

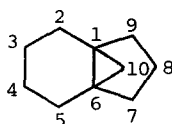
THE EFFECT OF RING STRAIN ON ^{13}C CHEMICAL SHIFTS

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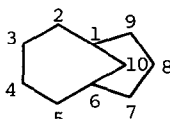
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It has been well established that the ^{13}C chemical shift of ring carbon atoms normally moves to higher field with decreasing ring size both for carbocyclic¹ and saturated heterocyclic² compounds. Recent work³ has shown that in compounds where two of the cyclopropane ring carbon atoms have 'inverted' tetrahedral geometry, i.e. all four constituents are in one hemisphere, the ^{13}C n.m.r. signals of the carbon atoms in the ring are dramatically deshielded relative to those of normal cyclopropane absorptions³. In one example introduction of a cyclopropane ring into the carbon framework of a benzhomoadamantane led to an actual increase in chemical shift in all of the carbon atoms in cyclopropane ring formation.

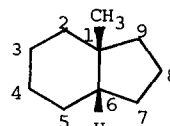
In order to see if this usual n.m.r. behaviour is unique to compounds containing carbons with 'inverted' tetrahedral geometry we have prepared the 'moderately' strained propellane tricyclo[4,3,1^{1,6}]decane (1) and its bicyclic relatives (2 & 3). The ^{13}C n.m.r.



(1)



(2)



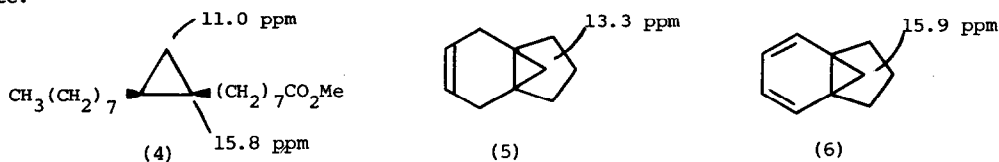
(3)

spectra of these compounds have been assigned using standard decoupling techniques, comparison with model compounds and deuterium labelling. The latter technique was necessary to distinguish unambiguously between $\text{C}_{2,5}$ and $\text{C}_{7,9}$ in compounds (1) and (3), and between C_8 and C_{10} in compounds (1) and (2). Spectral data are summarised in the Table.

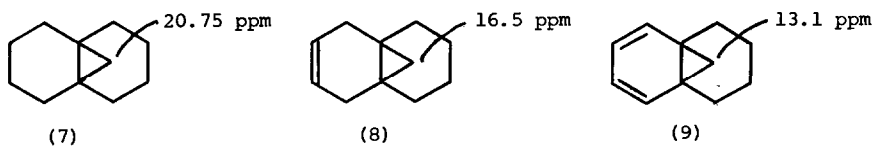
Table, ^{13}C Chemical Shift (ppm) for the C_{10} Hydrocarbons (1), (2) & (3)

Carbons	Compound		
	(1)	(2)	(3)
1,6	26.65	30.5	40.6 (1), 45.05 (6)
2,5	29.45	34.6 ↖	33.8 (2), 26.8 (5)
7,9	35.65	32.8 ↖ ?	29.05 (7), 38.3 (9)
10	16.65	32.05	26.8 (Me)
3,4	21.85	28.0	22.5 (3), 22.9 (4)
8	21.2	19.4	20.75

Comparison of the results for compounds (1) & (2) shows that formation of the cyclopropyl ring causes the methylene carbon C_{10} to shift to higher field by 15.43 ppm and the methine carbons C_1 & C_6 by 3.35 ppm. In order to obtain another value for an expected shift on cyclopropane ring formation we prepared the disubstituted cyclopropane (4) from methyl oleate.



Comparison with the chemical shift of the mid-chain carbon atoms of methyl stearate (30.0 ppm) shows changes of -19.0 ppm for the methylene and -14.2 ppm for the methine proton. Thus, although formation of a cyclopropane ring in the 'moderately' strained propellane (1) led to increased shielding of the cyclopropyl carbons, the shifts were not as large as those obtained for (4) nor those obtained by comparison of nortricyclene with norbornene³. The ^{13}C n.m.r. spectra of the unsaturated compounds (5) and (6) together with the higher homologues (7), (8) & (9) were also assigned. The ^{13}C shifts of the bridging carbons are seen to move to higher fields on introducing successive double bonds into the bicycloundecane series (7, 8 & 9) but



the trend does not persist throughout the bicyclodecane series (1, 5 & 6). The decrease in shielding for the bridging cyclopropyl carbon in (6) as compared with that in (5) could be associated with the large amount of strain in the former molecule. We feel that these results coupled with those of Duddeck and Klein represent an interesting challenge to theoretical chemistry. What degree of bond angle distortion is necessary to remove the usual shielding effects which are associated with cyclopropane ring formation?

The presence of an inverted carbon in the benzohomoadamantane carbon also led to a deshielding of carbons more remote from the cyclopropane ring. Comparison of the δ values for C3, 4 & 8 in compounds (1, 2 & 3) show no abnormal deshielding in (1). Further examination of the spectra of these molecules shows the delicate balance of conformation effects on chemical shifts. Although the carbons 2 & 5 in the six-membered ring are at higher field than carbons 7 & 9 in the five-membered ring in both of compounds (1) & (3) the converse is true for cyclopentane and cyclohexane.

References

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