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Nortricyclylcarbinyl Carbocations. Structural Hybrids of Cyclopropylcarbinyl and Bridged 2-Norbornyl Carbocations

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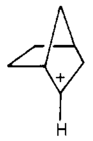
Abstract: Nortricyclylcarbinyl cations **3**, containing a tertiary, secondary, or primary C_1' center, were prepared in situ. The preparation of the primary system allows the first unequivocal observaton of the NMR properties of a "static" primary cyclopropylcarbinyl cation. All three types have a "bisected" structure and exhibit electron delocalization changes which are progressive within the series and which therefore indicate that the primary ion is not structurally unique. These cations are thermally much more stable than simple cyclopropylcarbinyl cations and this, and the question of why the ions are static, is probed and discussed. Nortricyclylcarbinyl cations can also be regarded as vinyl-bridged 2-norbornyl cations and the question arises as to whether this "character" is enhanced in the properties of these ions. This question is not easily answered on experimental grounds, but theoretical calculations in the following article provide evidence that this is the case.

Both the 2-norbornyl cation **1** and the primary cyclopropylcarbinyl cation **2** have a long and well-known history of controversy, centered primarily on questions of structure (geometry, electron delocalization, etc.).[1]



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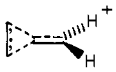

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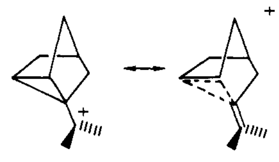
Undaunted, the present study reports an investigation of a carbocation system incorporating features of *both* a bridged 2-norbornyl cation and the "bisected" cyclopropylcarbinyl structure, i.e., cation **3**.[2]

The nortricyclylcarbinyl system **3** has been only sparsely studied[3] and no solvolysis rate studies have been published. This cation, which is written and named as a "bisected" cyclopropylcarbinyl system in **3C** can also be considered as a vinyl-bridged 2-norbornyl cation **3V**, with the actual structure expected, of course, to be somewhere in between.



3C 3V

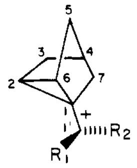
The parent "bisected" cyclopropylcarbinyl cation is also some composite of similar "extreme" structures, a point often made by Dewar[4] and many others.

The nortricyclylcarbinyl system **3** is of interest in the following connections.

(1) This tricyclic ring, for reasons made clear in the Results and Discussion, is very likely the simplest supporting skeletal structure capable of allowing one to observe a static "bisected" primary cyclopropylcarbinyl cation, a cation type unknown before the present study and from which one can obtain valuable NMR parameters. One also has the unique opportunity here to compare the properties of homologous primary, secondary, and tertiary cyclopropylcarbinyl cations.

(2) Since the ion is also a bridged 2-norbornyl cation, one can ask whether "extreme structure" **3V** is favored in the **3C** ↔ **3V** "mix" over the equivalent situation in the simple cyclopropylcarbinyl system. There is, of course, a large amount of evidence suggesting that the bicyclo[2.2.1]heptane framework is uniquely well suited for such bonding.[1a,b]

In this study, we have prepared and investigated the homologous cation series **3** (written in the cyclopropylcarbinyl resonance form),

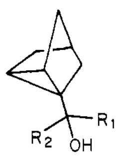


3a, $R_1 = R_2 = H$
b, $R_1 = H, R_2 = CH_3$
c, $R_1 = CH_3, R_2 = H$
d, $R_1 = R_2 = CH_3$

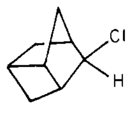
including some NMR measurements on neutral reference compounds related to these. Some deuterium-substituted ions were also prepared in connection with the question of whether these cations are indeed *static* structures.

Results and Discussion

The ions were prepared from the corresponding nortricyclyl alcohols **4a**, **4b**, and **4c**. The primary cation can also be prepared from the tricyclic chloride **5**.[2]



4a, $R_1 = R_2 = H$
b, $R_1 = H, R_2 = CH_3$
c, $R_1 = R_2 = CH_3$



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Stability of the Cations. Cations **3a–d** are remarkably stable toward rearrangement, and the reasons for this are discussed later. The primary cation is stable to about −20 °C before general

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[1] Reviews: (a) Olah, G. A. *Acc. Chem. Res.* **1976**, *9*, 41. (b) Sargent, G. D. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds., Wiley-Interscience: New York, 1972, Vol III, p 1099. (c) Wiberg, K. B.; Hess, B. A.; Ashe, A. S. *Ibid.*, **1295**. (d) Richey, H. G. *Ibid.*, 1201. (e) Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977; Chapters 5 and 6.

[2] Reported, in part, in communication form: Schmitz, L. R.; Sorensen, T. S. *Tetrahedron Lett.* **1981**, *22*, 1191–1194.

[3] (a) Hart, H.; Martin, R. A. *J. Am. Chem. Soc.* **1960**, *82*, 6362. (b) Gaitonde, M.; Vatakencharry, P. A.; Dev. S. *Tetrahedron Lett.* **1964**, 2007. (c) Richey, H. G.; Garbacik, T. J.; Dull, D. L.; Grant, J. E. *J. Org. Chem.* **1964**, *29*, 3095. (d) Richey, H. G.; Grant, J. E.; Garbacik, T. J.; Dull, D. L. *Ibid.* **1965**, *30*, 3909. (e) Jennings, B. H.; Herschback, G. B. *Ibid.* **1965**, *30*, 3902.

[4] (a) Dewar, M. J. S.; Marchand, A. P. *Ann. Rev. Phys. Chem.* **1965**, *16*, 321. (b) Dewar, M. J. S.; Haddon, R. C.; Komornicki, A.; Rzepa, H. *J. Am. Chem. Soc.* **1977**, *99*, 377.

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Table I. ^{1}H NMR Chemical Shifts[a] and Coupling Constants for Cations 3a-d

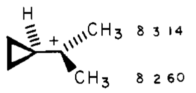
cation	^{1}H chem shifts[a]: H-1'	H-2-(H-6)	H-3(H-5)	H-4	H-7	other
3a[b]	7.83 (anti) 7.61 (syn)	5.95	1.91 1.82 (AB, 14)	2.62	1.63	
3b[c]	8.35 (q, 6.8)	5.12	1.71 1.65 (AB, 13.2)	2.45	1.47	2.21 (CH_3, d, 6.8)
3c[c]	8.98 (q, 7.0)	5.31	*d*	*d*	*d*	2.10 (CH_3, d, 7.0)
3d[e]		4.67	1.69 1.62 (AB, 13.4)	2.36	1.48	2.36 (anti-CH_3) 2.19 (syn-CH_3)

[a] Coupling constants (Hz) in parentheses and chemical shifts in δ (ppm). [b] −115 °C. [c] −80 °C. [d] Obscured by the peaks from 3b. [e] −20 °C.

decomposition gradually sets in. Cations **3b** and **3c** are stable for a time at room temperature, and **3d** is stable up to nearly +100 °C. Furthermore **3d** is quite stable in acids as weak as 96% H_2SO_4 and is a potentially suitable candidate for preparing a stable crystalline salt for X-ray analysis.

NMR Spectra. Proton and ^{13}C NMR parameters for cations **3a–d** are reported in Tables I and II, including ^{13}C–^1H coupling constants. The ^{1}H NMR spectra are remarkably free of resolvable coupling, only the methylene protons at C-2(C-6) showing up as an AB "quartet" under high-field (200-MHz) conditions. In addition, in **3b** and **3c**, there is the expected coupling between the C-1′ proton and methyl group. Where applicable, ^{1}H and ^{13}C assignments have been correlated by specific ^{1}H decoupling of ^{13}C NMR spectra.

The NMR spectra of **3a–d** are completely consistent with the bisected geometry shown (overall C_s symmetry). The ^{1}H chemical shift difference shown by the two C-1′ substituents is particularly diagnostic for this geometry, as was originally shown by Olah and Pittman[5] for the dimethylcyclopropylcarbinyl cation **6**. Thus,



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the two C-1′ protons in **3a** have an ^{1}H chemical shift difference of 0.22 ppm, the two methyl groups in **3d**, a difference of 0.17 ppm, and the protons in **3b** and **3c**, a difference of 0.63 ppm. In the ^{13}C NMR spectrum of **3d**, the two C-1′ methyl groups differ by 3.53 ppm. The higher field signal is assigned to the methyl group syn to the cyclopropane ring.

Charge Delocalization in 3a–d. The diagnostic carbons are those on the β-cyclopropyl position (C-2, C-6) and on C-1′. A ^{13}C chemical shift comparison of these in cations **3a–d** is shown in Figure 1. It should be noted from this that the shifts in the "primary" ion are almost exactly what one would have predicted from a linear extrapolation of the secondary and tertiary ion results; i.e., there is no structural "break" involved here (for the significance of this, see later).

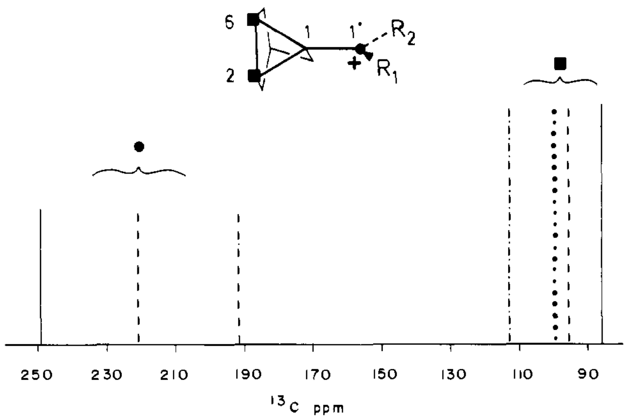


Figure 1. Comparison of the ^{13}C NMR chemical shifts (C-1′ and C-2-(C-6)) in cations **3a–d**: $R_1 = R_2 = H$ (**3a**), ---; $R_1 = H$, $R_2 = CH_3$ (**3b**), - - -; $R_1 = CH_3$, $R_2 = H$ (**3c**), ···; $R_1 = R_2 = CH_3$ (**3d**); —. Note that as C-1′ moves upfield, C-2(C-6) moves downfield.

If one accepts a linear correlation between charge density and ^{13}C chemical shift,[6] then the observed shift changes in **3a–d** are completely consistent with a greater proportion of extreme structure **3V** in the ion description as one goes from tertiary to secondary to primary cation, a result one expects, but one which has been obscured in the literature because of the special structural status which has often been accorded the primary parent cyclopropylcarbinyl cation.

Considering that the charge on the C-2(C-6) carbon peak is shared by two carbons, compared to that on the single C-1′ atom, there is a noticeable constancy in the upfield and downfield shifts (see Figure 1). Thus, in going from tertiary ion **3d** to the primary ion **3a**, the C-1′ carbon shifts upfield by 58.1 ppm, while the C-2(C-6) carbons shift downfield a total of 2 × 26.4 = 52.8 ppm. This is, of course, again consistent with the idea of a fixed total charge (1+), which is only shifting internally as one varies the structure.[7]

C-1, C-1′ Rotation Barriers. The primary ion **3a** shows no hint of any rotation process, on the NMR kinetic time scale, up to −20 °C, where decomposition gradually sets in. In the secondary ions **3b** and **3c**, i.e., the syn and anti isomers, we again see no evidence for any rapid rotation process interconverting these. Both **3b** and **3c** are present in the initial low-temperature preparation starting from alcohol **4b**, and we do not know whether the mixture is an equilibrium one or not. There is, in any case, no experimentally detectable change in this ratio as one warms the solution, ratio **3b**/**3c** ≈ 12. This system is apparently the first one giving both syn and anti isomers since there is no report of this in the simple 1′-methylcyclopropylcarbinyl cation case.[8] The preference for the anti isomer **3b** is expected.[9]

Table II. ^{13}C NMR Chemical Shifts[a] and Coupling Constants for Cations 3a–d and Related Carbonyl Compounds

compd	^{13}C chem shifts: 1	1'	2 and 6	3 and 5	4	7	other
3a[b]	113.5	191.4 (171)	112.9 (190.9)	39.8 (140)	36.5 (155 ± 10)	31.0 (137)	
3b[c]	97.0	220.8 (170.9)	95.4 (188.7)	38.4 (137)	34.1 (147)	29.2 (137)	27.1 (CH_3, 129)
3c[c,d]		...	99.8	...	...	...	
3d[e]	84.2	249.6	86.1 (184.2)	38.1 (140)	33.0 (*f*)	31.4 (133)	33.7 (anti-CH_3, 129) 30.2 (syn-CH_3, 129)
ketone 16	36.5	...	25.3 (179.9)	33.7 (132)	31.1 (148.3)	33.1 (132)	207.0 (C=O) 27.2 (148, CH_3)
ester 15	26.2	...	23.3 (179.5)	33.5 (133.7)	31.1 (150.1)	33.2 (133.6)	174.8 (C=O) 51.3 (146.1, CH_3)

[a] Coupling constants (Hz) in parentheses and chemical shifts in δ (ppm). [b] −118 °C. [c] −90 °C. [d] A minor population isomer which was basically characterized by ^{1}H NMR. The S/N of the ^{13}C spectra was such that only the peak listed here could be confidently identified. [e] −112 °C. [f] Peaks are badly overlapped.

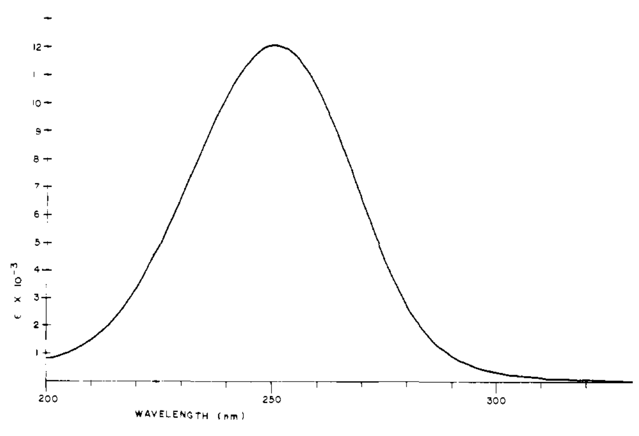
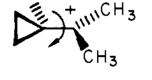


Figure 2. Ultraviolet spectrum of cation **3d** in 96% H_2SO_4.

For the tertiary ion **3d**, ^{13}C NMR spectra were used to estimate a minimum rate for the rotation barrier. The two methyls are found at 30.2 and 33.7 ppm, and up to +80 °C, there is only a slight suggestion that the lines may be broader than at lower temperatures. Simulating the ^{13}C line width at 80 °C, assuming a dynamic exchange process, we arrive at a minimum barrier of 18 kcal/mol; i.e., this could be the barrier, or the barrier could be still higher if the slight line broadening was caused by other factors. The barrier *would not be lower than this.* Molecular orbital calculations (STO-3G) on this barrier give a value of 17.7 kcal/mol.

The rotation barrier in the parent dimethyl cation **6** is reported[10] as 13.7 kcal/mol, so that there is obviously some factor present in **3d** which significantly increases the barrier.



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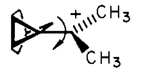
exptl E'_a = 13.7 kcal/mol
calcd STO-3G/MNDO = 13.2 kcal/mol



3d

exptl $\Delta G^{\ddagger} \geqslant 18$ kcal/mol
calcd STO-3G/MNDO = 17.7 kcal/mol

Ultraviolet Spectra. The parent dimethylcyclopropylcarbinyl cation **6**, in FSO_3H solution, has a λ_{max} at 289 nm (ϵ_{max} 10 800) and the published[11] spectrum shows a second, shorter wavelength, peak and strong end absorption at about 210 nm. Cation **3d** is stable in 96% H_2SO_4, and excellent UV solvent which is blank down to about 200 nm and which therefore permits one to accurately look for higher energy transitions. The UV spectrum of **3d** is shown in Figure 2. Compared to **6**, the λ_{max} is shifted a remarkable 38 nm to lower wavelength. There is also no sign of any further intense absorption down to 200 nm and the next UV transition must be quite high in energy (therefore the short wavelength absorption in the spectrum of **6** is probably spurious).

The band at 251 nm in **3d** is assignable to a strongly polarized transition from the HOMO π-MO to the lowest antibonding MO (see following article).

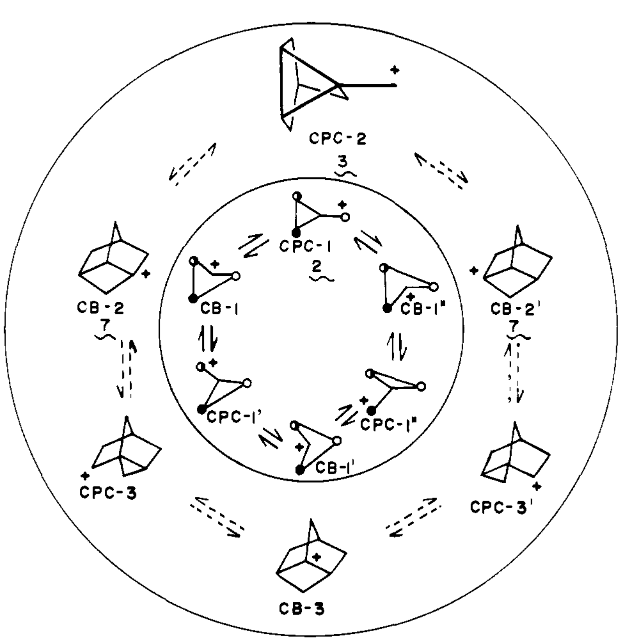
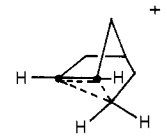


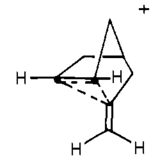
Figure 3. Comparison of the cyclopropylcarbinyl-cyclobutyl cation rearrangement pathway for the parent system **2** (inner circle) and for the nortricyclylcarbinyl cation **3** (outer circle). The evidence suggests that only cation **3**, in the outer circle, is present in our solutions, whereas all species in the inner circle are populated and in rapid equilibrium in solutions of the parent system.

^{13}C-^1H Coupling Constants. As expected from previous work on secondary and tertiary cyclopropylcarbinyl cations,[12] the $^{13}C_\beta$–$^1H_\beta$ (C-2 and C-6 in **3**) coupling constants decrease slightly in the order primary > secondary > tertiary > ketone or ester (Table II). In the primary case, we can compare the chemical shift and coupling constant with that of the 2-norbornyl cation, as shown.



1 (written in the
postulated bridged form)

$\delta(^{13}C)$ 125 [$J(^{13}C-^1H)$ = 184.5 Hz][13]



3a

$\delta(^{13}C)$ 112.6 [$J(^{13}C-^1H)$ = 190.9 Hz]

Although somewhat similar, these results are likely fortuitous because cation **3a**, according to MO calculations,[14] still retains a considerable cyclopropylcarbinyl "character".

Why Is It Possible To Observe a "Static" Primary Cyclopropylcarbinyl Cation in 3a? This question arises if we illustrate why the parent, primary, cyclopropylcarbinyl cation **2** is *not* static *nor* the sole species involved in the stable ion solution.[15]

A partial structural graph of the parent $C_4H_7^+$ system involving possible cyclopropylcarbinyl and cyclobutyl cations is shown in

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(5) Pittman, C. U.; Olah, G. A. *J. Am. Chem. Soc.* **1965**, *87*, 2998, 5123.

(6) (a) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468. (b) Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 5801.

(7) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683.

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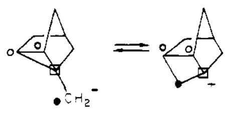
Table III. Temperature Dependence of the ^{13}C Chemical Shifts for Cations 3a and 8

		carbon chemical shift[b]					
ion	temp[a]	C-1'	C-1	C-2(C-6)	C-3(C-5)	C-4	C-7
3a[c]	−25	189.6		112.0	39.8	36.7	31.4
	−47	190.1		112.2	39.8	36.6	31.2
	−74.5	190.6	113.1	112.4	39.7	36.5	31.1
	−101.5	191.2	113.1	112.6	39.8	36.4	31.0
	−118	191.6	113.0	112.8	39.8	36.4	31.0
8[d]	−29			111.5	39.7	36.6	31.2
	−72.5			112.0	39.7	36.5	31.0
	−102			112.3	39.7	36.4	30.9

[a] °C. [b] Peaks (δ) were measured relative to the CH_3 carbon of internal *tert*-butyl cation; this was assigned a chemical shift of δ 48.05 by using a prior calibration. Errors are estimated as ±0.2 ppm. [c] For the possible equilibrium



in which the population of 7 should increase with increasing temperature, one would expect carbon (·) to move upfield (as found), carbon (▫) to move downfield (not found), and carbon (○) to move upfield (as found). Other carbons should not change much (as found). [d] Compared to 3a, the chemical shifts observed are barely changed.

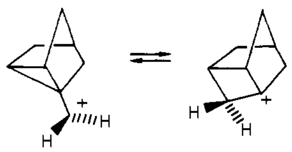
Figure 3 (inner circle). The corresponding cycle for cation **3a** etc. is shown in the outer circle of Figure 3.

Attempts to observe the NMR spectral properties of what might have been **2** fail for two reasons: (a) the ion solution appears to be a rapidly interconverting equilibrium mixture of *two* populated $C_4H_7^+$ species,[15] one of which may be **2**, and (b) even with the assumption that **2** is present, the three methylene carbons in the ^{13}C or ^1H NMR are completely averaged by the Figure 3 sequence and hence the associated chemical shifts are rather uninformative. In contrast, cation **3a** seems, at first sight, highly preferable compared to the rather strained-looking "partners" in the outer circle of Figure 3; i.e., we would not expect these to exist in measurable amounts. However, we were forced for a number of reasons to reconsider whether cation **7a** might contribute in a minor way to the NMR parameters of **3a**.

(1) The ^{13}C NMR chemical shifts observed for **3a** solutions were very slightly temperature dependent and were in the approximate direction expected if cation **7a** were a very minor, but not negligible, partner.

(2) Molecular orbital calculations placed cation **7a** respectably close in energy to **3a**. Thus, MNDO calculations (fully-optimized geometries) have **7a** 16.4 kcal/mol higher than **3a**, but STO-3G calculations, using the same geometries, result in **7a** being 9 kcal/mol *lower* in energy than **3a**.

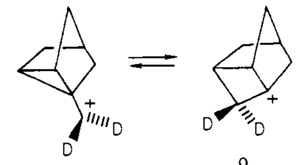
(3) The 1-methylcyclobutyl cation has been postulated to be *nonplanar* and to have sp^3 hybridization at the C^+ center,[16] so that **7a** may be more stable than anticipated for a bridgehead cation.



3a 7a (populated?)

The temperature dependence of the ^{13}C shifts in **3a** is shown in Table III. The magnitude of these shifts is insufficient, however, to permit any unambiguous interpretation. Further experiments were therefore undertaken.

I. The dideuterio ion **8** might be expected on the basis of known solvolysis data to be *less* stable relative to the cyclobutyl partner **9**, than in the proton case. For example, the solvolysis of **10** shows $k_H/k_D = 1.319$, whereas **11** shows $k_H/k_D = 0.928$,[17] i.e., **8** should be destablized relative to **3a** and **9** stabilized relative to **7a**. If indeed **7a** were a very small populated contributor to the **3a** solution, then in the deuterated case, we would expect ^{13}C NMR chemical shift changes appropriate for a larger proportion of the cyclobutyl partner.[18] However, preparation and characterization of the dideuterio ion **8** (using the corresponding alcohol) shows that the ^{13}C shifts (Table III) are virtually identical with those of the proton analogue **3a** and therefore inconsistent with a larger population of the hypothetical cyclobutyl partner **9**.



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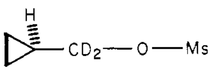

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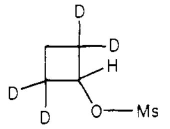
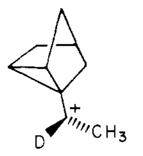


11

II. The secondary and tertiary ions **3b** and **3d** also show small ^{13}C shift changes with temperature. These are about half the magnitude of those in **3a** but show comparable shift directions. However, even if one interprets the **3a** results in terms of an equilibrium mixture of **3a** and **7a**, the equilibrium concentration of **7a** could be no more than a few percent.[19] It is inconceivable that the much more stable ions **3b** and **3d** would have any measureable population of their corresponding cyclobutyl cation "partners" and therefore the temperature vs. chemical shift changes must be due to other causes. In addition, the monodeuterio cation **12** shows no significant ^{13}C shift differences compared to **3b**.



12

The above results make it fairly certain that we are dealing only with a single species in all three cases. The temperature vs. chemical shift changes may be due to dependence of the ^{13}C shifts on a ring vibrational mode in **3a–d**.[20]

For many years, the observable cation obtained from cyclopropylcarbinol or cyclobutanol was thought to be a single ion and the unusual chemical shifts which were observed, compared to the secondary and tertiary counterparts, led to the postulate of various "nonclassical" structures. This situation changed in 1978 when it was found that at least two populated cations (in rapid equilibrium) contribute to the observed spectra.[15] The "bisected" cyclopropylcarbinyl cation **2** was suggested as a possibility for one of the species (the minor). Since we find a near linear extrapolation of the C-1′ and C-2(C-6) carbon shifts in **3a–d**, one is now on reasonably safe ground in extrapolating the chemical shifts of the known simple secondary and tertiary cyclopropylcarbinyl cations to give NMR parameters estimates of the "static", bisected, primary cyclopropylcarbinyl cation.

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

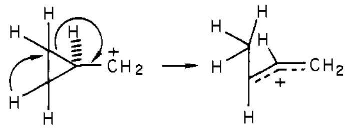
(17) Goricnik, B.; Majerski, Z.; Borcič, S.; Sunko, D. E. *J. Org. Chem.* **1973**, *38*, 1881.

(18) (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.

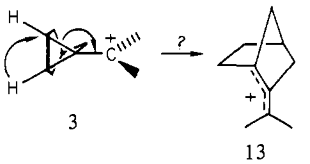
(19) A conservative estimate based on the total change in chemical shift (2 ppm for the C-1′ carbon) over the extreme temperature range, compared to the difference in chemical shift for this carbon in **3a** and **7** (at least 100 ppm).

(20) (a) Altman, L. J.; Laungamin, D.; Gunnarsson, G.; Wennerström, H.; Forsen, S. *J. Am. Chem. Soc.* **1978**, *100*, 8266. (b) Marshall, T. W. *Mol. Phys.* **1961**, *4*, 61.

Why Are Ions 3a–d Thermally Fairly Stable? A common fate of cyclopropylcarbinyl cations is an ultimate conversion to more stable allyl cations,[21] often limiting the thermal stability of the former. Connected with each cyclopropylcarbinyl cation in the inner Figure 3 circle is a corresponding allyl cation, whose formation one can rationalize as

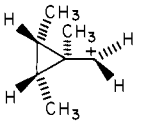


The cyclopropylcarbinyl cations **3a–d** do not suffer this fate because the corresponding allyl cation **13** is clearly of high energy.



The nortricyclene skeletal structure thus has the ability to prevent both of the usual cyclopropylcarbinyl rearrangements. Yet this simple framework retains the C_s symmetry of a "bisected" ion and probably causes a minimum of distortion of the basic cyclopropylcarbinyl cation structure.

Is There Extra Vinyl Bridging "Character" in the Structure of Cations 3a–d? The observable 2-norbornyl cation is postulated to have a symmetrically bridged structure,[22] which may be the result of a particularly favorable geometry inherent in a bicyclo[2.2.1]heptane ring. It is not unreasonable, therefore, to speculate that **3a** might have a higher vinyl-bridging "character" than a similarly-substituted simple cyclopropylcarbinyl cation, e.g., **14**. Cation **14** is not stable, however, under observable ion conditions so that one has no opportunity for meaningful comparisions.



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We have therefore carried out a series of MO calculations,[14] which suggest not only that the nortricyclylcarbinyl cations have a higher vinyl-bridging "character" but also that the primary ion **3a** is actually somewhat better represented by extreme structure **3V** than by **3C**; i.e., the ion is marginally closer to a vinyl-bridged 2-norbornyl cation. This conclusion is also consistent with the higher C-1, C-1′ rotation barrier found for **3d** compared to the model cation **6**.

Experimental Section

1-(Hydroxymethyl)tricyclo[2.2.1.0^{2,6}]heptane (4a) was prepared by $LiAlH_4$ reduction of methyl 1-tricyclo[2.2.1.0^{2,6}]heptanecarboxylate (**15**). This alcohol has been previously prepared by $LiAlH_4$ reduction of the corresponding acid:[23] bp 51–53 °C (0.6 torr) (lit.[23] 50–54 °C (0.8 torr)); ^1H NMR (60 MHz in $CDCl_3$) δ 3.78 (2 H, s), 3.29 (1 H, br), 2.02 (1 H, br), 1.6–1.2 (6 H, m), 1.08 (2 H, br); ^{13}C NMR (22.63 MHz in $CDCl_3$) δ 63.8, 35.0, 33.9 (2 C), 31.7, 26.1, 15.7 (2 C).

1-(Hydroxydideuteriomethyl)tricyclo[2.2.1.0^{2,6}]heptane was obtained by $LiAlD_4$ reduction in an analogous reaction to the above. There is the expected absence of ^1H peak at δ 3.78 and ^{13}C peak at δ 63.8 in the NMR spectra.

Methyl 1-Tricyclo[2.2.1.0^{2,6}]heptanecarboxylate (15). Into a cooled, 0 °C ether solution of the known acid[23] was distilled an excess of diazomethane/ether. The reaction was allowed to stand 1 h at 0 °C and 2 h at 25 °C. Excess diazomethane was destroyed with glacial acetic acid and the mixture washed once with water, 10% NaOH, and saturated NaCl solution and then dried over $MgSO_4$. Evaporation of solvent gave a 96% yield of the ester (pure by GLC) as a liquid: ^1H NMR (60 MHz in $CDCl_3$) δ 3.60 (3 H, s), 2.05 (1 H, m), 1.83 (2 H), 1.47 (2 H, d), 1.36 (4 H); ^{13}C NMR (22.63 MHz in $CDCl_3$) δ 174.8, 51.3, 33.5 (2 C), 33.2, 31.1, 26.2, and 23.3 (2 C); IR (neat film) 1724 cm^{-1}.

1-(1-Hydroxyethyl)tricyclo[2.2.1.0^{2,6}]heptane (4b) was prepared by the method of Hart and Martin.[23]

2-(1-Tricyclo[2.2.1.0^{2,6}]heptyl)-2-hydroxypropane (4c) was obtained as a liquid by the addition of $CH_3Li{\cdot}LiBr$ in ether to the known[23] 1-acetyltricyclo[2.2.1.0^{2,6}]heptane (**16**). The product of ether evaporation, after the usual workup, was essentially pure: ^1H NMR (60 MHz in $CDCl_3$) δ 2.05 (1 H, br m), 1.62 (1 H, br, OH), 1.41–1.1 (12 H, complex, including a sharp singlet at 1.2 ppm for the CH_3 groups); ^{13}C NMR (22.63 MHz in $CFCl_3$) δ 69.7, 35.0, 34.3 (2 C), 33.8, 32.2 28.9 (2 C), and 14.5 (2 C); IR (neat film) 3412 cm^{-1}.

2-(1-Tricyclo[2.2.1.0^{2,6}]heptyl)propene (17). Although alcohol **4c** survives gas chromatography using direct on column (glass) injection, preparative GLC on a Varian Model 90-P (metal injector and column) resulted in complete dehydration. The pure alkene **17** was collected (20% Carbowax 20M on Chromosorb W): ^1H NMR (90 MHz in $CDCl_3$) δ 4.72 (2 H, br), 2.02 (1 H, br), 1.7–1.2 (11 H); ^{13}C NMR (22.63 MHz in $CDCl_3$) δ 145.6, 107.2, 35.9, 34.0 (2 C), 31.2, 20.8, 18.7 (2 C). This material was used for cation preparations in connection with UV spectroscopy.

A mixture of ***exo*- and *endo*-2-chlorotricyclo[3.2.1.0^{3,6}]octane** was prepared by stirring a $CFCl_3$ solution of *exo*-2-tricyclo[3.2.1.0^{3,6}]octanol[24] with excess PCl_5 for 1.75 h at 0 °C. The resulting reaction mixture was washed with water and dried over K_2CO_3. Removal of the $CFCl_3$ yielded the title chlorides, the presence of two isomers being shown by the ^{13}C NMR spectrum. The exo isomer has been previously reported.[25]

Preparation of Cations. Ion **3a** was prepared by the addition of a $CFCl_3$ solution of **4a** to a −78 °C solution of 1:2 SbF_5–FSO_3H/SO_2ClF (1:5 SbF_5/SO_2ClF was also used). The dideuterio analogue of **3a** (**8**) was prepared by the same procedure. Ion **3a** was also prepared by the addition of a mixture of *exo*- and *endo*-2-chlorotricyclo[3.2.1.0^{3,6}]octane in $CFCl_3$ solution to a cooled (ca. −130 °C) 1:4:2 $SbF_5/SO_2ClF/SO_2F_2$ solution contained in an NMR tube. Ions **3b** and **3d** were prepared from the corresponding alcohols as above. Successful preparations of these ions were obtained by using 1:2 SbF_5–FSO_3H/SO_2ClF, FSO_3H/SO_2ClF, and neat FSO_3H. Ion **3d** was also prepared by extraction of a pentane solution of the alcohol into 96% H_2SO_4 at 0 °C.

NMR Spectroscopy. All ^1H NMR chemical shifts are in parts per million (δ). The 200-MHz ^1H NMR spectra of cations were recorded on a Varian XL-200 spectrometer with the instrument locked on an insert of $(CD_3)_2O$ containing a small amount of Me_4Si-h_{12} which served as a reference. Under these conditions, Me_4Si has a value of δ 0.416 relative to Me_4Si in SO_2ClF being assigned a value of δ 0.0. ^{13}C NMR spectra of ions (22.63 MHz) were obtained by using a Brüker WH-90 spectrometer. The ^{19}F NMR signal of SO_2ClF was used as a lock. The spectra were referenced to internal $CFCl_3$, taking the center of the doublet as 117.9 ppm. Temperatures were calibrated and measured as previously reported.[26]

UV Spectroscopy. Alkene **17** was slowly extracted from a dilute, purified, pentane solution into the acid at 0 °C. Measurements were made by using 1-mm cells and a Cary 219 spectrometer.

NMR Line-Broadening Simulations Involving 3d. A standard two-site exchange program was used, matching the line width of ^{13}C NMR spectra measured at +81 °C. Intrinic line widths were taken from the sharpest spectra obtained (at lower temperatures). For the two CH_3 carbons of **3d** this gives $k \leq 40\ s^{-1}$ and $\Delta G^{*} \geq 18.2$ kcal/mol.

MO Calculations. These were carried out as described in the following article.[14] The MNDO geometries were completely optimized in all cases.

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Registry No. 3a, 78607-00-8; **3b**, 80997-28-0; **3d**, 80997-29-1; **4a**, 20647-97-6; **4b**, 20647-99-8; **4c**, 70722-70-2; **8**, 80997-31-5; **15**, 23235-44-1; **16**, 22482-71-9; **17**, 4696-12-2; 1-(hydroxydideuteriomethyl)tricyclo[2.2.1.0^{2,6}]heptane, 80997-32-6; *exo*-2-chlorotricyclo[3.2.1.0^{3,6}]octane, 81075-65-2; *endo*-2-chlorotricyclo[3.2.1.0^{3,6}]octane, 41564-23-2; *exo*-2-tricyclo[3.2.1.0^{3,6}]octane, 6239-89-0.

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