Tetrahedron. Vol. 31, pp. 1571 to 1575. Pergamon Press 1975. Printed in Great Britain

^{13}C NUCLEAR MAGNETIC RESONANCE SPECTRA OF 2-SUBSTITUTED BICYCLO(3.3.1)NONAN-9-ONES

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(*Received in the UK 24 January 1975; Accepted for publication 10 February 1975*)

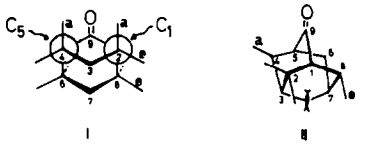
Abstract—^{13}C-NMR spectra of isomeric 2-substituted bicyclo(3.3.1)nonan-9-ones have been recorded to examine variation of ^{13}C-shieldings with stereochemistry. The observed shieldings are discussed in terms of the electronic and steric effects. Besides quite regular sterically induced γ-upfield shifts, remarkable anti-γ-carbon shieldings are reported.

INTRODUCTION AND GENERAL CONSIDERATIONS

Substituent effects on ^{13}C-chemical shifts have received continuing attention[1-3] as they provide useful information about stereochemistry.[4] Bicyclic[5-11] and polycyclic[12-16] systems, which often exhibit rigid and defined molecular geometry, are therefore suitable model compounds for examination of the electronic and steric effects on carbon shielding. Thus we have studied the behaviour of the bicyclo(3.3.1)nonane framework in ^{13}C-NMR spectroscopy.

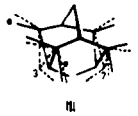
According to the relative energy minima, bicyclo(3.3.1)nonane (3) may exist in the double chair, boat-chair and double boat conformation. But the most stable conformer is the chair-chair one, which predominates despite strong interactions of the *endo* hydrogens at C-3 and C-7. However, stabilisation of the chair-boat arrangement may be achieved by introducing *endo* substituents at C-3 of the bicyclo(3.3.1)nonane.[17]

Similar stereochemistry is observed in bicyclo(3.3.1)nonan - 9 - one (1). In the case of 2-substituted bicyclo(3.3.1)nonan - 9 - ones, the X-ray, IR, and NMR spectroscopic evidence demonstrate that twin chair conformation is favoured, although the energy difference between the chair-chair and chair-boat conformation must be smaller for the 9-keto compound than in the parent hydrocarbon, as flagpole interaction is lacking in the former. In order to show the significant interactions, Newman-projection (I) is drawn in addition to the three dimensional representation (II) of bicyclo(3.3.1)nonan - 9 - one (1) in an idealized geometry.



I

Thus, it can be seen that two identical 1.3-diaxial arrangements of *exo* hydrogens are found at C-2..C-4 and C-6..C-8. A second type of *gauche* interactions are the identical interring repulsions of *endo* hydrogens at C-2..C-8 and C-4..C-6, which could be rationalized as 1,3-diequatorial interactions. As it can be seen on Dreiding models composed of ideal chairs, both distances of sterically interacting hydrogens, *exo*-C_2-H..C_4-H and *endo*-C_2-H..C_8-H are identical. However this is only true when the C-3..C-7 repulsion is neglected. As a consequence of this repulsion both rings are distinctly flattened to relieve steric crowding in the double chair conformation (III). This fact is reflected in the increase of the C-3..C-7



III

distance to 3.1 Å instead of 2·5 Å in an ideal twin-chair framework of bicyclo(3.3.1)nonan - 9 - one (1).[18,19] If an *exo* or *endo* hydrogen at C-2 is now replaced by a functional group, steric crowding is increased at C-4 or C-8, respectively. Each of these two nonbonded interactions is superimposed by C-3..C-7 repulsion. In the case of an *exo* group fixed at C-2 crowding between C_4-H (*exo*) and the substituent is diminished by increasing C-3..C-7 distance, whereas in *endo* compounds flattening should increase steric congestion owing to the diminished separation of the functional group and the *endo* hydrogen at C-8.

Assignments

Bearing in mind CMR values of bicyclo(3.3.1) nonane 3 and bicyclo(3.3.1)nonan - 9 - one (1), the problem of individual assignments of the 2-substituted keto compounds (6–13) is facilitated. The absorptions of the methin carbons C-1, C-2 and C-5 are distinguished from the others by off resonance decoupling and then assigned by consideration of the expected substituent parameters. The signals of C-7 and C-6 were taken as the closest to the values of the corresponding carbon in the parent ketone. The sterically influenced carbons C-4 in *exo* and C-8 in *endo* isomers are normally estimated to be shielded in the neighbourhood of C-7. A comparison of the sterically induced γ-effects in isomeric 2 - hydroxy - bicyclo(3.3.1)nonanes seems to justify this assignment.[20] Thus the remaining absorptions for C-3 and the sterically uncrowded γ-carbons C-8 and C-4, respectively, can be

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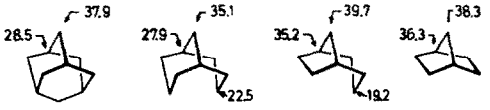
differentiated, when one takes into account the expected β-substituent effects. A priori there is no reason, why assignment of C-3 and C-4 or C-8 might not be reversed. However, interchanging assignment would not lead on principle to other conclusions, as shieldings of these carbons do not differ remarkably. The assignment of the remaining keto group, the acetyl- and tosyl-carbons are obvious on the basis of signal multiplicities and the characteristic chemical shifts.

RESULTS AND DISCUSSION

Chemical shifts of bridgehead and methylene carbons. The CMR spectrum of bicyclo(3.3.1)nonane (**3**) contains four lines in accordance with the C_{2v}-symmetry of the molecule. Although methylene shifts do not appear to be sensitive to strain in bicyclic compounds, bridgehead carbon values indicate that bicyclo(3.3.1)nonane (**3**) can be related to adamantane (**2**).[12,13]

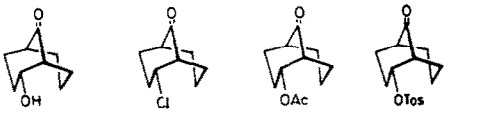


2 **3** **4** **5**

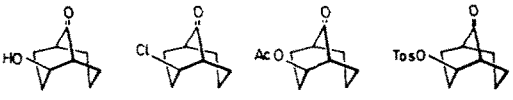
However it must be notified that bridgehead ^{13}C-resonances differ remarkably on proceeding from bicyclo(3.3.1)nonane (**5**) to bicyclo(3.2.1)octane (**4**),[20] whereas these shieldings are similar in the latter compound and norbornane (**5**).[7] This may reflect that the conclusion to strain is rather inadequate when one considers solely bridgehead carbon shifts. But it may be generalized that bridgehead carbons in bicyclo(n.2.1) hydrocarbons absorb in a range of 36 ∓ 2 ppm. The latter seems to be confirmed by the corresponding tertiary carbon in bicyclo(4.2.1)nonane,[20] which is found in the predicted range.

As a result of twofold *gauche* arrangement highest shieldings are observed for C-3,7 (22·5 ppm) in bicyclo(3.3.1)nonane (**3**). Turning to the bicyclo(3.3.1)nonan - 9 - one (**1**), C-3,7 absorptions (20·5 ppm) are additionally shifted to higher field in comparison to the parent hydrocarbon (**3**). But primarily as a result of two diaxial nonbonded interactions effective at C-3,7 in **3** and **1**, higher shielding is calculated, if one compares value of the corresponding carbon (C-4, 20·3 ppm) in *trans* - 2,6 - dimethyl - cyclohexanone[21] which exhibits only one "across the ring" nonbonded interaction at C-4. Therefore, we think that steric crowding by *endo* hydrogens at C-3,7 does not determine C-3,7 high field absorption. In contrast, it is conceivable that C-3 is deshielded owing to δ-steric crowding at C-7 (and vice versa), thus cancelling partly γ-sterically induced shift (this would correspond to ϵ-interaction of the two axial - *endo* - hydrogens at C-3,7). This assumption would violate the general association of steric crowding with ^{13}C-upfield shift, but agree with other findings at sterically perturbed δ-carbon.[4,25] Also higher shieldings of C-3 in bicyclo(3.2.1)octane (19·2 ppm) and bicyclo(3.2.1)octan - 8 - one (17·4 ppm)[20] compared to the corresponding carbons in the bicyclo(3.3.1)nonane system, might confirm the assumption of downfield shift owing to δ-hindrance found in the latter compounds.

(b) *General substituent effects.* As it can be seen on shieldings in substituted cyclohexanes,[22] the magnitude of substituent effects depends on the nature and the orientation of the functional group. Thus, an equatorial OH group tends to deshield α- and β-carbons more than axial OH in cyclohexanols.[23] The CMR evidence from the norbornane system appears to confirm these phenomena.[5-8] On the contrary, as can be concluded from data of Table 1, the epimeric 2-substituted bicyclo(3.3.1)nonan-9-ones (**6–13**) show more pronounced deshielding (3·4 – 4·7 ppm) of α-carbons in the *exo* isomers (**7**, **9**, **11** and **13**).

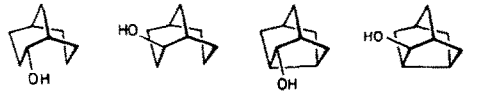


6 **8** **10** **12**



7 **9** **11** **13**

It could be envisaged that this fact is due to smaller steric interaction in the case of axial substituents. Vice versa a diminished α-effect in the *endo* compounds (**6**, **8**, **10** and **12**) might reflect higher steric crowding. This would only be true if one neglects the possible steric compression between the π-cloud of the CO function and the substituent in *exo* isomers. Furthermore, the difference of α-parameters appears too high to be explained only by steric arguments. Therefore one might conclude that the lower electronic density at C-2 in *exo* compounds is a result of the through space electronic interaction between the axial substituent and the spatially neighbouring CO group (Fig. VII). This fact would imply that the underlying reason for the observed α-effects in 2-substituted bicyclo(3.3.1)nonan - 9 - ones (**6–13**) is mainly electronic in origin. But in absence of the electronic effect of the CO function, the relation of α-effects and steric hindrance is seen in 2 - hydroxy - bicyclo(3.3.1)nonanes (**14**, **15**)[20] and hydroxy-noradamantanoles (**16** and **17**),[24] which exhibit smaller α-effects in the *exo* molecules as a cause of additional nonbonding 1,3-interaction with *syn* hydrogen at C-9.



14 **15** **16** **17**

Thus the difference of the carbinyl carbons $\delta_2^{endo} - \delta_2^{exo}$ in **14**, **15** and **16**, **17** are 1·8 and 2·7 ppm, respectively, whereas C-2 carbons in the keto-alcohols (**6** and **7**) differ by −3·4 ppm.

Considering β-effects at the bridgehead carbons C-1, only small differences are noticeable, while β-C-3 methylene carbons follow the general trend, which predicts greater deshielding for equatorial substituents.

The relation of steric interaction and γ-substituent effects has undoubtedly been proved to be one of the most significant and disputed phenomenon in CMR. In the compounds **6–13** γ-effects should be operative at C-4, C-8 and C-9. It is interesting to notice that steric γ-effect exhibits at the same time a non steric counterpart in each isomer. Thus in *exo* compounds the functional group is

Table 1. ^{13}C-chemical shifts of bicyclo(3.3.1)nonane (3) and derivatives of bicyclo(3.3.1)nonan - 9 - one (1)[a]

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9
bicyclo(3.3.1) nonane (3)	27.9	31.6	22.5	31.6	27.9	31.6	22.5	31.6	35.1
bicyclo(3.3.1) nonan-9-one (1)	46.5	34.2	20.5	34.2	46.5	34.2	20.5	34.2	221.7
endo-2-hydroxy-bicyclo(3.3.1) nonan-9-one (6)	54.4	73.4	29.5	27.7	45.2	34.0	20.8	27.2	219.3
exo-2-hydroxy-bicyclo(3.3.1) nonan-9-one (7)	54.7	76.8	28.5	29.1	46.2	34.5	19.6	30.6	220.1
endo-2-chloro-bicyclo(3.3.1) nonan-9-one (8)	53.9	61.7	31.5	29.8	44.9	34.0	20.4	28.8	215.8
exo-2-chloro-bicyclo(3.3.1) nonan-9-one (9)	54.6	65.5	28.4	29.9	45.5	34.7	19.6	32.7	216.1
endo-2-acetoxy-bicyclo(3.3.1) nonan-9-one (10) [b]	51.2	74.7	28.8	27.7	45.5	34.5	20.9	26.7	216.6
exo-2-acetoxy-bicyclo(3.3.1) nonan-9-one (11) [c]	51.1	78.2	26.2	28.8	45.8	34.7	19.5	30.8	217.8
endo-2-tosyloxy-bicyclo(3.3.1) nonan-9-one (12) [d]	51.9	81.7	28.2	27.5	44.8	34.0	20.3	26.7	215.0
exo-2-tosyloxy-bicyclo(3.3.1) nonan-9-one (13) [e]	51.7	86.4	27.1	27.8	45.5	34.8	19.3	30.9	215.5

a) chemical shifts in ppm relative to TMS.

b) values for the acetyl group: 169.9 (CO); 21.2 (CH_3)

c) values for the acetyl group: 169.9 (CO); 21.0 (CH_3)

d) values for the tosyl group: 144.9;133.8;129.9;127.5;21.5

e) values for the tosyl group: 143.9;134.2;129.9;127.5;21.6.

Table 2. Substituent effects in 2-substituted bicyclo(3.3.1) nonan - 9 - ones (6–13)[a,b]

	C-1 (β)	C-2 (α)	C-3 (β)	C-4 (γ)	C-5 (δ)	C-6 (ε)	C-7 (δ)	C-8 (γ)	C-9 (γ)
(6) endo-OH	7.9	39.2	9.0	-6.5	-1.3	-0.2	0.3	-7.0	-2.4
(7) exo-OH	8.2	42.6	8.0	-5.1	-0.3	0.3	-0.9	-3.6	-1.6
(8) endo-Cl	7.4	27.5	11.0	-4.4	-1.6	-0.2	-0.1	-5.4	-5.9
(9) exo-Cl	8.1	31.3	7.9	-4.3	-1.0	0.5	-0.9	-1.5	-5.5
(10) endo-OAc	4.7	40.5	8.3	-6.5	-1.0	0.3	0.4	-7.5	-5.1
(11) exo-OAc	4.6	44.0	5.7	-5.4	-0.7	0.5	-1.0	-3.4	-3.9
(12) endo-OTos	5.4	47.5	7.7	-6.7	-1.7	-0.2	-0.2	-7.5	-6.7
(13) exo-OTos	5.2	52.2	6.6	-6.4	-1.0	0.6	-1.2	-3.3	-6.2

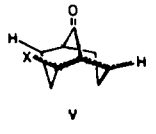
a) substituent effects are in ppm relative to bicyclo(3.3.1)nonan-9-one (1); a minus sign denotes a highfield shift on substitution.

b) greek letters in parantheses represent the kind of substituent effect on the corresponding carbon

gauche oriented with respect to C-3..C-4 bond, resulting in *syn* diaxial arrangements of the substituents and H-4-*exo*. The hydrogen attached to C-8 is far removed and no steric interaction is possible here. However, in *endo* isomers steric crowding occurs at C_8-H *endo*, whereas C_4-H *exo* cannot be influenced sterically. Therefore, C-4 is shifted to higher field in the *exo* isomers, while C-8 shows a marked upfield shift in the corresponding *endo* epimers. As one would expect the diamagnetic shift of the sterically compressed γ-carbon is more pronounced in *endo* compounds as a result of flattening both rings. However, shieldings of the steric γ-carbons do not differ remarkably in corresponding isomers. Therefore, the question arises, in which way the expected much stronger diequatorial 1,3-interaction can minimize steric crowding in *endo* compounds. As the bridge head angle is already enlarged in *exo* - 2 - chloroketone (9)[19] because of diequatorial interaction of *endo* hydrogens at C-2 and C-8, it is reasonable to suppose that the angle C-2..C-1..C-8 at the tertiary bridgehead carbon is more increased in *endo* molecules owing to stronger steric compression. This fact

IV

at the same time increases the C-3..C-7 separation and effects stronger distortion and angular strain of the bicyclo skeleton. Turning to the sterically uncrowded anti - γ - carbons C-8 in *exo*, and C-4 in *endo* epimers, a diamagnetic shift is observed in each case. As bicyclo(3.3.1)nonan - 9 - one skeleton provides W-orientation (consider functional group X and anti - γ - carbon - hydrogen bond, figure V, VI), the pronounced higher shieldings in *endo* and *exo* compounds (6–13) can

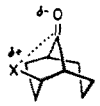


V

VI

be explained according to Grutzner's conception:[5] This means that the high field shift is attributable to the overlap between the back lobes of the binding orbitals at C-2, C-4, 8. The smaller magnitude of the electronically induced anti - γ - effect in the *exo* compounds may be due to greater distortion of the plane W-arrangement by flattening both rings and higher angle at the middle carbon of the propanic fragment ($C_2..C_1..C_8$). We think it is important to point out that the size of the diamagnetic anti - γ - shift is nearly in the order of the steric γ-shift in *endo* molecules, thus making differentiation sometimes difficult.

However the situation seems rather confusing if one compares 2-substituted adamantanes.[12,13] No sizeable upfield shift can be observed at the sterically uncrowded anti - γ - carbons, although ideal W-arrangement must be expected here. These findings are confirmed by comparison of 2 - hydroxy - bicyclo(3.3.1)nonanes (**14** and **15**),[20] which exhibit only sizeable diamagnetic shifts at the sterically congested γ-carbons. To explain the abnormal high shieldings of the anti - γ - carbons in 2-substituted bicyclo(3.3.1)nonan - 9 - ones (**6–13**), we suppose that the electronically induced anti - γ - effect appears to be consequence of changed electronic properties and higher steric strain in this system. Finally the substituent at position C-2 may exert its γ-influence at the keto function C-9. Independent of stereochemistry, carbonyl carbon is shifted to higher field. As the magnitude of the upfield shift is more pronounced in chloro-, acetoxy and tosyloxy-ketones (**8–13**), a partial hydrogen bridge participation resulting in low field shift cannot be excluded in hydroxy ketones (**6** and **7**). In order to explain higher shieldings in *exo* compounds, through space electronic interaction and possible steric influence must be taken into account. Thus electron donation from the heteroatom lone electron pair would change the polarization of the carbonyl - π - bond (Fig. VII), as also indicated by heterocyclic 8-membered ring ketones.[26] Evidence for the



VII

steric repulsion of the *exo* substituent and the carbonyl - π - bond is supported only in the solid state of *exo* - 2 - chloro - bicyclo(3.3.1)nonan - 9 - one (**9**), where the O atom is slightly displaced from the plane of carbons C-1..C-5..C-9.[19] In *endo* compounds (**6**, **8**, **10** and **12**), steric and through space electronic influence must be excluded. Therefore the underlying cause for the upfield shift of the carbonyl carbon is due to the electronic through - σ - bond transmission along the anti peri planar arrangement of $X–C_2–C_1–C_9$ chain. The importance of the substituent orientation towards the CO group is demonstrated by alkaline ring cleavage fragmentation only with *endo* - 2 - substituted bicyclo(3.3.1)nonan - 9 - ones to afford carboxy-cyclooctenes.[17] Further arguments for through bond effects along three σ-bonds are supported by photo electron spectra of azaadamantanones, in which the interaction of the π-CO-orbitals and the heteroatom lone electron pair is indicated.[27]

Although δ-effects prove to be small, a clear trend can be observed, as anti-δ-carbons with maximum separation from the substituent tend to exhibit higher shieldings. Thus, δ-C-5 bridgehead carbons are shifted more upfield in *endo* than in *exo* counterparts, while δ-C-7 carbons are more deshielded in *endo* than in *exo* molecules.

CONCLUSION

The findings of appreciable upfield anti-γ-carbon diamagnetic shifts, indicate that the useful application of the latter ones on structural elucidation may be restricted under certain circumstances. As at present time anti-γ-effect cannot be explained satisfactorily, this subject will need further investigations.

EXPERIMENTAL

^{13}C Puls Fourier Transform spectra were obtained under broad band decoupling conditions with a Bruker HFX-90 NMR spectrometer operating at 22·63 MHz.

Samples were obtained in 10 mm tubes as approximately 1M solns in $CDCl_3$. The ^2H resonance of the solvent served as lock signal. Chemical shifts were initially measured relative to the central line of the $CDCl_3$-triplet and then converted to the TMS standard by using the following relationship:

$$\delta_{TMS} = \delta_{CDCl_3} - 77{\cdot}1 \text{ ppm}.$$

The precision of the individual shielding values is ±0,2ppm. Off resonance decoupling experiments were carried out with the proton frequency offset approx. 400 Hz from the center of the proton spectral region.

The bicyclic compounds used in this investigation were all prepared by known methods;[28–34] the *endo*/*exo* mixtures (**6**/**7**, **8**/**9**, and **10**/**11**) were separated by column chromatography of the crude reaction mixtures on Silicagel 60 (Merck, 70–230 mesh ASTM) and using light-petroleum 30/50-ether mixtures (1–40% ether) as an eluent.

Bicyclo(3.3.1)*nonane* (**3**). Bicyclo(3.3.1)nonene was hydrogenated (Pd/C in MeOH) and **3** isolated by cristallization from MeOH at −80°.

Bicyclo(3.3.1)*nonan* - 9 - *one* (**1**). Bicyclo(3.3.1)non - 2 - en - 9 - *one was hydrogenated (Pd/C in MeOH) followed by dichromate*[31] oxidation of the product because of the formation of little amounts of bicyclo(3.3.1)nonan - 9 - ol. The resulting ketone (**1**) was purified by vacuum sublimation (100° at 12 mm).

Acknowledgements—We thank Professor W. Parker, University of Stirling, Scotland, for kindly supplying us with *endo* - 2 - hydroxy - bicyclo(3.3.1)nonane. The gift of the epimeric mixture of (**6**)/(**7**) as well as of tosylates (**12**) and (**13**) by Professor W. Kraus, University of Stuttgart-Hohenheim is gratefully acknowledged. A. H. thanks the Deutsche Forschungsgemeinschaft for financial support.

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