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STEREOELECTRONIC INTERPRETATION OF THE UNUSUAL PERLIN EFFECTS AND ^{1}H NMR CHEMICAL SHIFTS IN 1,3-OXATHIANE

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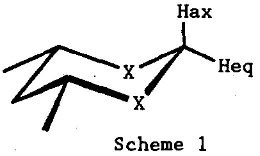
Abstract. Interpretation of "anomalous" Perlin effects and ^{1}H NMR chemical shifts in 1,3-oxathiane seems plausible by consideration of the relative importance of stereoelectronic interactions in this heterocycle.

Introduction.

The original studies of Perlin and Casu[1] laid the foundation for the development of useful correlations between C-H bond orientation and the magnitude of the corresponding ^1J coupling constants. For example, it has been observed that the magnitude of the one-bond coupling constants for an axial C-H bond adjacent to oxygen or nitrogen in a six membered ring is 8-10 Hz smaller than ^1J for the corresponding C-H equatorial bond; i.e. $^1J_{C-Heq} > {}^1J_{C-Hax}$. This observation has been interpreted in terms of an n → σ* stereoelectronic interaction between a pair of nonbonded electrons on oxygen or nitrogen and the axial, antiperiplanar adjacent C-H bond.[2]

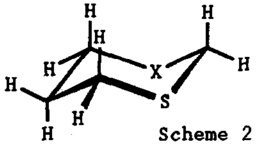
A pertinent example is *cis*-4,6-dimethyl-1,3-dioxane (1, Scheme 1) where $^1J[C(2)-H_{ax}] = 157.4$ Hz is smaller than $^1J[C(2)-H_{eq}] = 167.5$ Hz.[3] In contrast with this situation, Bailey et al.[4] discovered that the dithiane analogue 2 (Scheme 1) exhibits an opposite behavior; that is, $^1J[C(2)-H_{ax}] = 154.1$ Hz > ^1J $[C(2)-H_{eq}] = 144.9$ Hz.



1, X = O
2, X = S

Scheme 1

More recently, Juaristi and Cuevas[5] reported that a reversal of the relative magnitudes of the coupling constants [$^1J_{C-Hax} > {}^1J_{C-Heq}$; "reverse" Perlin Effect] is actually observed for all C-H bond pairs in 1,3-dithiane (3, Scheme 2). This finding appears to support the existence of a dominant stereoelectronic interaction between the relevant fragment orbitals in the equatorial C-H bonds and antiperiplanar C-S bonds, as previously suggested by Wolfe, et al.[6] The present note describes our observations in 1,3-oxathiane (4, Scheme 2), a system which could provide relevant information concerning the relative magnitude of stereoelectronic interactions involving oxygen *vis-a-vis* sulfur.



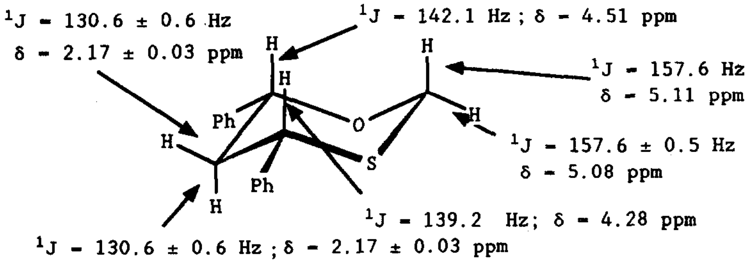
3, X = S
4, X = O

Scheme 2

Results.

A. *cis*-4,6-Diphenyl-1,3-oxathiane (5).[7]

Proton-coupled ^{13}C, and high-resolution ^{1}H NMR spectra of 5 afforded the data indicated in Scheme 3. Most interestingly, similar coupling constants $^{1}J_{C-H_{ax}} \cong {}^{1}J_{C-H_{eq}}$ are observed both at C(2) and C(5), suggesting a balance of the effect(s) responsible for a "normal" $^{1}J_{C-H_{ax}} < {}^{1}J_{C-H_{eq}}$ for C-H bonds in cyclohexane[8] or adjacent to oxygen,[1-3] but a "reverse" trend (i.e., $^{1}J_{C-H_{eq}} < {}^{1}J_{C-H_{ax}}$) when the C-$H_{eq}$ is antiperiplanar to C-S bonds (see the introduction).

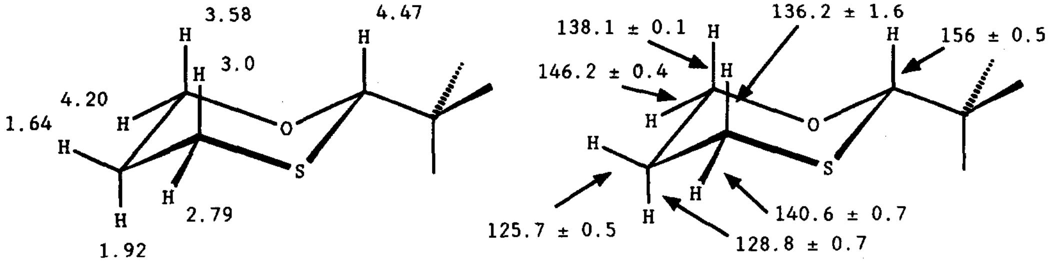


Scheme 3

B. 2-*tert*-Butyl-1,3-oxathiane (6).

Proton-coupled ^{13}C, and high-resolution ^{1}H NMR spectra of 6 permitted the unequivocal assignments presented in Scheme 4. Thus, anomalous chemical shift behavior ($\delta H_{ax} > \delta H_{eq}$) is observed for the methylene protons at C(4) and C(5). By contrast, the protons at C(6) (adjacent to oxygen) exhibit the normal $\delta H_{ax} < \delta H_{eq}$.

On the other hand, for the methylene C_4-H bonds adjacent to sulfur $^{1}J_{C-H_{ax}} < {}^{1}J_{C-H_{eq}}$ (normal Perlin effect), in contrast with the observation in 1,3-dithiane.[5] Nevertheless, at C(5) $^{1}J_{C-H_{ax}} \cong {}^{1}J_{C-H_{eq}}$ (near *balance* of Perlin effects), and for the methylene adjacent to oxygen $^{1}J_{C-H_{ax}} < {}^{1}J_{C-H_{eq}}$ (*normal* Perlin effect).

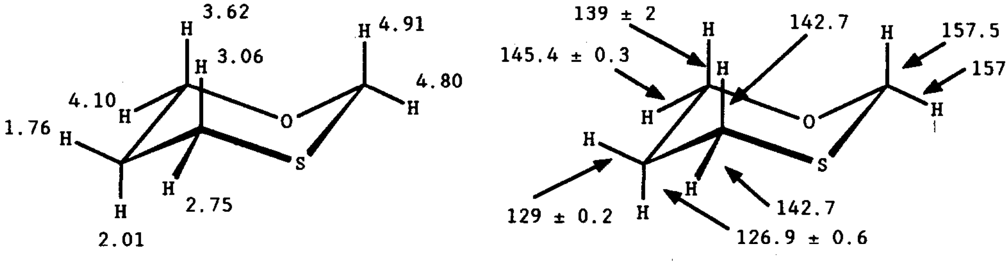


(^{1}H chemical shifts) Scheme 4 ($^{1}J_{C-H}$ coupling constants)

C. <u>Low-temperature Spectra of 1,3-Oxathiane</u> (<u>4</u>).

At -90 °C, ring inversion of the unsubstituted heterocycle is slowed sufficiently so that the individual chemical shifts and coupling constants could be measured. This study was important in view of the previous observation that the *t*-butyl group at C(2) distorts the ring,[9] so that some of the NMR data from <u>6</u> may not be representative of those in the parent system.

The data collected in Scheme 5 (solvent CD_2Cl_2) confirm the anomalous chemical shifts for the axial and equatorial hydrogens at C(2), C(4), and C(5); that is, $\delta H_{ax} > \delta H_{eq}$. Interestingly, a near *balance* of Perlin effects is observed for the C-H coupling constants in these carbons. On the other hand, *normal* chemical shifts and Perlin effects are found at C(6).



(^1H chemical shifts) ($^1J_{C-H}$ coupling constants)

Scheme 5

<u>Discussion</u>.

Three pieces of information seem to be essential for the understanding of the unusual Perlin effects and proton chemical shifts reported above:

(1) the observation made by Eliel et al.[10] that diamagnetic bond anisotropies alone[11] do *not* properly account for the anomalous shifts at C(2) in 1,3-dithiane,

(2) the proposal of Wolfe et al.[6] that the smaller coupling constant for $^1J_{C-H_{eq}}$ at C(2) in 1,3-dithiane originates from the weaker nature of this bond, as a result of $\sigma_{C-H} \rightarrow \sigma^*_{C-S}$ or $\sigma_{C-S} \rightarrow \sigma^*_{C-H}$ stereoelectronic (antiperiplanar) orbital interactions, and

(3) the finding by Juaristi and Cuevas[5] that *all* equatorial bonds in 1,3-dithiane are antiperiplanar to C-S bonds, and do exhibit smaller $^1J_{C-H_{eq}}$ coupling constants.

We consider that the anomalous chemical shifts for the axial and equatorial protons at C(2), C(4) and C(5) are the result of relevant contributions by the $\sigma_{C-S} \rightarrow \sigma^*_{C-H}$ two-electron two-orbital interactions. This stereoelectronic effect causes an upfield shift for the antiperiplanar, equatorial hydrogens, as well as a concomitant decrease on the $C-H_{eq}$ coupling constants, which is nearly balanced by the normal Perlin effect.[12] On the "oxygen-part" of the molecule, however, the well accepted $n_O \rightarrow \sigma^*_{C-H}$ interaction appears to be dominant.

Examination of the observed $^1J_{C-H}$ coupling constants in cyclohexane ($^1J_{C-H_{ax}}$= 122

Hz; $^1J_{C-H_{eq}}$= 126 Hz),[8] 1,3-dithiane,[4,5,13] 1,3-dioxane,[3,13] and 1,3-oxathiane (this work; Section C) suggests the following heteroatom effects: α-oxygen = +21 Hz; α-sulfur = +16 Hz; β-oxygen = +3 Hz; β-sulfur = +4 Hz; γ-oxygen = +3 Hz; antiperiplanar n_O = -2 Hz, antiperiplanar σ_{C-S} = -7 Hz.[14] A full discussion will be presented in a forthcoming full paper.

Acknowledgments. We are grateful to Professor W.F. Bailey for suggesting the study of Perlin effects in 1,3-oxathiane, and for additional comments, to Professor B.M. Pinto for a careful reading of this manuscript, to G. Uribe for recording the NMR spectra, and to CONACYT (project no. E0242) for partial financial support.

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(14)We are indebted to one rewiewer for suggesting this method of increments to analyze the observed heteroatom effects on $^1J(^{13}C-H)$.

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