labeled duplex. As might be anticipated, none of the simulated isotropic spectra provide an especially good fit to the dynamic signature of the distinctly anisotropic[10] long duplex DNA. The spectrum does, however, contain features found in isotropic simulations in the 20–100 ns τ_r range.[11] For the present purposes, the signature of a large DNA duplex is easily distinguished from that of the hairpin and single-stranded forms.[12]

The spectra presented here suggest that spin-labeled DNA in combination with EPR is a simple and powerful tool for the structural evaluation of regions of DNA suspected not to exist in the B form.[13] Large and characteristic differences between duplex and unpaired bases should permit detection of the latter in DNA of any size. Furthermore, the EPR method is not subject to one major problem common to all chemical reactivity probes, that of dynamic equilibration of conformations. In fact, the nanosecond time scale of the EPR method should permit quantitation of such equilibria (e.g., duplex/cruciform equilibria). This spin label method of structure evaluation may also find use as a preliminary characterization of small DNA's whose study by NMR or X-ray diffraction is contemplated. Whether spin probes will reveal distinct signatures for other nucleic acid structures (e.g., A-, Z-, and bent DNA, RNA structures) remains to be found.

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(10) Barkley, M. D.; Zimm, B. H. *J. Chem. Phys.* **1979**, *70*, 2991.

(11) Both theoretical and experimental studies are underway to understand the observed spectra.

(12) Bobst has reported minor differences in the single- and double-stranded forms of a less rigidly tethered spin-labeled DNA (see: Bobst, A. M.; Kao, S.-C.; Toppin, R. C.; Ireland, J. C.; Thomas, I. E. *J. Mol. Biol.* **1984**, *173*, 63). However, extensive motion of the spin probe independent of the DNA caused the resulting spectra for even long duplex DNA to be dominated by a subnanosecond motion, seriously compromising the sensitivity of such probes to the motional processes characteristic of DNA.

(13) To what extent motion of the nitroxide independent of the attached base has affected the EPR signatures recorded here is unknown. The cited τ_r values should not be assumed to reflect exclusively motion of the pyrimidine heterocycle.

Stereoselective Circumambulatory Methyl Migrations in the Nonamethylcyclopentylium Ion

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Degenerate 1,2-rearrangements of carbocations are usually very rapid, and dynamic NMR spectroscopy has been used to determine the barriers of such processes.[1] Saunders reported a barrier of 3.1 kcal/mol for the 1,2-H shift in the dimethylcyclopentyl cation **1**.[2] As the barriers for 1,2-H and 1,2-CH_3 migrations are of similar magnitude in the tetramethyl- and pentamethylethyl cation,[3] one can estimate the bridged cation **2a** to be 3–4 kcal/mol less stable than the open cation **2b**.

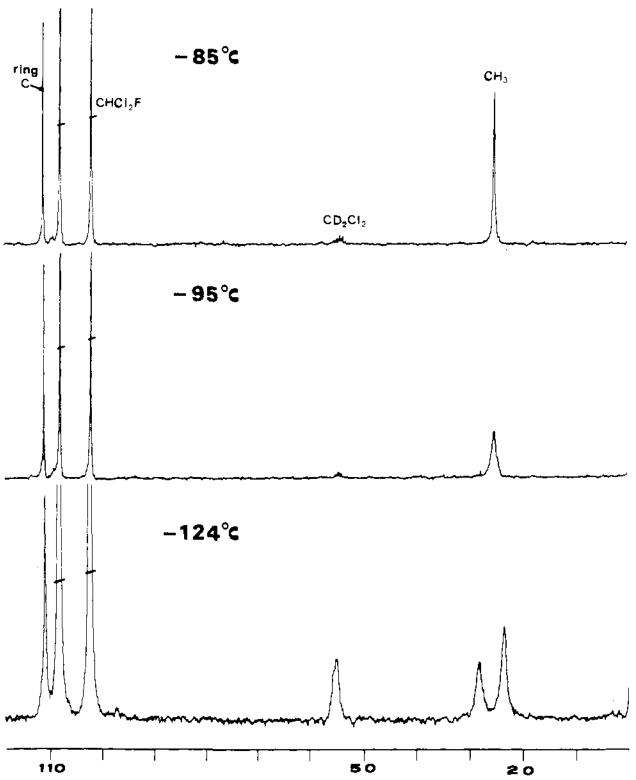
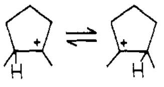
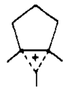


Figure 1. ^{13}C NMR spectra of the nonamethylcyclopentylium ion in $FSO_3H/SbF_5/SO_2ClF/CHCl_2F$.



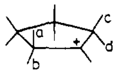
1a **1b**



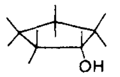
2a

2b

It should be possible to overcompensate this small energy difference by torsional strain, and we had speculated that the nonamethylcyclopentylium ion **3** might possess a methyl-bridged structure, since the classical structure **3a** incorporates four adjacent quaternary carbon centers.



3a



4

When nonamethylcyclopentanol **4**,[4a] prepared from octamethylcyclopentanone[4b,c] and CH_3Li, was dissolved in a solution of FSO_3H/SbF_5 in SO_2ClF[5] at −90 °C, a single peak (δ 1.86) was observed in the 200 MHz ^1H NMR spectrum, indicating total scrambling of all methyl groups, analogous to the spectra previously reported for the unsubstituted cyclopentylium ion.[6] Decomposition of **3** with formation of *tert*-butyl cations takes place at $T > -70$ °C. When the solution of **3** in $SO_2ClF/CHCl_2F$ was cooled, the ^1H NMR signal broadened, and, at −137 °C, two resonances at δ 2.00 and 1.63 with relative intensities 5:4 were observed.

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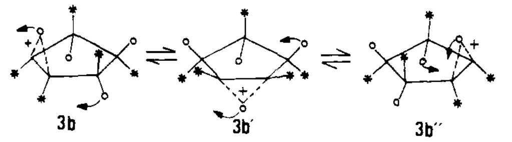
Line shape analysis[7] of the 200 MHz ^{1}H NMR spectra taken between −103 and −137 °C yields $\Delta\nu$ = 82 Hz and k_A = 246 s^{-1} and k_B = 308 s^{-1} (−120 °C) for the exchange between A and B with a population ratio P_A:P_B = 5:4. A barrier of $\Delta G^{\ddagger}$ (−120 °C) = 7.0 kcal/mol is thus obtained for the process which equalizes all methyl groups.

In accord with the ^{1}H NMR spectra, the 50 MHz ^{13}C NMR spectrum taken at −80 °C showed only two resonances at δ 110.88 (ring C) and δ 25.42 (CH$_3$). When the solution was cooled at −124 °C, the methyl signal was split into two resonances at δ 28.17 and 23.57 (ratio 4:5),[8] while the δ 110.88 signal remained sharp (Figure 1). The signal of the ring carbons does not show line broadening even at −135 °C, indicating a barrier of less than 2.5 kcal/mol for the circumambulatory process.

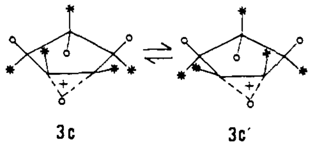
These spectra indicate that rapid circumambulatory methyl migrations take place, while a set of four methyl groups remains separate from a second set of five methyls. This observation excludes the C_{2v} ground-state geometry **3a** of the title cation, since in this case the migrations of the methyl groups a, b, c, and d had equal probability, and all methyl groups should become equivalent during the circumambulatory process.

The methyl-bridged cation **3b**, however, might account for the observed 4:5 methyl splitting, since the 1,2-methyl migrations can be expected to proceed with inversion at the ring carbons.[9] As shown in eq 1, only the dotted methyl groups will circumambulate, while the starred methyls move up and down at fixed ring positions. Scrambling between the two sets of methyl groups does not take place.

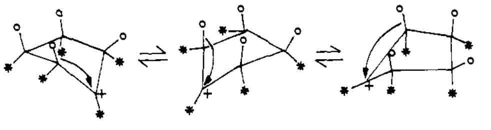
A similar behavior can be expected for the partially bridged structures **3c**, and the rate of the equilibration **3c** ⇄ **3c′** can be assumed to be higher or lower than the rate of the methyl migrations.



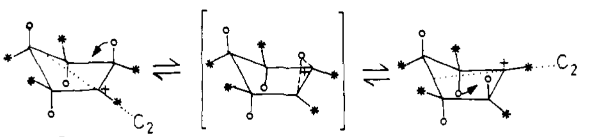
3b **3b′** **3b″** (1)



3c **3c′** (2)



3d **3d′** **3d″** (3)



3e **3e′** (4)

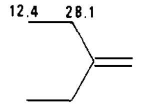
It is possible, however, to explain the nonequivalence of the two sets of methyl groups also with the assumption of classical carbenium ions with a nonplanar five-membered ring. If the ground state were a nonbridged cation with C_s symmetry (**3d**), the dotted methyl groups, which are adjacent to the carbenium center, can be expected to migrate preferentially, since they possess the proper orientation for interaction with the vacant p orbital. 1,2-Migration might generate a second nonplanar ring (**3d′**), and the four migrating methyl groups above the ring may remain separate from the nonmigrating five methyls below the ring.

In a classical carbenium ion with C_2 symmetry (**3e**), the methyl groups in axial position (dotted) are colinear with the empty p orbital and have a greater migrating ability than the equatorial methyl groups. This structure may account for the observed 4:5 splitting, if the axial and equatorial methyl groups retain their individual steric positions during the methyl shifts, as indicated by eq 4.

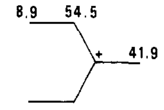
If one eliminates the classical structure **3d**, which was found to be 4.5 kcal/mol less stable than **3e** on the basis of force field calculations,[10] one has to consider structures **3b**,**c** and **e** as potential ground-state geometries.

The total ^{13}C chemical shift difference between carbocations and the corresponding saturated hydrocarbons has been used as a probe for bridging.[11] Whereas $\Delta\delta$ values of 350 ppm or more were found for classical cations, smaller shift differences were usually observed for bridged cations. For cation **3**, the sum of chemical shifts is calculated to be approximately 340–350 ppm greater than in the corresponding saturated hydrocarbon,[4a] thus favoring a classical, perhaps a weakly bridged structure (**3e** or **3c**).

In trivalent carbenium ions, carbon atoms directly attached to the carbenium center are usually strongly deshielded, while carbons in β position experience a slight upfield shift (see compounds **5** and **6**).[12]



5



6

In the carbenium ions **3d** or **3e**, the set of starred methyl groups which includes the methyl group directly attached to the carbenium center, is therefore expected to absorb at lower field, if the shift difference of the nonequivalent β-methyl groups is assumed to be small. Since the five-methyl ^{13}C NMR signal of **3** absorbs at higher field than the four-methyl signal, classical ground-state structures are disfavored.

On the basis of chemical shift considerations, the partially bridged structure **3c** thus appears to be most probable, but the alternatives **3b** and **3e** cannot be excluded. It should be mentioned that in analogy to our finding 1,2-hydride shifts have recently been reported to be faster in the *all-trans*-1,2,3,4,5-pentamethylcyclopentyl cation than in the all-cis isomer.[13] Since the circumambulatory process cannot be frozen out at −135 °C, isotope labeling[1b] and/or solid-state NMR experiments[14] will be needed to obtain unequivocal evidence for the structure of **3**.

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Registry No. 3, 119009-90-4; **4**, 103457-83-6.

Supplementary Material Available: Experimental and simulated 200 MHz ^{1}H NMR spectra (6 pages) of **3**. Ordering information is given on any current masthead page.

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[8] The pulse sequence of 1.3 s (35° pulses) warranted complete longitudinal relaxation, and the 4:5 averaged signal coincides with the chemical shift observed in the completely degenerate cation.

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