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^{17}O NMR CHEMICAL SHIFTS *VERSUS* STRUCTURE RELATIONSHIPS IN OXIRANES [1]

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Summary: Natural-abundance ^{17}O NMR spectra have been measured for twenty one oxiranes. Their chemical shifts covering a 100 ppm range were interpreted in terms of the paramagnetic β- and diamagnetic γ-effects. In addition, through-space orbital interaction between the ethylenic π and the Walsh orbitals of the oxirane ring was suggested by a lowfield shift in norbornadiene *exo*-oxide.

We have shown that natural-abundance ^{17}O NMR spectroscopy which is now easily accessible by chemists as a result of recent advances in FT NMR instrumentation can be extremely useful for elucidating the structure and chemical bonding of oxygen-containing compounds. Chemical shifts covering a more than 1000 ppm range are explained in terms of empirical rules which are in principle quite similar to those used to interpret ^{13}C NMR data.[2] In order to demonstrate the usefulness of ^{17}O NMR as a structural probe of more subtle changes in structure and chemical bonding, we have now examined a series of oxiranes.[3]

Just as in ^{1}H and ^{13}C NMR of cyclopropanes, oxiranes, and aziridines, the oxygen nuclei of oxiranes are most highly shielded among the ether family. Introduction of methyl groups to the three-membered ring leads to a gradual downfield shift as shown in Table 1: a 33 ppm downfield shift by one methyl group (**1** → **3**) and 59, 63, and 66 ppm shifts by two methyl groups (**14**, **15** and **16** relative to **1**, respectively). The third methyl group appears to induce a downfield shift of 25 ppm (**10** → **18**). The resonance shift of tetramethyloxirane **21** is 47, 43, and 40 ppm downfield from those of dimethyloxiranes **14**, **15**, and **16**, respectively. Thus, whereas the effects of polysubstitution are levelling off, there still holds an approximate additivity; one methyl group has the effect of inducing a *ca*. 30 ppm downfield shift. The value can be compared with 9.4 ppm of the β-methyl parameter in the additivity rule for the ^{13}C chemical

Table 1. ^{17}O chemical shifts of typical oxiranes and ^{13}C chemical shift data for the methylene carbons of structurally related cyclopropanes.

oxirane	no.	$\delta^{17}O$	$\delta^{13}C$	oxirane	no.	$\delta^{17}O$	$\delta^{13}C$
ethylene oxide	**1**	-49	-3.8	cycloheptene oxide	**12**	4	
1,2-butylene oxide	**2**	-18		cyclooctene oxide	**13**	9	
propylene oxide	**3**	-16	6.0	isobutylene oxide	**14**	10	14.1
norbornene *exo*-oxide	**4**	-15	1.2	*cis*-2-butene oxide	**15**	14	
epichlorohydrin	**5**	-14		*trans*-2-butene oxide	**16**	17	
cyclopentene oxide	**6**	-8	5.8	benzonorbornadiene *exo*-oxide	**17**	37.5	14.9
1,4-dihydronaphthalene oxide	**7**	-8	3.0	1-methylcyclohexene oxide	**18**	28	
styrene oxide	**8**	-6	9.1	α-pinene oxide	**19**	34	
cycloocta-1,5-diene dioxide	**9**	2		norbornadiene *exo*-oxide	**20**	53	19.2
cyclohexene oxide	**10**	3	10.5	2,3-dimethyl-2-butene oxide	**21**	57	
cyclohexa-1,4-diene oxide	**11**	1	6.5				

shifts of alkanes.[4]

In this connection, it seemed of interest to plot ^{17}O shifts of oxiranes against ^{13}C shifts of the corresponding carbon atoms in the structurally related cyclopropanes. A line of reasonably good correlation (r = 0.935) with a slope of 3.83 was obtained as shown in Figure 1.[5] It is thus demonstrated that a similar mechanism is playing in determining the ^{13}C and ^{17}O shifts, although the latter being about four times more sensitive. The common mechanism in question would be paramagnetic screening. According to Pople's approximate expression, the local paramagnetic screening constant is given by Eq. 1,

$$\sigma_p^A = -\frac{e^2\hbar^2\langle r^{-3}\rangle}{2m^2c^2(\Delta E)}[Q_{AA} + \sum_{A\neq B} Q_{AB}] \qquad (1)$$

whereQ's are constitutive terms and ΔE is a mean or effective excitation energy. Other things being equal between structurally related epoxides and cyclopropanes, the slope in Figure 1 should correspond to the ratio of $\langle r^{-3}\rangle_O$ to $\langle r^{-3}\rangle_C$, where $\langle r^{-3}\rangle$ is the mean inverse cube of the 2p electron radius. It amounts theoretically to 2.74 and experimentally to 2.96 for acyclic ethers,[6] for example. A larger value found here for oxiranes *vs*. cyclopropanes appears to show that changes in ΔE is more dependent on a subtle structural change in oxiranes than in cyclopropanes. Thus it is possible that a minor change in chemical bonding and/or orbital interactions which may not be found in cyclopropanes by ^{13}C NMR could be found by ^{17}O NMR of oxiranes.

An upfield shift of ^{17}O resonance in norbornene *exo*-oxide **4** by 18 ppm

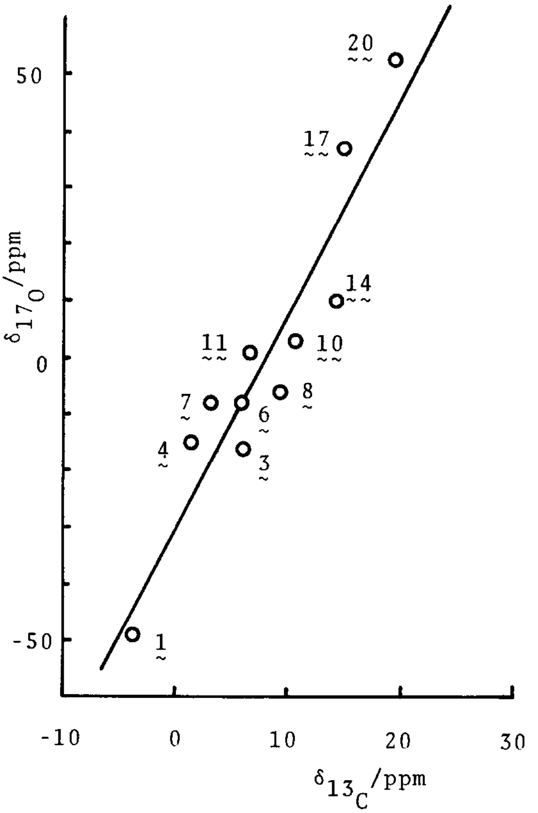

Figure 1. Plots of the ^{17}O chemical shifts of oxiranes *vs*. the ^{13}C chemical shifts of cyclopropanes.

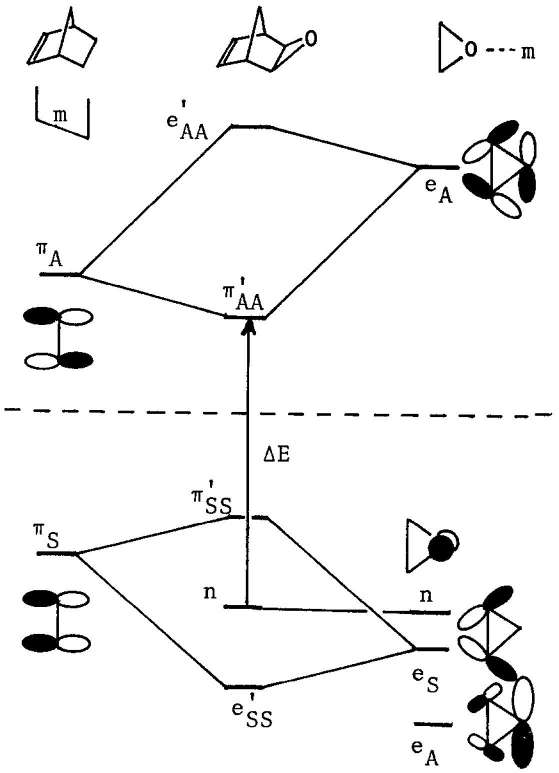

Figure 3. Correlation diagram for the construction of the molecular orbitals of norbornadiene *exo*-oxide

relative to cyclohexene oxide 10 can be ascribed to the γ-effect. A similar but diminished amount of the effect is already evident in the corresponding cyclopropane derivatives as summarized in Figure 2. The steric γ-effect of an *exo*-cyclopropane ring on the methano-bridge carbon has been pointed out by the present authors;[7] the ^{13}C shift values of the tricyclic hydrocarbons are smaller by 11.5, 11.0, and 12.1 ppm than those of norbornane, norbornene, and benzonorbornene, respectively (Figure 2). Similar γ-effects in ^{13}C shifts due to an *exo*-oxirane ring are obtained as reported:[7,8] Δδ of -12.0, -8.1, and -9.9 ppm for 4, 20, and 17, respectively. It can be regarded as the counteraction of this γ-effect which is observed for the ^{17}O shift of 4 and described above.

The downfield ^{17}O shifts by 52 and 45 ppm in 20 and 17 relative to 11 and 7, respectively, and ^{13}C shifts by 12.7 and 11.9 ppm of the cyclopropane methylene in the corresponding tricyclohydrocarbons are unusual and may require some orbital interactions as follows to be taken into account. Just as through-space interaction between the π-orbitals in norbornadiene,[9] a significant overlap is expected between the π-orbital and the Walsh orbital of the oxirane ring beneath the carbon skeleton of norbornadiene exo-oxide **20**. The π* level of the ethylenic moiety mixes with the antibonding Walsh orbital to effect lowering of the π* orbital (see Figure 3). As a result, an effective n→π* excitation energy ΔE in Eq. 1 decreases and the paramagnetic screening will increase to give a downfield shift.

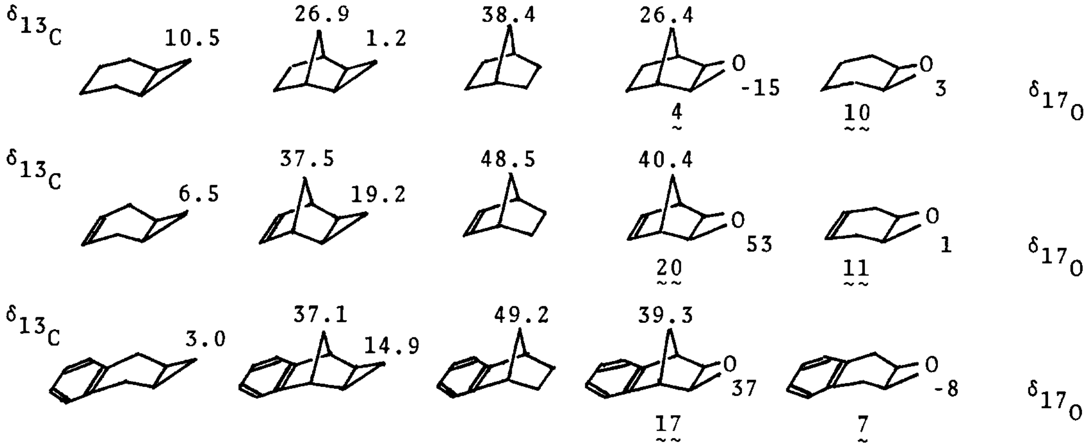

Figure 2. The γ-effects on ^{13}C and ^{17}O chemical shifts.

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