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OXYGEN-17 NUCLEAR MAGNETIC RESONANCE

THE EFFECTS OF REMOTE UNSATURATION ON ^{17}O-CHEMICAL SHIFTS IN POLYCYCLIC ETHERS

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Abstract —Natural-abundance ^{17}O-NMR spectra of 7-oxanorbornane, *exo*-3-oxatricyclo[3.2.1.0^{2,4}]octane and their unsaturated derivatives (*endo* cyclic and *exo*cyclic double bonds) have been measured. Linear correlation laws were observed for δ_O/δ_C of these ethers/corresponding hydrocarbons. The "cyclization shifts" for δ_O in ethers were not correlated by the "cyclization shifts" for δ_C of the corresponding hydrocarbons.

The endocyclic double bond in 2-norbornene derivatives exerts a remarkable downfield shift effect of 10–17 ppm on the bridge carbon C-7 chemical shift (δ_C) relative to the corresponding saturated analogs.[1] This so-called "norbornene effect" is not observed in acyclic, monocyclic hydrocarbons[2] and in the bicyclo[2.2.2]octane series.[3] Downfield shift effects *ca* 29 ppm and 46 ppm were observed on the δ_C of the γ-carbons C-5,6 by introducing an endocyclic double bond in bicyclo[2.1.1]hexane and, respectively, tricyclo[2.1.1.0^{5,6}]hexane.[4] Downfield shift effects on δ_C of C-7 were also observed in norbornane derivatives by annelation with a benzene ring,[5] an *endo*-cyclopropane ring[5,6] or an *endo*-epoxide ring.[7] On the other hand, 2-methylenenorbornanes,[8] 2-norbornanones[9] and 2,3-dimethylenenorbornanes[10] display a δ_{C-7} very similar to that of the corresponding norbornane derivatives. Qualitative interpretations based on frontier molecular orbitals (FMO) have been proposed for the effects on δ_C mentioned above.[4,6a,11] The differences noticed between the bicyclo[2.1.1]hexane, tricyclo[2.1.1.0^{5,6}]hexane and norbornanes, in one hand, and bicyclo[2.2.2]octanes, monocyclic and acyclic hydrocarbons in the other hand, suggest that strain effects and conformation effects (e.g. distance between the γ-carbons and the unsaturated function) intervene, perhaps by affecting the balance between the effects due to change of the $\langle r^{-3}\rangle_{2p}\sum_B Q_{AB}$ term and to change of the "mean excitation energy" (ΔE), assuming the Karplus and Pople paramagnetic term[12]

$$\sigma^A_{para} = (-e^2h^2/2m^2c^2)(\Delta E^{-1})\langle r^{-3}\rangle_{2p}\sum_{B\neq A} Q_{AB}$$

to be the dominant contribution to the carbon screening.

We have shown that ^{17}O-chemical shifts (δ_O) of 31 aliphatic ethers ROR′ correlate with δ_C for methylene groups of the corresponding alkanes R–CH$_2$–R′. The constant of proportionality could be related to the orbital expansion term

$$\langle r^{-3}\rangle_{2p}(\delta_O = 2.96\delta_C - 92.6\,\text{ppm}).^{13a,14}$$

Therefore, δ_O of 7-oxanorbornane and its unsaturated derivatives should bring data that, perhaps, will improve our understanding of the origin of the "C-7 norbornene effect". The δ_C of the H$_2$C(3) in the *exo*-tricyclo[3.2.1.0^{2,4}]octane is also affected by the unsaturation introduced at C-6,7 (cyclopropane homoconjugated with an ethylene, *s-cis*-butadiene function). We have also measured the δ_O of the corresponding *exo*-3-oxatricyclo[3.2.1.0^{2,4}]octane derivatives and we shall show that the δ_O/δ_C correlation laws for the epoxide/cyclopropane and oxanorbornane/norbornane families are not the same as that observed for alicyclic, aliphatic ethers/hydrocarbons.

EXPERIMENTAL

The ethers **1**, **10** and the epoxide **31** were from Fluka AG, Buchs, Switzerland. The other compounds for which δ_O or δ_C are reported for the first time were prepared according to known procedures: i.e. **2**.[15] **4**,[16] **5**,[10a] **6**,[17] **7**,[18] **8**,[19] **9**,[17] **18**,[18] **19**,[19] **22**,[20] **28**.[21] The tris-epoxides **37**[22a] and **38**[22b] and 7-oxanorbornadiene (**3**)[23] were kindly provided by Prof. H. Prinzbach, University of Freiburg i. Brsg., Germany. Natural-abundance ^{17}O-NMR spectra of the bicyclic ethers were recorded using 2 M de-gassed solutions in CDCl$_3$ (room T) on a Bruker WP 200 spectrometer (27.145 MHz, spectrum width: 25 KHz or 50 KHz, 16K data points); no lock signal was used. The values of δ_O are referenced to internal 0.3-M dioxane ($\delta_O = -2.0$ ppm) and are reported to H$_2$O ($\delta_O = 0.0$ ppm). Natural-abundance ^{17}O-NMR spectra of aliphatic and monocyclic ethers were recorded on a Bruker HX90 using the conditions reported elsewhere[13b] (12.2 MHz, spectrum width: 12 KHz, 8K data points, room T). The values of δ_O are referenced to internal 2M nitromethane ($\delta_O = 602.5$ ppm) and are reported to H$_2$O ($\delta_O = 0.0$ ppm). The proton signal of nitromethane was used as lock signal. The δ_O are accurate to ±2 ppm; positive sign refers to downfield shifts.

RESULTS AND DISCUSSION

The δ_O of 7-oxanorbornane (**1**) and its unsaturated derivatives **2**–**9** are reported in Table 1 together with

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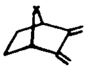
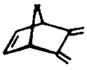
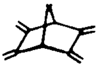
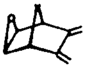
Table 1. δ_O of 7-oxanorbornanes **1**–**9**, tetrahydrofuran (**10**) and 3,4-dihydrofuran (**15**), and δ_C of the corresponding hydrocarbons **11**–**14**, **16**–**21** (δ_O, δ_C in ppm)

						
δ_0(X=O):	1: 85.5	2: 110	3: 192.5	4: 86.5	5: 107	6: 123.5
δ_C(X=CH_2):	11: 39.2[9a]	12: 48.8[9a]	13: 75.2[9a]	14: 39.3[10a]		
						
δ_0(X=O):	7: 113.5	8: 89	9: 53.5	10: 14(16.2[32])	15: -7	
δ_C(X=CH_2):	17: 51.4[10a]	18: 40.4	19: 26.2[10a]	20: 26.5[4]	16: 23.1[4]	21: 24.3[10b]

the δ_C of $H_2C(7)$ of the corresponding norbornanes **11**–**19**. A linear correlation law (r = 0.996, 7 points)

$$\delta_O(\text{oxanorbornanes}) = 2.84\ \delta_C(\text{C-7, norbornanes})\text{-}25.68\ \text{ppm}$$

was obtained for the bicyclic ethers **1**–**4**, **7**–**9** and the hydrocarbons **11**–**14**, **17**–**19**. This law is approximately parallel to that observed for the acyclic aliphatic ethers/alcanes;[13a,14] it deviates from it essentially by a different intercept ($\Delta\delta_O \simeq 67$ ppm), the O atoms of the 7-oxanorbornanes being relatively more deshielded than the O atoms in aliphatic ethers. This deviation is related to the differential effect of cyclization ("cyclization shifts") on δ_O and δ_C, respectively, between ethers and hydrocarbons. In ^{13}C-NMR, the cyclopropanes[25] display δ_C at higher field than in propanes, corresponding to a "cyclization shift" of *ca* −20 ppm (see Table 2). This "cyclization shift" fades with increase of the ring size.[25] In ^{17}O-NMR, the "cyclization shift" remains relatively small for monocyclic ethers (Table 2). It appears therefore, that the large "cyclization shift" of *ca* +33 ppm measured for the 7-oxanorbornane family is specific to this bicyclic family (*cf* PES data[28]). It has an opposite sign to the *ca* −10 ppm "cyclization shift" recognized for norbornane (Table 2).

The Karplus–Pople theory of paramagnetic shift[12] allows one to rationalize qualitatively the deshielding effect observed for the "cyclization shift" on δ_O of 7-oxanorbornanes. According to this theory, it was calculated that the $\sum_{B} Q_{AB}$ term (representing the local electron density at atom A) equals 2 for a tetracoordinated C atom; it equals 5/3 for a sp^3 hybridized O atom. It can be shown[14] that this term (for C) is independent of the carbon hybridization, whereas, considering strained molecules where hybridization of the O atom could be different from sp^3, this term varies between 2 and 4/3. The value $\sum_{B} Q_{OB} = 2$ is reached when the bond angle C–O–C equals 90°. The downfield "cyclization shift" of 33 ppm for **1** vs diisopropylether represents *ca* 1/6 of the paramagnetic contribution to δ_O (estimated to *ca*

Table 2. "Cyclization shifts" ($\Delta\delta_X^{cycl}$, ppm) on δ_O of ethers and δ_C of the corresponding hydrocarbons

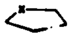
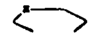
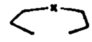
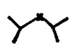
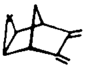
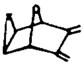
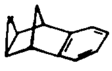
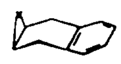
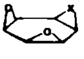
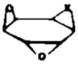
						
δ_0(X=O):	-56(-49[24])	- 52.5	- 20.5	- 22.5	- 14.	6.5
$\Delta\delta_0^{cycl}$:	- 3.5		+ 2.		+ 7.5	
δ_C(X=CH_2):	-3.8[25]	15.9[26]	22.1[25]	24.9[26]	25.3[25]	34.4[26]
$\Delta\delta_C^{cycl}$:	- 19.7		- 2.8		- 9.1	
						
δ_0(X=O):	5.(8.8[33])	1.5	0.	- 3.5	85.5	52.5
$\Delta\delta_0^{cycl}$:	3.5		3.5		+ 33.	
δ_C(X=CH_2):	26.6[25]	31.9[26]	28.2[25]	29.3[26]	39.2[9a]	49.0[27]
$\Delta\delta_C^{cycl}$:	- 5.3		- 1.1		- 9.8	

Table 3. δ_O of the epoxides **9, 19, 22–25, 31–33, 37, 38** and δ_C of the corresponding CH_2 group in the analogous hydrocarbons **26–30, 34–36** (ppm)

						
δ_O(X=O):	**22**: - 14(-15[24])	**23**: 53[24]	**19**: - 1.	**9**: - 1.5	**24**: 37.5[24]	**25**: - 8.[24]
δ_C(X=CH$_2$):	**26**: 1.0[6b](1.2[24])	**27**: 19.2[24]	**28**: 4.2[21]		**29**: 14.9[24]	**30**: 3.[24]
						
δ_O(X=O):	**31**: 0.(3.[24])	**32**: 1.[24]	**33**: -8.[24]	**37**: - 14.5	**38**: 10.	**38**: 6.
δ_C(X=CH$_2$):	**34**: 10.6[24]	**35**: 6.5[24]	**36**: 5.8[24]			

200 ppm[29]). Therefore, the "cyclization shift" as defined in Table 2 for 7-oxanorbornane and the other cyclic ethers might be due to a change in the $\sum_{O} Q_{OB}$ term. Because of that, linear correlations between δ_O and δ_C can be expected only for families of very similar compounds.

The δ_O of the 3-oxatricyclo[3.2.1.0^{2,4}]octanes **9, 19, 22–24** and related epoxides **25, 31–33, 37, 38** are reported in Table 3 with the δ_C of $H_2C(3)$ of the corresponding tricyclo[3.2.1.0^{2,4}]octanes **26–29** and the related cyclopropane derivatives **30, 34–36**. An apparent linear correlation law (r = 0.999, 4 points)

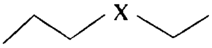
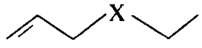
$$\delta_O(\text{3-oxatricyclo}[3.2.1.0^{2,4}]\text{octanes}) = 3.66\delta_C(\text{tricyclo}[3.2.1.0^{2,4}]\text{octanes}) - 17.07\,\text{ppm}$$

is observed. It is not parallel to the δ_O/δ_C correlation law of the acyclic ethers/hydrocarbons (*cf* Fig. 1). It must be pointed out that the ethylene oxide/cyclopropane data deviates from this law, whereas the δ_O and δ_C of the epoxides **25, 31–33** (that are *cis*-disubstituted epoxides like the 3-oxatricyclo-[3.2.1.0^{2,4}]octanes) and, respectively, the corresponding hydrocarbons **30, 34–36** can be fitted together with the data of the epoxide/cyclopropane of the tricyclic family with a law (r = 0.944, 8 points)

$$\delta_O = 3.64\delta_C - 22.4\,\text{ppm}$$

that is not very different from the above linear correlation (Fig. 1). The number of points at hand is certainly insufficient to allow any meaningful distinction to be made now between the bicyclic and tricyclic systems described here.

It is interesting to note, however, that the introduction of a double-bond β,γ to the oxygen function in the 7-oxanorbornanes induces a net deshielding effect on the δ_O (*ca* 25–82 ppm) of the ether (compare **2** with **1**, **3** with **2** and **7** with **4**). Thus, the "norbornene effect" noticed for the hydrocarbons is definitively paralleled by an "oxanorbornene effect" in 7-oxanorbornanes. Contrastingly, the introduction of a β,γ-unsaturation in tetrahydrofuran (**10**) leads to a relatively important upfield effect (*ca* 21 ppm) (*cf* **15** with **10**) that is correlated by a very small upfield effect in the corresponding hydrocarbons (*cf* **16** with **20** and also **21**). In the acyclic series, however, no effect is observed on δ_O and δ_C by the β,γ-unsaturation; e.g.

δ_O(X=O):	1.5	1.5 ppm
δ_C(X=CH$_2$):	31.9	31.7 ppm

A downfield effect (*ca* 68 ppm) is observed for the δ_O of the *exo*-3-oxatricyclo[3.2.1.0^{2,4}]octanes (*cf* **23** with **22**[24]), the double bond being in this case γ,δ to the oxygen function. Such an effect becomes unsignificant in the family of the 7-oxabicyclo[4.1.0]heptanes **31, 32**.

An unsignificant downfield effect (*ca* 2–3 ppm per diene function) was measured for δ_O of 7-oxanorbornane when one or two exocyclic s-*cis*-butadiene groups substitute C-2,3 and C-5,6 (compare **4** with **1**, **7** with **2**, **8** with **4**, **1**). A somewhat larger downfield effect (*ca* 13 ppm) was observed on δ_O of the 3-oxatricyclo[3.2.1.0^{2,4}]octane (*cf* **19** with **22**, Table 3).

The effects described above could be attributed in part to transannular interactions.[30] To a first approximation, an account of the charge transfer (inevitably accompanied by change in the mean excitation energy) between the epoxide or cyclopropane group and the homoconjugated unsaturated functions in *exo*-tricyclo[3.2.1.0^{2,4}]octanes can be anticipated by the FMO theory.[24] Thereby, one could perhaps "rationalize" the larger downfield effects induced by the endocyclic double bond than by the exocyclic s-*cis*-butadiene function by invoking the smaller LUMO coefficients of the diene (than LUMO of an ethylene) overlapping with a relatively low-lying subjacent HOMO of the epoxide.[31] Nevertheless, it is unclear to us how such qualitative treatment could make a "reasonable" account for the much larger differential effect of the endocyclic double bond vs exocyclic s-*cis*-butadiene on δ_O of 7-oxanorbornanes (and δ_C of norbornanes). The MO's shapes and energy sequencing of ethylene oxide,[31] puckered tetrahydrofuran[32] and 2,5-dihydrofuran[32] show many "similitudes". Furthermore, it is not obvious why the above mentioned effects are not larger at the centers γ (norbornane family: direct conjugation or hyperconjugation between the 5-membered ring and the olefins) than at the centers δ to the unsaturated

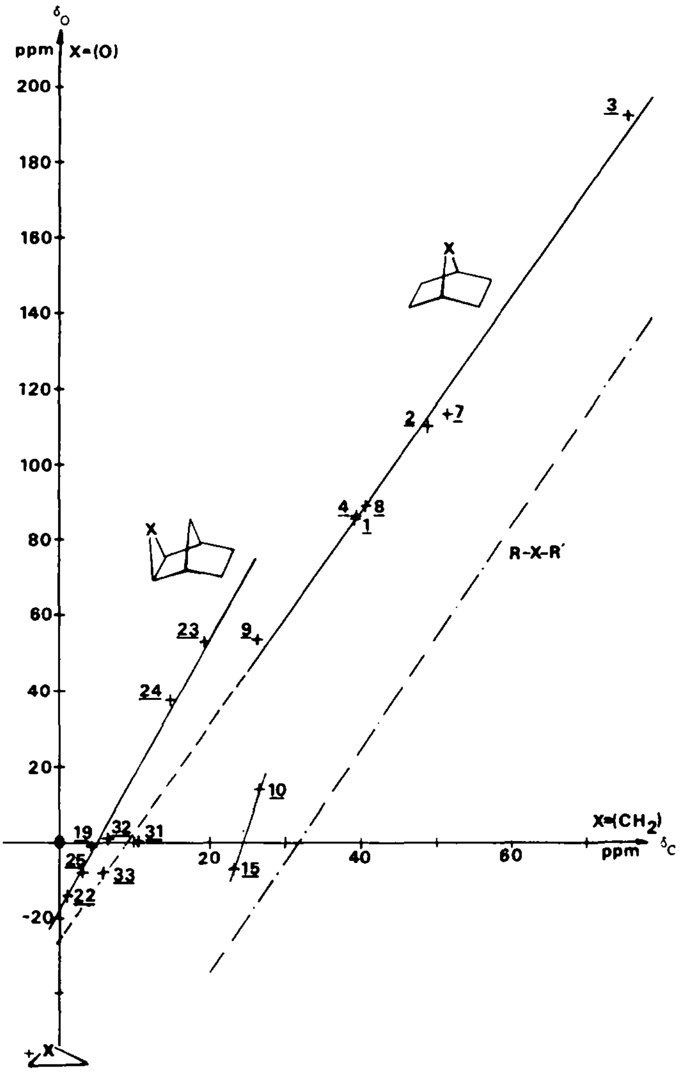


Fig. 1. Correlations between δ_O of ethers and δ_C of the corresponding CH_2 groups in the analogous hydrocarbons (*cf* data in Tables 1–3)

functions (O-3 and C-3 in the tricyclo-[3.2.1.0^{2,4}]octane family). It is established that variations of the mean excitation energy[12] has a definite contribution to δ_C and δ_O in very similar compounds.[13,14] As long as no simple relation can be defined between these variations and the variation of electron densities as a function of the structures, one can hope only for tentative explanations.

Finally, we observed that the α-Me substituent effect on δ_O (16–20 ppm) of 2,3-bis(methylene)-7-oxanorbornane (*cf* **4–6**, Table 1) was somewhat larger than the Me effect (derived from the comparison of the δ_O of diisopropylether (52.5 ppm), isopropyltertbutylether (62.5 ppm) and diterbutylether (76 ppm). It is slightly smaller than the β-methyl substituent effects reported for the δ_O of tetrahydrofuran and tetrahydropyran.[33]

The differences observed for the δ_O of the *cis*- (**37**) and *trans*-trioxa-tris-σ-homobenzene (**38**) witnesses the importance of conformational and configurational factors.[33,34] These factors, undoubtedly, are intervening also in differentiating the various β,γ-unsaturation effects on δ_O and δ_C reported here (e.g.: *cf* the downfield "norbornene" and "oxanorbornene effects" on, respectively, δ_C and δ_O with the upfield β,γ-unsaturation effects in respectively cyclopentane and tetrahydrofuran[35]).

CONCLUSION

An endocyclic double bond at C-2,3 and C-5,6 of 7-oxanorbornanes and at C-6,7 of *exo*-3-oxatricyclo-[3.2.1.0^{2,4}]octanes induce remarkable downfield shifts on δ_O. Contrastingly, an exocyclic *s-cis*-butadiene at the same positions leads to much smaller downfield shifts. These effects are proportional to the effects observed on δ_C in the corresponding hydrocarbons. The correlation laws δ_O/δ_{C-7} for 7-oxanorbornanes/norbornanes approximately parallels the correlation law reported for acyclic, aliphatic ethers/hydrocarbons. The "cyclization shifts" on δ_O for ethers are not correlated by the "cyclization shifts" on δ_C for the corresponding hydrocarbons.

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