CH_3)[4] and the 1-adamantyl (**2**) cations[3a,5] are well studied, but the 2-adamantyl cation (**1**, R = H) has not been detected under stable ion conditions despite repeated attempts;[5b,6] intermolecular rearrangement to **2** occurs instead.[5b,6,7] This problem can be overcome by blocking all four bridgehead positions by methyl groups.[8] The structures and behavior of the resulting 1,3,5,7-tetramethyl-2-adamantyl cations (**3**: secondary, R = H; tertiary, R = CH_3) are of particular interest because of their high symmetry. The four β, γ skeletal C–C bonds (C_3C_4, C_3C_{10}, C_1C_8, and C_1C_9) can help delocalize the positive charge through hyperconjugation and/or bridging.[9,10] The ^1H NMR spectrum of **3** (R = CH_3) at −72 °C corresponds to that expected of a static, tertiary ion (five signals). In contrast, the ^1H NMR spectrum of the corresponding secondary cation, **3** (R = H), posed interpretive problems.[8] Below −47 °C, the spectrum also shows five proton signals, but most of these have chemical shifts significantly different from those of the corresponding peaks of **3** (R = CH_3). In addition, the chemical shift of the C^+-H proton (R = H in **3**) at 5.1 ppm is more than 8 ppm displaced from that of the 2-propyl cation.[3b] Both static classical (**3**, R = H) and static bridged (e.g., **5a**) structures are excluded by this evidence, but rapidly equilibrating sets of four equivalent classical tetramethylprotoadamantyl ions (**4a–d**) or of four equivalent bridged ions (**5a–d**) are structural alternatives consistent with the number of proton signals observed and their chemical shifts.[8] Although solvolysis data provide evidence favoring the bridged ion interpretation,[8,11-13] continuing skepticism concerning the reality of three-center two-electron bonding in carbocations[13] and specific criticisms[14] of our earlier conclusions have stimulated us



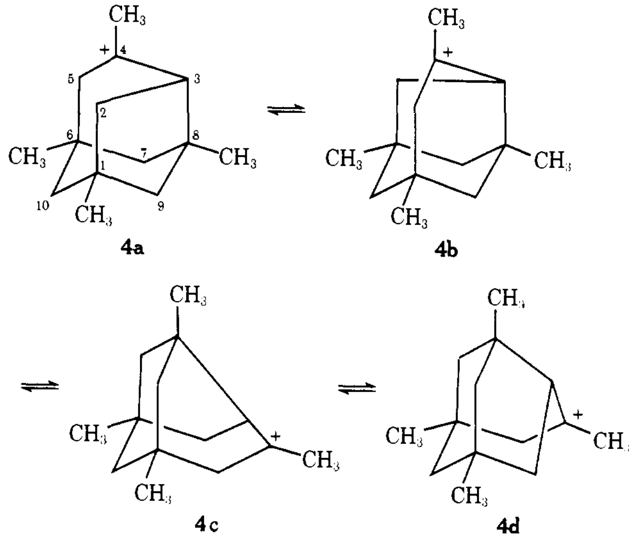
1



2



3



0002-7863/80/1502-0683$01.00/0

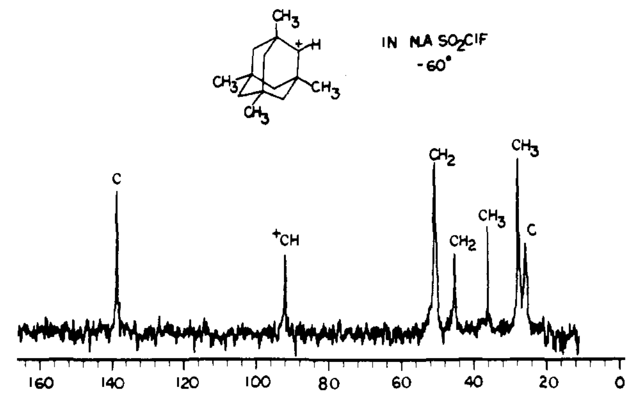
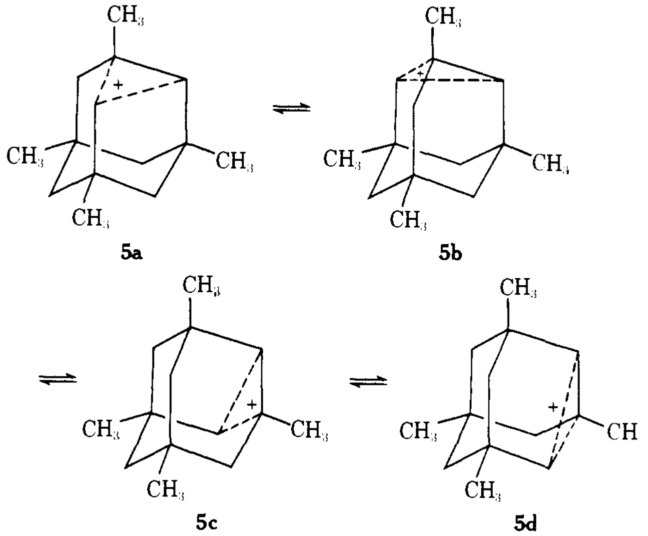


Figure 1. Proton-decoupled ^{13}C NMR spectrum of ion 3 (R = H) at −60 °C. The structure shown is a formal representation (see text).



5a 5b 5c 5d

to obtain ^{13}C NMR information in superacid media on the structures of 3 (R = H and R = CH_3) and related species.

Results

Figure 1 shows the proton decoupled ^{13}C NMR spectrum of the 1,3,5,7-tetramethyl-2-adamantyl cation (formally represented by 3, R = H). Even though the number of signals is consistent with the symmetry of structure 3 (R = H), the ^{13}C chemical shifts (Table I), like the ^1H chemical shifts,[8] deviate markedly from those expected for a static, secondary ion. The corresponding tertiary ion, the 1,2,3,5,7-pentamethyl-2-adamantyl cation (3, R = CH_3), provides a good model for comparison. At −80 °C, its ^{13}C NMR spectrum (Figure 2, bottom) is that of a static, classical species. The spectrum of 3 (R = CH_3) can be calculated with high accuracy (Table I) from that of the 2-methyl-2-adamantyl cation (1, R = CH_3)[4] by using chemical-shift increments based on substitution of adamantane by bridgehead methyl groups[15] as well as the expected additive influence of methyl groups on carbenium ion ^{13}C chemical shifts.[16,17] The spectra of 3 (R = H) (Figure 1) and of 3 (R = CH_3) (Figure 2, bottom) have little in common, as far as the resonance positions of corresponding carbons are concerned (compare Table I). Furthermore, the calculated ^{13}C spectrum of 3 (R = H) does not agree at all with observation (Table I). This contrasts with the success of such calculations on 3 (R = CH_3) and the general finding of additivity of ^{13}C chemical shifts with adamantane derivatives.[15]

At higher temperatures, the ^{13}C spectrum of 3 (R = CH_3) shows an almost exact averaging of the chemical shifts of C_1, C_2, and C_3 and of the methyls attached to these positions (Figure 2, top, and Table I). Except for a small temperature effect (ca. 1 ppm), the positions of all the remaining signals remain unchanged. The previously described[8] degenerate adamantyl ⇌ protoadamantyl ⇌ protoadamantyl ⇌ adamantyl skeletal rearrangement involving a set of equivalent tertiary ions, 3, 6, and 7 (R = CH_3) (Scheme I), is responsible for this behavior.

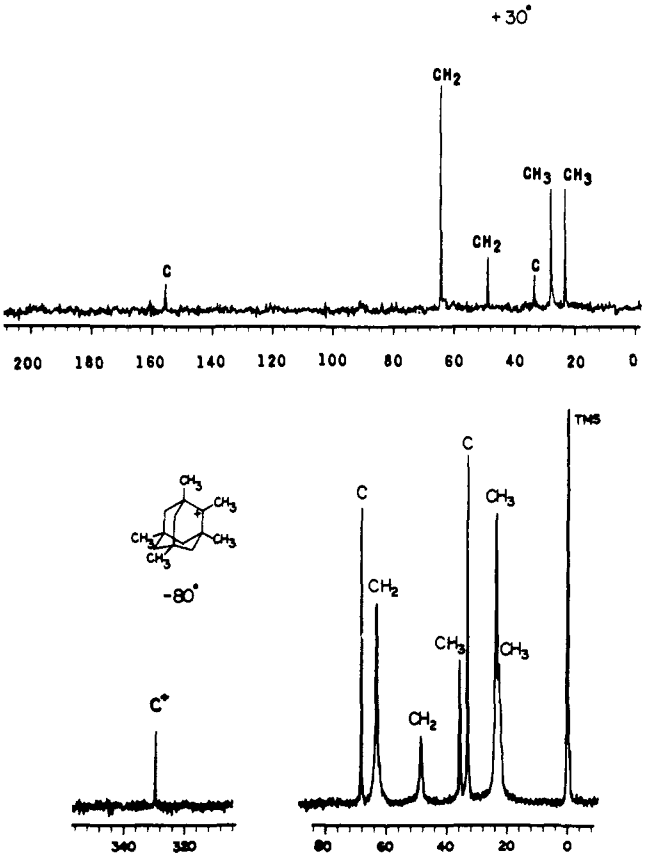


Figure 2. Proton-decoupled ^{13}C NMR spectra of ion 3 (R = CH_3) at −80 (below) and at +30 °C (above).

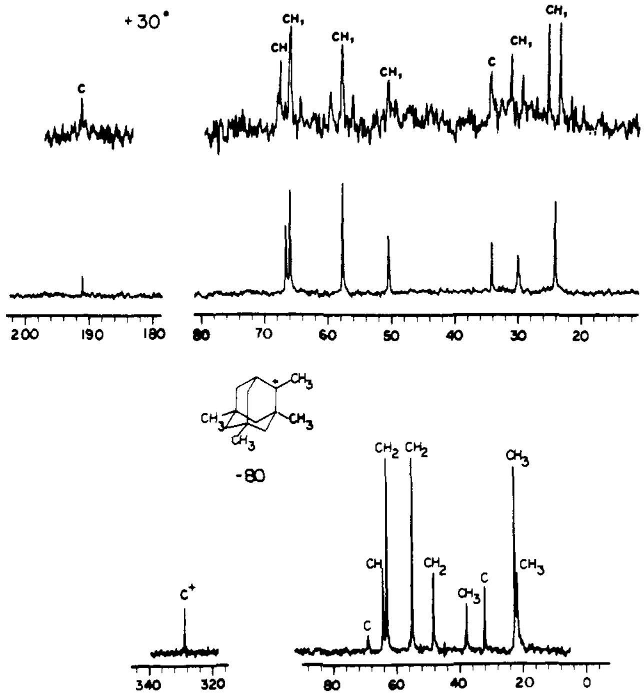


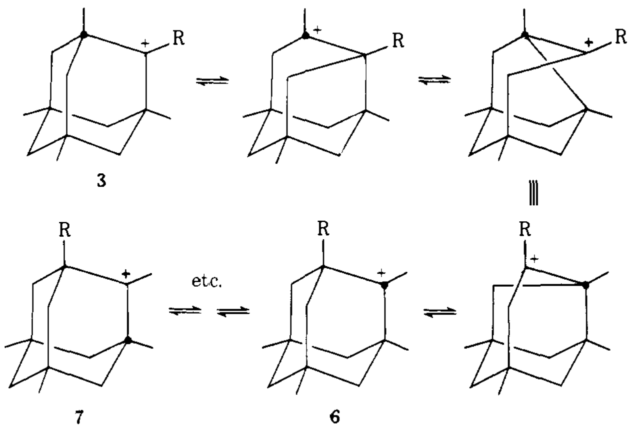
Figure 3. Proton-decoupled ^{13}C NMR spectra of ion 6 (R = H) at −80 (below) and at +30 °C (above). The proton-coupled spectrum at +30 °C is also shown above the decoupled spectrum at the top.

Table I. ^{13}C Chemical Shifts^{a} of 2-Adamantyl Cations and of 4-Protoadamantyl Derivatives

cation	C_1	C_2	C_3	C_4, C_{10}	C_5, C_7	C_6	C_8, C_9	C_1 CH_3	C_2 CH_3	C_3 CH_3	$C_{5,7}$ CH_3
1, R = CH_3	66.3	323.0	66.3	52.6	29.1	36.6	52.6		41.2		
3, R = CH_3, −80 °C	68.3	329.7	68.3	63.7	33.2	48.4	63.7	23.7	35.9	23.7	22.2
calcd	(69.7)^{b}	(323.6)^{b}	(69.7)^{b}	(64.8)^{b}	(32.5)^{b}	(48.8)^{b}	(64.8)^{b}				
+30 °C	156.0	156.0	156.0	64.8	33.9	49.2	64.8	28.4	28.4	28.4	23.8
3, R = H, −60 °C	138.6	92.3	138.6	51.0	26.2	45.7	51.0	38.4		38.4	28.1
calcd	(72.3)^{b}	(315.1)^{b}	(72.3)^{b}	(65.5)^{b}	(33.7)^{b}	(48.4)^{b}	(65.6)^{b}				
4a, calcd	(303.4)^{c}	(76.8)^{c}	(50.4)^{c}	(49.7)^{c} (C_9)	(34.7)^{c} (C_1)	(48.7)^{c}	(56.4)^{c} (C_2)				
	(C_4)	(C_3)	(C_8)	(56.2)^{c} (C_7)	(52.0)^{c} (C_6)	(C_{10})	(68.7)^{c} (C_5)				
4a–d, av calcd	(176.8)	(76.8)	(176.8)	(57.7)	(43.4)	(48.7)	(57.7)				
8	251.6	52.7	39.3 (C_8)	35.0 (C_9)	30.2 (C_1)	34.0	42.8 (C_2)				
	(C_4)	(C_3)				(C_{10})					
				41.5 (C_7)	40.9 (C_6)		44.6 (C_5)				
6, R = H, −80 °C	70.0	328.5	65.3	56.1	33.2	49.3	64.1	23.7	38.9		23.0
calcd	(69.1)^{b}	(322.8)^{b}	(68.1)^{b}	(57.9)^{b}	(31.9)^{b}	(49.6)^{b}	(65.6)^{b}				
+30 °C	190.8	190.8	66.3	57.4	34.0	50.2	65.7	29.9	29.9		24.0

[a] In parts per million, relative to external Me_4Si. [b] Calculated values based on the chemical shifts of **1** (R = CH_3) and methyl increments of ref 16 for the carbocation center and of ref 15 for the remaining positions. To calculate **3**, R = H, experimental chemical shifts for **3**, R = CH_3 (−80 °C), and the cation increments of ref 15 were used. [c] Calculated values for the hypothetical static tertiary species, **4a**. Protonated 4-protoadamantanone (**8**) was used to model the hypothetical static 4-methyl-4-protoadamantyl cation by using the protonated adamantanone (**9**) vs. 2-methyl-2-adamantyl cation (**1**, R = CH_3) chemical shift differences (ref 4): α = 55.9, β = 18.8, γ = 8.3, δ = 1.7, and ϵ = 1.3 ppm. Values for **4a** were then calculated by the procedure of footnote *b*. See text.

Scheme I. Illustration of the Adamantyl ⇌ Protoadamantyl ⇌ Protoadamantyl ⇌ Adamantyl Skeletal Rearrangement^{a}



^{a}One of the ring atoms is labeled for clarity.

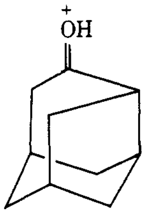
The same skeletal rearrangement of the secondary cation **3** (R = H) is not degenerate, but leads to the more stable isomer, the tertiary 1,2,5,7-tetramethyl-2-adamantyl cation, **6** (R = H).[8] This occurs at temperatures above −45 °C. The spectra are shown in Figure 3. At −80 °C, **6** (R = H) is a static classical ion displaying the ten carbon resonances as expected from C_s symmetry (Figure 3, bottom). As shown in Table I, the chemical shifts can also be calculated accurately using group increments. Also like **3** (R = CH_3), **6** (R = H) undergoes rapid degenerate rearrangement to **7** (R = H) at 30 °C, as indicated by the eight carbon resonances observed in its proton-decoupled ^{13}C spectrum (Figure 3, top). In this case, only C_1 and C_2 (and their attached methyl groups) exchange (**6** ⇌ **7**, R = H); their chemical shifts are averaged (although not as exactly as are those of **3** (R = CH_3) at +30 and −80 °C, Table I) as a consequence.

Structure of the 1,3,5,7-Tetramethyl-2-adamantyl Cation (3, R = H). We now turn to the central question of this paper: What is the best way to describe the nature of the secondary cation, **3** (R = H)? Three possibilities will be analyzed: a static trivalent (classical) structure, a rapidly equilibrating set of such classical structures, and a rapidly equilibrating set of unsymmetrically bridged (nonclassical) structures.

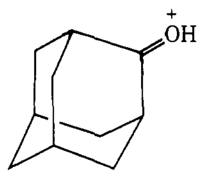
The resonance at 92.3 ppm (a doublet in the off-resonance spectrum) assigned to C_2, the "carbonium carbon" in **3** (R = H), is more than 200 ppm removed from the resonances associated with static classical cations in saturated systems.[16,17] This discrepancy is emphasized by the spectrum calculated for the hypothetical static, classical cation **3** (R = H) (Table I). There is no agreement with the observed values, unlike the situation with **3** (R = CH_3) and with **6** (R = H). The static, classical structure **3** (R = H) is not a viable possibility for this species.

We next consider the rapidly equilibrating set of four classical 1,4,6,8-tetramethyl-4-protoadamantyl cations **4a–d** (R = H). On time average, such a set (perhaps with some **3** (R = H) in equilibrium) will have symmetry properties consistent with the observed spectrum (Figure 1). The most deshielded carbons in this spectrum are C_1 and C_3 in **3** (R = H) (equivalent to C_4 and C_8 in **4a**) which are expected to bear much of the charge under such circumstances. The signals for the methyls attached to these positions are also shifted some 10 ppm to lower fields.

The spectrum for a hypothetical static 1,4,6,8-tetramethyl-4-protoadamantyl cation (e.g., **4a** (R = H)) was calculated (Table I) based on the ^{13}C spectrum of protonated 4-protoadamantanone (**8**) and conversion increments (Table I, footnote *c*) derived from the chemical-shift differences observed between protonated 2-adamantanone (**9**) and the 2-methyl-2-adamantyl cation (**1**, R = CH_3).[4] Such procedures are approximate, but should give reasonably good estimates for the chemical shifts of **4a** (R = H). From this estimate, the calculated spectrum of a rapidly equilibrating mixture of ions **4a–d** can be obtained (Table I).



8



9

Even allowing for some uncertainty in these estimates, there seems to be no way to reconcile the observed spectrum of the 1,3,5,7-tetramethyl-2-adamantyl cation with that calculated

Table II. Total ^{13}C Chemical-Shift Differences between Carbocations and Corresponding Hydrocarbons^{a}

carbocation	^{13}C chemical shift sum	hydrocarbon	^{13}C chemical shift sum	total chemical shift difference
A. Classical Ions				
2-propyl	423	propane	47	376
2-methyl-2-propyl	478	2-methylpropane	98	380
2-methyl-2-butyl	491	2-methylbutane	117	374
3-methyl-3-pentyl	505	3-methylpentane	137	369
2,3-dimethyl-2-butyl	524	2,3-dimethylbutane	145	379
2,2,3-trimethyl-3-butyl	563	2,2,3-trimethylbutane	185	378
cyclopentyl	496	cyclopentane	133	364
1-bicyclo[4.4.0]decyl	710^{b}	*trans*-decalin	344	367
1-methylcyclooctyl	659^{c}	methylcyclooctane	(263)	396
1-methylcycloheptyl	593^{c}	methylcycloheptane	(247)	346
1-methylcyclohexyl	573	methylcyclohexane	211	362
1-methylcyclopentyl	558	methylcyclopentane	184	374
3-pent-2-enyl	669^{d}	2-pentene	(313)	356
cyclopentenyl	712^{e}	cyclopentene	350	362
cyclohexenyl	647^{e}	cyclohexene	352	296
benzenium	877^{f}	1,4-cyclohexadiene	548^{g}	329
1,2-dimethylcyclopentyl	$583^{b,h}$	1,2-dimethylcyclopentane	(229)	354
1,2-dimethylcyclohexyl	$603^{b,h}$	*trans*-1,2-dimethylcyclohexane	250	353
3-nortricyclyl	703^{i}	nortricyclene	159	544
3-methyl-3-nortricyclyl	696^{i}	3-methylnortricyclene	(200)	496
1-cyclopropyl-1-ethyl (**23**)	468^{j}	ethylcyclopropane	(66)	402
1-cyclopropyl-1-methylethyl	512^{j}	(2-propyl)cyclopropane	(94)	418
8,9-dehydro-2-adamantyl	819^{k}	2,4-dehydroadamantane	(268)	551
1-tricyclo[3.2.2.0^{2,4}]nonyl	768^{l}	tricyclo[3.2.2.0^{2,4}]nonane	180^{l}	588
syn-tetracyclo[3.3.2.0^{2,4}.0^{6,8}]-1-decyl	773^{l}	tetracyclo[3.3.2.0^{2,4}.0^{6,8}]decane	146^{l}	627
1-pentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecyl	746^{l}	pentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane	104^{l}	643
2-methyl-2-bicyclo[2.2.2]octyl (**17**)	626^{c}	2-methylbicyclo[2.2.2]octane	241^{m}	385
2-methyl-2-bicyclo[3.2.1]octyl	632^{c}	*exo*-2-methylbicyclo[3.2.1]octane	277^{n}	355
2-methyl-2-bicyclo[2.1.1]hexyl (**21**)	644	2-methylbicyclo[2.1.1]hexane	$(251)^{p}$	393
1-adamantyl (**2**)	857	adamantane	342^{s}	515
3-homoadamantyl	755^{hh}	homoadamantane	(374)	381
endo-2-tricyclo[4.2.1.0^{2,6}]decyl	725^{ii}	*endo*-tricyclo[4.2.1.0^{2,6}]decane	(328)	397
1-bicyclo[3.3.0]octyl	664^{b}	bicyclo[3.3.0]octane	(230)	434
1-bicyclo[3.3.3]undecyl	765^{jj}	bicyclo[3.3.3]undecane	(285)	480
11-methyl-11-tricyclo[4.4.1.0^{1,6}]undecyl	785^{kk}	11-methyl-11-tricyclo[4.4.1.0^{2,6}]undecane	(340)	445
2-methyl-8,9-dehydro-2-adamantyl	832^{ll}	2-methyl-8,9-dehydroadamantane	(300)	532
2,4-dehydro-4-homoadamantyl	775^{mm}	2,4-dehydrohomoadamantane	(360)	415
3-tricyclo[3.2.1.0^{2,7}]octyl	625^{nn}	tricyclo[3.2.1.0^{2,7}]octane	(192)	433
2-bicyclo[4.1.0]hexyl	568^{oo}	bicyclo[4.1.0]hexane	113	455
2-bicyclo[3.1.0]hex-3-enyl	842^{pp}	bicyclo[3.1.0]hex-3-ene	374	468
2-methyl-2-adamantyl (**1**, R = CH$_3$)	802^{r}	2-methyladamantane	373^{s}	430
1,2,3,5,7-pentamethyl-2-adamantyl (**3**, R = CH$_3$)	977	1,2,3,5,7-pentamethyladamantane	$(605)^{s}$	372
B. Nonclassical Ions				
2-norbornyl	408^{t}	norbornane	233	175
7-norbornenyl (**11**)	454^{u}	norbornene (**10**)	455	−1
		tricyclo[3.2.0.0^{2,7}]heptane	$(159)^{v}$	295
7-methyl-7-norbornenyl	516^{u}	7-*anti*-methylnorbornene	479	37
7-norbornadienyl	655^{w}	norbornadiene	751	−96
trishomocyclopropenyl	$66^{q,x}$	bicyclo[3.1.0]hexane	115^{y}	−48
8-tricyclo[4.1.0.0^{2,5}]octyl	155^{z}	tricyclo[4.1.0.0^{2,5}]octane	$(233)^{y}$	−78
9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl (**12**)	307^{aa}	pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane	(280)	27
1,5-dimethyltricyclo[2.1.0.0^{2,5}]pent-3-yl	286^{bb}	1,5-dimethyl[2.1.0.0^{2,5}]pentane	(139)	147
cyclopropylcarbinyl	280^{i}	methylcyclopropane	49^{cc}	231
		cyclobutane	93	187
1-methyl-1-cyclobutyl (**13**, R = CH$_3$)	327^{dd}	methylcyclobutane	152	175
		1,1-dimethylcyclopropane	106^{cc}	221
1,3,5,7-tetramethyl-2-adamantyl	805	1,3,5,7-tetramethyladamantane	552^{s}	253
C. Borderline and Special Cases Discussed in Text				
2-butyl	385	butane	76	309
2-methyl-2-norbornyl (**16**)	578^{ee}	2-*exo*-methylnorbornane	274	304
1,2-dimethyl-2-norbornyl (**18**)	582^{h}	1,2-dimethylnorbornane	(308)	274
2,3-dimethyl-2-norbornyl	601^{h}	2,3-dimethylnorbornane	(314)	287
2-bicyclo[2.1.1]hexyl (**20**)	506^{o}	bicyclo[2.1.1]hexane	210	296
homocyclopropenium	502^{qq}	cyclobutene	(320)	182
1,1′-dimethylcyclopropylcarbinyl (**22**)	451^{ff}	1-ethyl-1-methylcyclopropane	(125)	326
cyclooctyl (**24**, R = H, $n + m = 8$)	521^{gg}	cyclooctane	222	299
cyclononyl (**24**, R = H, $n + m = 9$)	465^{gg}	cyclononane	243	222
cyclodecyl (**24**, R = H, $n + m = 10$)	602^{gg}	cyclodecane	262	340
1,6-dimethylcyclodecyl (**24**, R = CH$_3$, $n = m = 5$)	573^{gg}	1,6-dimethylcyclodecane	(332)	241

Table II. (*Continued*)

carbocation	^{13}C chemical shift sum	hydrocarbon	^{13}C chemical shift sum	total chemical shift difference
		D. Dications		
1,4-bicyclo[2.2.2]octyl	885[rr]	bicyclo[2.2.2]octane	204	681/2 = 341
1,5-bicyclo[3.3.3]undecyl	1115[jj]	bicyclo[3.3.3]undecane	(285)	830/2 = 415
2,5-dimethyl-2,5-hexyl	962[ss]	2,5-dimethylhexane	(204)	758/2 = 379

[a] Unless otherwise noted, data have been taken from ref 16 and 17 and Table I. Values for reference hydrocarbons in parentheses have been estimated from related compounds; see ref 17. [b] Olah, G. A.; Liang, G.; Westermann, P. W. *J. Org. Chem.* **1974,** *39,* 367. [c] Reference 42. [d] Olah, G. A.; Spear, R. J. *J. Am. Chem. Soc.* **1975,** *97,* 1539. [e] Olah, G. A.; Liang, G.; Mo, Y. K. *Ibid.* **1972,** *94,* 3544. Olah, G. A.; Liang, G. *Ibid.* **1975,** *97,* 1987. [f] Reference 23. [g] Reference 24. [h] Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1974,** *96,* 189. [i] Reference 25. [j] See ref 25, 27, and 36a. [k] Reference 26. [l] Reference 27. [m] Wenkert, E.; Cochran, D. W.; Gottlieb, H. E.; Hagaman, E. W.; Filko, R. B.; Matos, F. J. deA.; Madruga, M. I. L. M. *Helv. Chim. Acta* **1976,** *59,* 2437. [n] Lippmaa, E.; Pehk, T.; Belikova, N. A.; Bobyleva, A. A.; Kalinichenko, A. N.; Ordubodi, M. D.; Plate, A. F. *Org. Magn. Reson.* **1976,** *8,* 74. [o] Reference 3h. [p] Della, E. W.; Hine, P. T.; Patney, H. K. *J. Org. Chem.* **1977,** *42,* 2940. References 3a and 5. [q] Olah, G. A.; Prakash, G. K. S.; Rawdan, T. N.; Whittaker, D.; Rees, J. C. *J. Am. Chem. Soc.* **1979,** *101,* 3935. [r] Reference 4 and Table I. [s] Reference 15. At −70 °C and at −150 °C; for revised values at −150 °C, see ref 3i. [u] Reference 3g. [v] Value for nortricyclene used. [w] Reference 3e. [x] Masamune, S.; Sakai, M.; Kemp-Jones, A. V.; Nakashima, T. *Can. J. Chem.* **1974,** *52,* 855. [y] Christl, M. *Chem. Ber.* **1975,** *108,* 2781. [z] Masamune, S.; Sakai, M.; Kemp-Jones, A. V. *Can. J. Chem.* **1974,** *52,* 858. [aa] Reference 34. [bb] Masamune, S.; Sakai, M.; Ona, H.; Jones, A. J. *J. Am. Chem. Soc.* **1972,** *94,* 8956. [cc] Monti, J. P.; Faure, R.; Vincent, E. J. *Org. Magn. Reson.* **1975,** *7,* 637. [dd] Reference 20. [ee] Reference 41. [ff] Reference 57. [gg] Reference 49. [hh] Reference 5b. [ii] Olah, G. A., et al., unpublished. [jj] Olah, G. A.; Liang, G.; Schleyer, P. v. R.; Parker, W.; Watt, C. I. F. *J. Am. Chem. Soc.* **1977,** *99,* 966. [kk] Olah, G. A.; Liang, G.; Ledlie, D. B.; Costopoulos, H. G. *Ibid.* **1977,** *99,* 4196. [ll] Refererence 26. [mm] Olah, G. A.; Liang, G.; Babiak, K. A.; Morgan, T. K.; Murray, Jr., R. K. *Ibid.* **1976,** *98,* 576. [nn] Olah, G. A.; Liang, G. *Ibid.* **1976,** *98,* 7026. [oo] Olah, G. A., et al., submitted for publication. [pp] Olah, G. A.; Liang, G.; Jindal, S. P. *J. Org. Chem.* **1975,** *40,* 3259. [qq] Olah, G. A.; Staral, J. S.; Liang, G. *J. Am. Chem. Soc.* **1974,** *96,* 6233. [rr] Reference 27h. [ss] Olah, G. A.; Grant, J. L.; Spear, R. J.; Bollinger, M. J.; Serianz, A.; Sipos, G. *Ibid.* **1976,** *98,* 2501.

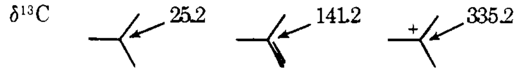
for the set of classical, rapidly equilibrating ions **4a–d** with or without admixture of some amount of the secondary classical species, **3** (R = H).

This leaves only the third possibility, the set of rapidly equilibrating unsymmetrically bridged ions **5a–d.** This confirms the earlier structural assignment.[8]

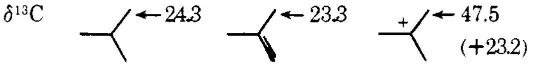
^{13}C Chemical Shifts and Carbocation Structures. The observed ^{13}C chemical shifts of the 1,3,5,7-tetramethyl-2-adamantyl cation do not agree with the calculated spectra for either the static classical (**3**, R = H) or the rapidly equilibrating classical (**4a–d**) models. Ideally, we should also calculate the spectrum of **5a,** take a positional average to approximate the equilibrating mixture **5a–d,** and compare the result with experiment. Unfortunately, this is not possible at present. Consequently, nonclassical structures, here as elsewhere, have been assigned not because of agreement with a model, but by the elimination of other possibilities. The inconsistency of this procedure, the possible existence of unknown effects, and the possible inappropriateness of the carbocation models employed for comparison purposes form the basis for criticisms of nonclassical assignments made in this manner.[13] We now answer these criticisms in detail.[18]

We first evaluate the ^{13}C chemical shift behavior of carbocations in a simple way which overcomes the complications associated with estimating the chemical shifts of individual carbons. The sum of the observed chemical shifts for all carbon atoms of a given carbocation is compared with the sum of all the carbon chemical shifts for the corresponding hydrocarbon.[19] For example, the sum of chemical shifts (vs. Me_4Si) for the 2-methyl-2-propyl cation is 478 ppm (335.2 ($\delta\ {}^{13}C_2$) + 3 × 47.5 ($\delta^{13}C_{1,3,4}$));[16] for 2-methyl-2-propane this sum is 98 ppm.[17] Thus, in going from 2-methyl-2-propane to the 2-methyl-2-propyl cation, a total deshielding of 478 − 98 = 380 ppm is observed.

This total deshielding can be rationalized in the following way.[20] The large (310 ppm) change in ^{13}C chemical shift of the central carbon atom in going from isobutane to the *tert*-butyl cation can be attributed partly to a $sp^3 \rightarrow sp^2$ hybridization change and partly to the presence of the positive charge.[17,20-22]



The remaining 70 ppm (380 − 310) of the total deshielding is then due to charge delocalization to the remaining carbons.



In the benzenium ion,[23] an example of quite a different type, the total deshielding relative to 1,4-cyclohexadiene (1,3-cyclohexadiene gives the same result)[24] is 329 ppm. This can be ascribed to an increase in one sp^2 center (ca. 124 ppm), to dienylic positive charge distribution to C_1, C_3, and C_5 (153.3 ppm = 2 × 62.5 + 28.3, see below),[21,22] and to the involvement of the other carbons, C_2, C_4, and C_6 (52 ppm = 26.5 + 2 × 12.8). Such assignments are rather primitive and ignore delocalization of charge to the hydrogens.[20] Nevertheless, the total ^{13}C deshielding differences appear to provide useful guides to the structural nature of carbocations.

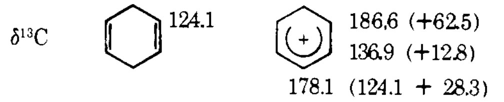


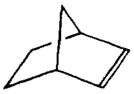
Table II summarizes the total chemical-shift differences exhibited by a great variety of carbocations. Ions with total ^{13}C chemical-shift differences larger than about 325 ppm have been gathered together in Table IIA. The structures of ions in this category have not been questioned and do not present interpretive problems. They include both static and rapidly equilibrating classical carbocations, allylic ions, the benzenium ion, and some secondary and tertiary cyclopropylcarbinyl cations. The chemical-shift differences span a rather wide range, but most fall between 350 and 390 ppm, despite the diversity of structures involved. A few exceptions are noted.

The 1-adamantyl cation (**2**) gives an especially large chemical-shift difference. The structure is classical but is unusual in that the "vacant" cationic orbital is fixed at a 180° dihedral angle with the three adjacent C–C bonds; an unusually large hyperconjugative transfer of positive charge to the remaining bridgehead carbons may result.[3a,5] In contrast, the β hydrogens do not hyperconjugate well because of the unfavorable 60° dihedral angles to the bridgehead cationic orbital. Consistent with this interpretation, the bridgehead ^{13}C

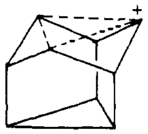
chemical shifts in **2** are unusually deshielded in comparison with acyclic β-C values.[5] The same is true for the ^{13}C chemical shifts of the γ carbons of the cyclopropylcarbinyl cations in Table IIA;[3g,25–27] these ions also tend to exhibit larger than normal total chemical shift differences. When the cyclopropylcarbinyl cation system is incorporated into a rigid cage structure, particularly large values are found, e.g., for the 3-nortricyclyl,[25] the 8,9-dehydro-2-adamantyl,[26] and the cyclopropane annulated 1-bicyclo[2.2.2]octyl cations.[27a]

The total chemical shift differences for the 2-methyl-2-adamantyl (**1**, R = CH_3) and the 1,2,3,5,7-pentamethyl-2-adamantyl (**3**, R = CH_3) cations, 430 and 372 ppm, respectively, are not abnormal. On this basis they can be assigned classical structures.

The other extreme is illustrated by the ions in Table IIB. The behavior is often quite remarkable. Some of the ions show *less* total deshielding than that of the parent olefins! Homoconjugation is quite different than allylic conjugation (Table IIA) in this respect. When an olefin is converted to an allyl cation, an increase of one sp^2 center occurs (as well as the increase in charge). In contrast, when norbornene (**10**) is converted to the bridged 7-norbornenyl cation (**11**), there is a net *loss* of *two* sp^2 centers, as all of the carbons involved in bridging are at least tetracoordinate. The effect of the charge in **11** seems to vanish, at least as far as the total ^{13}C chemical shifts are concerned![3e,g,28]


10


11


12

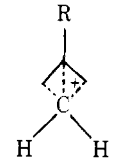
That carbon atoms involved in three-center two-electron (or in multicenter) bonding (e.g., in nonclassical ions) should exhibit smaller ^{13}C deshieldings than sp^2 carbon atoms (e.g., those in classical ions) is well founded. Ditchfield and Miller[29] have used ab initio methods to calculate the ^{13}C chemical shifts of the classical and the hydrogen-bridged ethyl cations. The ^{13}C chemical shift sum of classical $C_2H_5^+$ is 100 ppm less than that of the bridged form. It is unfortunate that this method has not yet been applied to ions with bridging carbon.

There is a quantitative parallel between the ^{13}C chemical shifts in carbocations and ^{11}B chemical shifts in corresponding boranes.[30] Not only are C$^+$ and B isoelectronic, but boron exhibits coordination numbers five and six in many of its compounds. Williams has taken advantage of this parallel to calculate successfully the ^{13}C NMR spectra of nonclassical cations.[31] It suffices here to note that ^{11}B chemical shifts of boron atoms with higher coordination to boron (e.g., at the apical position in nido boranes) are more shielded than those with lower coordination (e.g., at the basal positions of the same compounds).[32] The same is true of ^{13}C chemical shifts in the carboranes. Olah et al. have found that penta- and hexacoordinate carbons resonate at 25–65 ppm higher field than do tetracoordinate carbons in similar structures.[33]

Nonclassical cations, structures with higher carbon coordination, are thus expected to exhibit less ^{13}C deshielding than their classical alternatives. This is exactly what is found. All the ions in Table IIB have been assigned nonclassical structures (usually involving pentacoordinate carbon) by the original investigators. Coates' pentacyclononyl cation (**12**)[34] exhibits a total chemical shift difference of only 27 ppm. The value for the 2-norbornyl cation is larger, 175 ppm, but some 200 ppm less than typical values for classical cations (Table IIA). This analysis confirms the bridged structure for the 2-norbornyl cation.[3a,35]

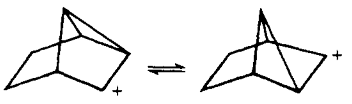
The value for the secondary 1,3,5,7-tetramethyl-2-adamantyl cation (**3**, R = H) is 253 ppm, 120 ppm lower than that for the corresponding tertiary ion **3** (R = CH_3). This behavior can be contrasted with that (Table IA) for classical secondary–tertiary pairs: 2-propyl (376) vs. 2-methyl-2-propyl (380) and cyclopentyl (364) vs. 1-methylcyclopentyl (374), where no significant changes occur. Our assignment of the set of rapidly equilibrating nonclassical structures, **5a–d**, to **3** (R = H)[8] is supported by this result.

A few comments on other ions in Table IIB are in order. The cyclopropylcarbinyl and 1-methylcyclobutyl cation chemical shift differences (231 and 175 ppm, respectively) are both much lower than those for secondary and tertiary cyclopropylcarbinyl ions (Table IIA). The unusual nature of the cyclopropylcarbinyl and of the 1-methylcyclobutyl ions, long recognized,[13a] has been emphasized by recent work and various interpretations offered.[20,36,37] Puckered nonclassical formulations (**13**, R = H or CH_3) appear increasingly attractive.



13

At one time, it was suggested that the 7-norbornenyl cation (**11**) might better be regarded as a rapidly equilibrating pair of cyclopropylcarbinyl cations, **14a** ⇌ **14b**.[38] Although subsequent investigations have made the latter alternative untenable,[3e,g,39] it has not been withdrawn by its proponent.[13a]

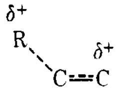

14a **14b**


15

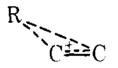
Formulations **14a** and **14b** imply classical cyclopropylcarbinyl character; on this basis total chemical shift differences of 400 ppm or more would be expected for this ion (Table IIA). Instead, almost no change (−1 ppm) is observed! If the tricycloalkane **15**, instead of norbornene (**10**), is used as the hydrocarbon reference, the total chemical shift difference is 295 ppm, still very much smaller than the value, 544 ppm, observed for the 3-nortricyclyl cation. Clearly, **11** and not **14a** ⇌ **14b** represents the structure of this species.

Borderline and Special Cases. Carbocations, like other electron-deficient species and in contrast to saturated hydrocarbons, tend to have rather flat potential-energy surfaces. Rearrangements involving low energy barriers are common. If these rearrangements, e.g., 1,2 shifts, occur between classical carbocations, bridged structures only a few kilocalories per mole higher in energy must be involved as transition states (or intermediates). Our proposed set of rapidly equilibrating nonclassical cations, **5a–d**, represents the opposite alternative. Here, the classical ion **3** (R = H) serves as the transition state (or intermediate) for the isomerizations among equivalent nonclassical species, **5a–d**. Each of these species, on symmetry grounds, is unsymmetrically bridged. That is, the bridging carbon has zero probability of being exactly equidistant to the two adjacent carbons. However, unsymmetrical bridging is possible even in cases where this is not required by symmetry.

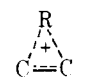
Carbocations afford a range of possibilities. Some nonclassical carbocations will be more stable than their classical counterparts. In other cases, the reverse will be true. In still other carbocations, classical and nonclassical forms will have nearly the same energy. Gradations of behavior are thus expected, even though the extremes—classical and nonclassical—can be clearly recognized. Charge delocalization will lead to a continuum ranging from hyperconjugation involving little geometrical change (i.e., in classical trivalent ions),[10] to partially bridged structures in which significant but unequal bonding to a second atom is taking place,[9a,b] to the limiting case where strong and equal bonding of the bridging atom or group to two atoms occurs symmetrically.[40]



hyperconjugation but no bridging



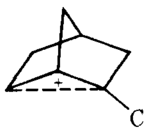
unsymmetrical bridging



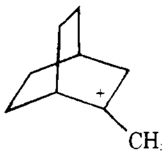
symmetrical bridging

Consider the total chemical shift difference criterion; values from nearly −100 to over +600 ppm are found for carbocations (Table II). Although there are two extreme categories (Tables IIA and IIB), intermediate values are observed. Data for a number of such borderline cases are presented in Table IIC. These merit some discussion.

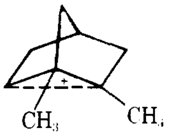
The 2-methyl-2-norbornyl cation has already been described by us as "partially σ delocalized".[3a,i,35,40,41] This implies heightened hyperconjugation involving some nuclear motion toward bridging (**16**). The total chemical shift difference, 304 ppm, is lower than that of typical tertiary cations, methylcyclopentyl (374 ppm), methylcyclohexyl (362), and especially 2-methyl-2-bicyclo[2.2.2]octyl (**17**) (385 ppm) and 2-methyl-2-bicyclo[3.2.1]octyl (355 ppm).[41,42]



16



17



18

The values, 287 and 274 ppm, respectively, for the 2,3-dimethyl[43,44] and the 1,2-dimethyl-2-norbornyl (**18**)[40,43] cations are lower than those (ca. 350 ppm) for the 1,2-dimethylcyclopentyl and the 1,2-dimethylcyclohexyl carbenium ions.[43]

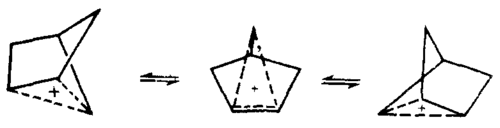
Our assignment (to **18**) of "a partially σ-delocalized carbonium ion structure undergoing a rapid 1,2 Wagner–Meerwein shift"[40] is also consistent with the results of the application of Saunders' major new investigational tool[45] to **18**. By labeling one of the methyl groups with deuterium, an isotopic perturbation is introduced which results in the splitting of carbon peaks which otherwise would give a single signal. The magnitude of this splitting, in general, varies from system to system in a significant way. Rapidly equilibrating carbocations undergo an isotopic perturbation of equilibrium, which results in relatively large splittings. Static ions, e.g., allylic[45b] or bridged,[45c] only undergo an isotopic perturbation of symmetry, and very small splittings result. With **18**, the splitting of intermediate magnitude observed[45a,c] indicates an intermediate situation with a low barrier between two structures which are partially delocalized.[46b]

We wish to stress two points. First, the work of Saunders[45,46] provides further evidence for the graduation of structure exhibited by carbocations. Second, the onset of bridging (heightened hyperconjugation) is necessarily subtle in its consequences, energetic and otherwise. Some probes, e.g., those based on ^{13}C chemical shifts, may be able to detect the onset of bridging before significant energetic changes are noted. Some indirect methods of study, e.g., the analysis of solvolysis rates and products,[47] may not be able to reveal small distinctions in the nature of carbocation *intermediates*. The direct observation of a carbocation in stable ion media should be inherently superior for this purpose. Environmental factors may also be important.

Does the 2-butyl cation have a bridged structure?[48] Recent results of Saunders indicate the barrier to 1,2-hydride shift in the 2-butyl cation to be unusually small, below (the value could be much smaller) 2.5 kcal/mol.[46] When energy differences between structural alternatives are so small, the species should exhibit some changes in properties. This appears to be reflected in a lowering of the total chemical shift difference from 374 ppm for 2-methyl-2-butyl to 309 ppm for 2-butyl. The isotopic perturbation splitting value is intermediate in magnitude,[45c] perhaps owing to partial hydrogen bridging. This means that data from 2-butyl should not be used to model classical secondary cation behavior;[13] values from the 2-propyl cation (static) or from the cyclopentyl cation (rapidly equilibrating, but with a hydride shift barrier of 3.5 kcal/mol)[46] should be used instead. Equilibrating tertiary cations, e.g., 2,3-dimethyl-2-butyl, 1,2-dimethylcyclopentyl, and 1,2-dimethylcyclohexyl, all have measured barriers above 3 kcal/mol and exhibit classical ^{13}C behavior (Table IIA) and large isotopic perturbations.[45c]

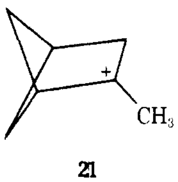
The structure of the rapidly equilibrating 2-bicyclo[2.1.1]hexyl cation has been variously described as being predominantly "classical"[3h] (**19a–c**) (on the basis of ^{13}C chemical shifts of individual carbon atoms) or as "nonclassical" (**20a–c**).[3f] The total chemical shift difference, 297 ppm, 100 ppm less than that for the 2-methyl-2-bicyclo[2.1.1]hexyl cation (Table IIA), indicates a pronounced nonclassical tendency. This is also shown by the small isotopic perturbation value.[45c] The similarity between the set **20a–c** of rapidly equilibrating nonclassical ions and our set, **5a–d**, should be noted.

19a **19b** **19c**

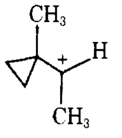


20a **20b** **20c**

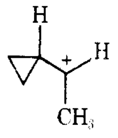
An increased degree of σ delocalization has been attributed by one of our groups to the 1,1′-dimethylcyclopropylcarbinyl cation (**22**).[37a] The total chemical shift difference, 326 ppm, is relatively large, but not as great as that of other secondary and tertiary cyclopropropylcarbinyl cations (Table IIA). For example, the value for **23** is 402 ppm. The very wide range of total chemical shift values for cyclopropylcarbinyl cations, from around 200 ppm for the parent (Table IIB) to over 600 ppm for polycyclic examples, emphasizes the variable nature of these species.



21

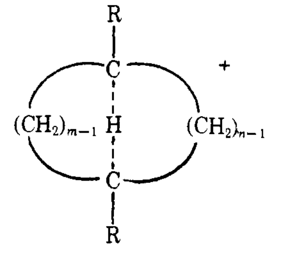


22



23

Sorensen's[49] transannularly hydride bridged middle ring cations, **24** (Table IIC), present a final set for consideration. Here, the use of total chemical shift differences based only on ^{13}C resonances seems particularly suspect since hydrogen rather than carbon bridging is involved. Furthermore, a more or less linear H bridge is indicated, rather than a triangular bridge as in a 1,2-hydride shift. This is emphasized by the peculiar proton chemical shifts exhibited by the bridging and by the methine (R = H in **24**) hydrogens.[49] When these methine hydrogens in the cyclodecyl cation (**24**, R = H, $n + m = 10$) are replaced by methyl groups (**24**, R = CH_3, $n = m = 5$), the total chemical shift difference actually *decreases* by nearly 100 ppm (from 340 to 241 ppm). Usually, tertiary ions show more classical character and higher total chemical shift values. Isotopic perturbation (very small splitting) shows the dimethyl cation to be nonclassical.[49d] In this species, the carbon spectra may better reflect the nature of the ion. In **24**, with R = H, some composite of carbon and hydrogen chemical shifts would probably provide a better structural index, since the hydrogens should be more directly involved in the nature of the charge distribution.



24

Assignments Based on Total Chemical Shift Differences. The range of total chemical shift differences observed (Table II) is very large, −96 to +643 ppm. How can one assign a structure to an ion on this basis? Although very large values are indicative of classical and very small values of nonclassical structures, we do not propose that the magnitude of the total chemical shift difference be used without taking the specific nature of the ion into account. The value for a given ion should be compared with those for related species, e.g., cyclopropylcarbinyl, allyl, alkyl, polycycloalkyl, etc. Comparison of a secondary ion with the corresponding methyl-substituted tertiary cation seems particularly apt. A significant decrease in nonclassical character in such secondary–tertiary comparisons results in large changes in total chemical shift differences. Classical secondary vs. tertiary ion comparisons showing small changes (isopropyl-*tert*-butyl = −4 ppm; cyclopentyl-methylcyclopentyl = −10 ppm) can, for example, be contrasted with 2-norbornyl-2-methyl-2-norbornyl = −129 ppm, **3** (R = CH_3)-**3** (R = H) = −119 ppm, 2-bicyclo[2.1.1]hexyl-2-methyl-2-bicyclo[2.1.1]hexyl = −97 ppm, and 2-butyl-2-methyl-2-butyl = −71 ppm.

Carbodications. Total chemical shift differences for three carbodications are included in Table IID. These species exhibit values which are *double* those typical of classical monocarbocations. The data for 1,4-bicyclo[2.2.2]octyl dication confirm that this species (rather than a rapidly exchanging halogenated monocation) was obtained in stable ion media.[27b] The inability of cyclopropane annulated bicyclo[2.2.2]octane systems to give similar dications[27a] remains unexplained.

Conclusions

1. The secondary 1,3,5,7-tetramethyl-2-adamantyl cation, formally represented by **3** (R = H), exists in stable ion media as a rapidly equilibrating set of unsymmetrically bridged ions, **5a–d**. The corresponding tertiary ion, **3** (R = CH_3), is a static classical species at low temperatures, but undergoes rapid degenerate rearrangement (Scheme I) at higher temperatures. A similar rearrangement sequence converts **5a–d** into **6** (R = H) above −45 °C.

2. The ^{13}C chemical shifts of **5a–d** cannot be reconciled with classical models. The assignment of nonclassical structure, made earlier on the basis of proton chemical shifts,[8] confirms a variety of solvolytic evidence[8,11-13] indicating a bridged structure for the 1-methyl-2-adamantyl cation.

3. In carbocations, the ^{13}C chemical shifts of carbonium carbons, those participating in multicenter bonding with higher coordination, are found at higher fields than those of carbenium (trivalent) carbons. This conclusion is supported by theoretical calculations,[29] by relationships between ^{11}B and ^{13}C chemical shifts in molecules with analogous structures,[30-33] and by the behavior of cations established to have classical or nonclassical structures.

4. The total ^{13}C chemical shift difference between a carbocation and its corresponding alkane provides a rough, but objective and easy to use, index of carbocation structure. Large differences, 350 ppm or greater, indicate classical carbocations. Values for nonclassical cations are much smaller, often 200 ppm or less (Table II). Comparison of values of closely related ions, e.g., a secondary with its methyl-substituted tertiary counterpart, should be made before assigning structures on this basis.

5. Many carbocations show intermediate behavior indicating partial bridging, heightened hyperconjugation, or enhanced delocalization. The isotopic chemical shift perturbation results of Saunders[45] lead to parallel conclusions.

Experimental Section

Materials. 4-Protoadamantanone,[11] 1,3,5,7-tetramethyl-2-chloroadamantane, and 1,2,3,5,7-pentamethyl-2-chloroadamantane were prepared by literature procedures[8] and sublimed under vacuum before use.

Preparation of 2-Adamantyl Cations. The stable cations were prepared by addition of the precursors in SO_2ClF solutions, under dry nitrogen atmospheres, to excess superacid (FSO_3H, FSO_3H-SbF_5, or SbF_5-SO_2ClF) precooled at either dry ice-acetone (ca. −78 °C) or liquid nitrogen-ethanol (ca. −135 °C) bath temperatures to give approximately 5–10% solutions. These carbocation solutions were then transferred under dry nitrogen into precooled NMR tubes for spectroscopic studies.

^{13}C NMR Spectroscopic Studies. The ^{13}C NMR spectra were obtained with a Varian XL-100-15 NMR spectrometer equipped with FT accessory, spin decoupler, and a variable-temperature probe. A Varian 620L computer was used to accumulate data. Fluorobenzene was used as external lock and all chemical shifts are referred to external Me_4Si (capillary, 5% ^{13}C enriched).

Acknowledgments. This work was supported by the National Science Foundation, the Fonds der Chemischen Industrie, and the Deutsche Forschungsgemeinschaft. We thank T. S. Sorensen and M. Saunders for stimulating discussions and for supplying information prior to publication.

References and Notes

(1) (a) The Chemistry of Protoadamantane. 7. Part 6: see ref 8. (b) Über σ-Bindungsverbrückte Carbonium-Ionen. 8. Part 7: Wenke, G.; Lenoir, D. *Tetrahedron* **1979,** *35*, 489. (c) Stable Carbocations. 210. From the University of Southern California.
(2) (a) Universität Erlangen-Nürnberg. (b) Technische Universität München. (c) Faculté des Sciences de Lyon. (d) Case Western Reserve University. (e) University of Southern California.
(3) (a) E.g., Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1973,** *12*, 173. (b) Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1969,** *91*, 5801. (c) Saunders, M.; Hagen, E. L. *Ibid.* **1968,** *90*, 2436, 6880. (d) Saunders, M.; Hagen, E. L.; Rosenfeld, J. *Ibid.* **1968,** *90*, 6882. (e) Olah, G. A.; Liang, G.; Mateescu, G. D.; Riemenschneider, J. L. *Ibid.* **1973,** *95*, 8698. (f) Seybold, G.; Vogel, P.; Saunders, M.; Wiberg, K. B. *Ibid.* **1973,** *95*, 2045. (g) Olah, G. A.; Liang, G. *Ibid.* **1975,** *97*, 6803. (h) Olah, G. A.; Liang, G.; Jindal, S. P. *Ibid.* **1976,** *98*, 2508. (i) Olah, G. A.; Prakash, G. K. S.; Liang, G. *Ibid.* **1977,** *99*, 5683. (j) Olah, G. A.; Donovan, D. J. *Ibid.* **1978**, *100*, 5163. (k) Olah, G. A. *Top. Curr. Chem.* **1970**, *80*, 19.
(4) Olah, G. A.; Liang, G.; Mateescu, G. D. *J. Org. Chem.* **1974,** *39*, 3750.
(5) (a) Schleyer, P. v. R.; Watts, W. E.; Fort, Jr., R. C.; Comisarow, M. B.; Olah, G. A. *J. Am. Chem. Soc.* **1964,** *86*, 5679. (b) Olah, G. A.; Liang, G. *Ibid.* **1973,** *95*, 194. (c) Mateescu, G. D. Ph.D. Thesis, Case Western Reserve University, 1971. (d) Sunko, D. E.; Hiršl-Starčević, S.; Pollack, S. K.; Hehre, W. J. *J. Am. Chem. Soc.* **1979,** *101*, 6163.
(6) Vogel, P.; Saunders, M.; Thielecke, W.; Schleyer, P. v. R. *Tetrahedron Lett.* **1971,** 1429. For evidence that the 2-adamantyl cation is stable in the gas phase, see: Wesdemiotis, C.; Schilling, M.; Schwarz, H. *Angew. Chem.*, In press.
(7) (a) Schleyer, P. v. R.; Lam, L. K. M.; Raber, D. J.; Fry, L. J.; McKervey, M. A.; Alford, J. R.; Cuddy, B. D.; Keizer, V. G.; Geluk, H. W.; Schlatmann, J. L. M. A. *J. Am. Chem. Soc.* **1970,** *92*, 5246. (b) Brouwer, D. M.; Hogeveen, H. *Recl. Trav. Chim. Pays-Bas* **1970,** *89*, 211.
(8) Lenoir, D.; Mison, P.; Hyson, E.; Schleyer, P. v. R.; Saunders, M.; Vogel, P.; Telkowski, L. A. *J. Am. Chem. Soc.* **1974,** *96*, 2157.

(9) Cf., e.g., (a) Radom, L.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 5935. (b) Olah, G. A.; Prakash, G. K. S.; Liang, G. *Ibid.* **1977**, *99*, 5683. (c) Hoffmann, R.; Mollere, P. D.; Heilbronner, E. *Ibid.* **1973**, *95*, 4860.

(10) Jensen, F. R.; Smart, B. E. *J. Am. Chem. Soc.* **1969**, *91*, 5688. Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *Ibid.* **1971**, *93*, 5715.

(11) (a) Lenoir, D.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 2138. (b) Lenoir, D.; Raber, D. J.; Schleyer, P. v. R. *Ibid.* **1974**, *96*, 2149. (c) Storesund, N. J.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1452. (d) Lenoir, D. *Chem. Ber.* **1973**, *106*, 78, 2366.

(12) Kovacevic, D.; Goricnik, B.; Majerski, Z. *J. Org. Chem.* **1978**, *43*, 4008.

(13) (a) Brown, H. C. (with comments by P. v. R. Schleyer) "The Nonclassical Ion Problem"; Plenum Press: New York, 1977. (b) Kramer, G. M. *Adv. Phys. Org. Chem.* **1975**, *11*, 177.

(14) Farcasiu, D. *J. Am. Chem. Soc.* **1976**, *98*, 5301. *J. Org. Chem.* **1978**, *43*, 3878.

(15) (a) Maciel, G. E.; Dorn, H. C.; Greene, R. L.; Kleschick, W. A.; Peterson, Jr., M. R.; Wahl, Jr., G. H. *Org. Magn. Reson.* **1974**, *6*, 178. The chemical-shift increments were $\alpha = 1.6$, $\beta = 6.9$, $\gamma = 0.6$, and $\delta = -0.8$ ppm for 1-methyladamantane substitution. (b) For other studies see Pehk, T.; Lippmaa, E.; Sevostjanova, V. V.; Krayuschkin, M. M.; Tarasova, A. E. *Org. Magn. Reson.* **1971**, *3*, 783. Also, Murakhovskaya, A. S.; Stepanyants, A. U.; Bagrii, Ye. I.; Frid, T. Yu; Zimina, K. I.; Sanin, P. I. *Neftekhimiya* **1974**, *14*, 220. Duddeck, H.; Hollowood, F.; Karim, A.; McKervey, M. A. *J. Chem. Soc., Perkin Trans. 2* **1979**, 360.

(16) The following increments were employed: $\alpha = 14.6$, $\beta = 0.8$ (tert), -4.0 (sec), $\gamma = -1.8$, and $\delta = -0.5$ ppm. Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5026.

(17) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972.

(18) Also see ref 13a, p 257.

(19) This procedure, "one very approximate way to test the whole molecule for charge delocalization", has also been suggested by Sorensen (ref 20). The use of *average* chemical shifts in unsymmetrical σ-delocalized systems has also been proposed (ref 21; also see ref 22).

(20) Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1977**, *99*, 6687.

(21) O'Brien, D. H.; Hart, A. J.; Russell, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410. These authors propose the relationship $\delta_{\mathrm{av}} = 289.5 - 156.3\,\rho_{\mathrm{av}}$, where ρ_{av} is the average π-electron density.

(22) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468. For symmetrical (D_{nh}) aromatic systems, the relationship $\delta = 288.5 - 159.5\rho$ holds well.

(23) Olah, G. A.; Staral, J. S.; Asencio, G.; Liang, G.; Forsyth, D. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6299.

(24) Olah, G. A.; Asencio, G.; Mayr, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *100*, 4347.

(25) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 1920.

(26) Olah, G. A.; Liang, G.; Babiak, K. A.; Ford, T. M.; Goff, D. L.; Morgan, Jr., T. K.; Murray, Jr., R. K. *J. Am. Chem. Soc.* **1978**, *100*, 1494.

(27) (a) de Meijere, A.; Schallner, O.; Weitemeyer, C.; Spielmann, W. *Chem. Ber.* **1979**, *112*, 908. (b) Olah, G. A.; Liang, G.; Schleyer, P. v. R.; Engler, E. M.; Dewar, M. J. S.; Bingham, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6829.

(28) Note the large negative value for the 7-norbornadienyl cation (Table IIB).

(29) Ditchfield, R.; Miller, D. P. *J. Am. Chem. Soc.* **1971**, *93*, 5287.

(30) (a) Nöth, R.; Wrackmeyer, B. *Chem. Ber.* **1974**, *107*, 3089. (b) Spielvogel, B. F.; Nutt, W. R.; Izydore, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 1609.

(31) Williams, R. E. Abstract S-12, Fourth International Meeting on Boron Chemistry, Snowbird, Utah, July 1979. Private communication.

(32) Eaton, G. R.; Lipscomb, W. N. "NMR Studies of Boron Hydrides and Related Compounds"; W. A. Benjamin: New York, 1969.

(33) Olah, G. A.; Prakash, G. K. S.; Liang, G.; Henold, K. L.; Haigh, G. B. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 5217.

(34) Coates, R. M.; Fretz, E. R. *J. Am. Chem. Soc.* **1975**, *97*, 2538; **1977**, *99*, 297. Brown, H. C.; Ravindranathan, M. *Ibid.* **1977**, *99*, 299.

(35) Olah, G. A. *Acc. Chem. Res.* **1976**, *9*, 41. Also see comments, ref 13a. Schleyer, P. v. R.; Allinger, N. L.; Yuh, Y.; Arnett, E. M.; Petro, C.; Pienta, N., *J. Am. Chem. Soc.*, submitted for publication. Arnett, E. M.; Pienta, N. *Ibid.*, in press. Also see ref 48b.

(36) (a) Olah, G. A.; Spear, R. J.; Hiberty, P. C.; Hehre, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 7470. (b) Olah, G. A.; Prakash, G. K. S.; Donovan, D. J.; Yavari, I. *Ibid.* **1978**, *100*, 7085. (c) Staral, J. S.; Yavari, I.; Roberts, J. D.; Prakash, G. K. S.; Donovan, D. J.; Olah, G. A. *Ibid.* **1978**, *100*, 8016. (d) Staral, J. S.; Roberts, J. D. *Ibid.* **1978**, *100*, 8018.

(37) (a) Olah, G. A.; Donovan, D. J.; Prakash, G. K. S. *Tetrahedron Lett.* **1978**, 4779. (b) Levi, B. A.; Blurock, E. S.; Hehre, W. J., *J. Am. Chem. Soc.*, **1979**, *101*, 5537.

(38) Brown, H. C.; Bell, H. M. *J. Am. Chem. Soc.* **1963**, *85*, 2324.

(39) Gassman, P. G.; Fentiman, Jr. A. F. *J. Am. Chem. Soc.* **1970**, *92*, 2549, and the citations given in ref 38.

(40) Olah, G. A.; DeMember, J. R.; Lui, C. Y.; Porter, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 1442.

(41) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1974**, *96*, 195.

(42) Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1978**, *100*, 1487.

(43) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1974**, *96*, 189.

(44) Jones, A. J.; Huang, E.; Haseltine, R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1975**, *97*, 1133.

(45) (a) Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070. (b) Saunders, M.; Kates, M. R. *Ibid.* **1977**, *99*, 8071. (c) Saunders, M.; Kates, M. R.; Wiberg, K. B.; Pratt, W. *Ibid.* **1977**, *99*, 8072.

(46) (a) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 7082. (b) Saunders, M.; Chandrasekhar, J.; Schleyer, P. v. R. In "Rearrangements in Ground and Excited States", DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 1.

(47) Brown, H. C.; Ravindranathan, M.; Rao, C. G.; Chloupek, F. J.; Rei, M.-H. *J. Org. Chem.* **1978**, *43*, 3667. Also see discussion in ref 13a, Chapter 9.

(48) (a) Dannenberg, J. J.; Weinwurzel, D. H.; Dill, K.; Goldberg, B. J. *Tetrahedron Lett.* **1972**, 1241. (b) Köhler, H.-J.; Lischka, H. *J. Am. Chem. Soc.* **1979**, *101*, 3479.

(49) (a) Kirchen, R. P.; Sorensen, T. S. *J. Chem. Soc., Chem. Commun.* **1978**, 769. (b) Kirchen, R. P.; Sorensen, T. S.; Wagstaff, K. *J. Am. Chem. Soc.* **1978**, *100*, 6761. (c) Kirchen, R. P.; Sorensen, T. S. *Ibid.*, in press. (d) Sorensen, T. S. *Ibid.*, submitted for publication.