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Manifestation of Stereoelectronic Effects on the Calculated Carbon−Hydrogen Bond Lengths and One Bond $^{1}J_{C-H}$ NMR Coupling Constants in Cyclohexane, Six-Membered Heterocycles, and Cyclohexanone Derivatives

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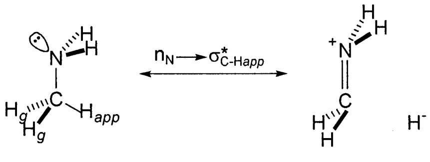
Abstract: Cyclohexane (**1**), oxygen-, sulfur-, and/or nitrogen-containing six-membered heterocycles **2**−**5**, cyclohexanone (**6**), and cyclohexanone derivatives **7**−**16** were studied theoretically [B3LYP/6-31G(d,p) and PP/IGLO−III//B3LYP/6-31G(d,p) methods] to determine the structural (in particular C−H bond distances) and spectroscopic (specifically, one bond $^{1}J_{C-H}$ NMR coupling constants) consequences of stereoelectronic hyperconjugative effects. The results confirm the importance of $n_X \rightarrow \sigma^*_{C-Happ}$ (where X = O, N), $\sigma_{C-Hax} \rightarrow \pi^*_{C=O}$, $\sigma_{S-C} \rightarrow \sigma^*_{C-Happ}$, $\sigma_{C-S} \rightarrow \sigma^*_{C-Happ}$, β-$n_O \rightarrow \sigma^*_{C-H}$, and $\sigma_{C-H} \rightarrow \sigma^*_{C-Happ}$ hyperconjugation, as advanced in previous theoretical models. Calculated r_{C-H} bond lengths and $^{1}J_{C-H}$ coupling constants for C−H bonds participating in more than one hyperconjugative interaction show additivity of the effects.

Introduction

Present-day interpretation of molecular structure and reactivity usually takes into account steric and electrostatic interactions, and increasingly, stereoelectronic effects. In particular, it is realized that the orientation between bonds and lone pairs in a molecule may lead to stereospecific bond cleavage and/or bond formation. This is, of course, of fundamental importance in areas such as diastereo- and enantioselective synthesis, and motivates continued interest in the understanding of the basic principles[3] and consequences[4] of stereoelectronic interactions.

Particularly useful in this area of study are spectroscopic manifestations of stereoelectronic interactions. Indeed, already in 1957 F. Bohlmann made the important observation that C−H bonds antiperiplanar (app) to a vicinal nitrogen lone pair in conformationally defined amines present characteristic stretching frequencies.[5] Subsequent model studies with methylamine indicated that the $C-H_{app}$ bond is longer and weaker than the $C-H_{gauche}$ bonds,[6] and these observations have been interpreted as the result of $n_N \rightarrow \sigma^*_{C-Happ}$ hyperconjugation (**A** ↔ **A′**; eq 1).



A **A′**

(1)

Hyperconjugative processes such as the one depicted in eq 1 benefit from a two electron−two orbital interaction between an occupied, high-energy donor orbital and an empty, low-energy acceptor orbital[3,7] (Scheme 1). Because this stabilizing orbital interaction is inversely proportional to the energy difference between the interacting orbitals, the strongest stabiliz-

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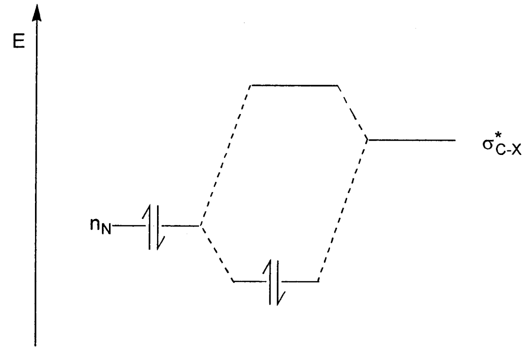
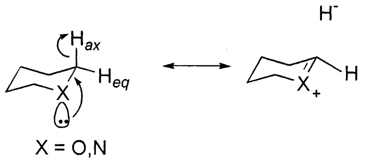
Scheme 1



ing interactions usually take place between the most effective donors and the most effective acceptors.

In another insightful observation, Perlin and Casu[8] reported that the magnitude of the one bond $^{13}C{-}^{1}H$ coupling constants for an axial C−H bond adjacent to oxygen or nitrogen in a six-membered ring is substantially smaller (by 8−10 Hz) than that of a $^{1}J_{C-H}$ for an equatorial C−H bond; that is, $^{1}J_{C-Hax} < {}^{1}J_{C-Heq}$.[8,9] This finding has been explained in terms of an $n_X \rightarrow \sigma^*_{C-Happ}$ (X = O, N) interaction between a pair of nonbonded electrons on oxygen or nitrogen and the axial (antiperiplanar) adjacent C−H bond; that is, double bond-no bond resonance[10] weakens the C−H_{ax} bond and attenuates the Fermi contribution to the one bond $^{13}C{-}^{1}H$ coupling constant (eq 2).[11−14] It has been proposed by Wolfe et al.[12] that stereoelectronic effects upon one-bond C−H coupling constants be termed "Perlin effects".



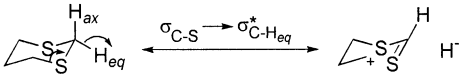
(2)

Nevertheless, Bailey et al.[15] discovered in 1988 that, in contrast with the situation in *cis*-4,6-dimethyl-1,3-dioxane (**B**, Chart 1) where $^{1}J_{C(2)-Hax} = 157.4$ Hz $< {}^{1}J_{C(2)-Heq} = 167.5$ Hz,[9a] the 1,3-dithiane analogue **C** (Chart 1) exhibits and opposite behavior: $^{1}J_{C(2)-Hax} = 154.1$ Hz $> {}^{1}J_{C(2)-Heq} = 144.9$ Hz.

Chart 1

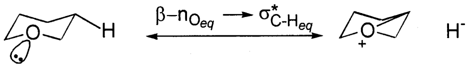
B **C**

This reversal of the relative magnitudes of the coupling constants was explained by Wolfe et al.[12,16] in terms of a dominant $\sigma_{C-S} \rightarrow \sigma^*_{C-Heq}$ or $\sigma_{C-Heq} \rightarrow \sigma^*_{S-C}$ (rather than $n_S \rightarrow \sigma^*_{C-Hax}$) interaction in **C** (eq 3). Juaristi and co-workers[17] provided experimental as well as theoretical support for such interpretation. Furthermore, the peculiar upfield chemical shifts observed for C(2)−H_{eq} in 1,3-dithiane and derivatives are in agreement with $\sigma_{C-S} \rightarrow \sigma^*_{C-Heq}$ hyperconjugation, instead of $\sigma_{C-Heq} \rightarrow \sigma^*_{S-C}$ interactions.[17c,18]



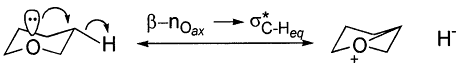
(3)

In a further development, Anderson et al.[19] reported evidence for a stereoelectronic interaction between a β-oxygen atom and equatorial C−H bonds in 1,3-dioxanes and 1,2,4-trioxanes, that afforded the "reversed" $^{1}J_{C-Hax} > {}^{1}J_{C-Heq}$ order. On the basis of intuitive arguments, Anderson et al.[19] suggest that "homo-anomeric" hyperconjugation between the equatorial lone pair on the β−oxygen and C−H_{eq} in a W-plan arrangement resulted in weaker bonds and, therefore, smaller one-bond C−H coupling constants (eq 4).



(4)

More recently, however, a computational study by Alabugin[13] led to the plausible conclusion that it is the axial (p-type), rather than the equatorial (s-type) lone pair at the β-oxygen atom, that is involved in the stereoelectronic interaction (eq 5).



(5)

Thus, the relative magnitude of one bond $^{13}C{-}^{1}H$ coupling constants in six-membered oxygen- and sulfur-containing heterocycles show the importance of various stereoelectronic hyperconjugative interactions through which electron density is transferred to suitably oriented acceptor C−H bonds ($n_O \rightarrow \sigma^*_{C-Happ}$,[8−17] $\sigma_{C-S} \rightarrow \sigma^*_{C-Happ}$,[12,13,16,17] and $\beta\text{-}n_{Oax} \rightarrow \sigma^*_{C-Heq}$[13]). Furthermore, it is now generally accepted that σ_{C-H} bonds are better donors than σ^*_{C-C} bonds,[4a,13,20] so that $\sigma_{C-Hax} \rightarrow \sigma^*_{C-Hax}$ stereoelectronic interactions must be considered in any systematic analysis of Perlin effects.

A different form of hyperconjugation has been documented for substituted π systems. In particular, sigma C−H bonds can

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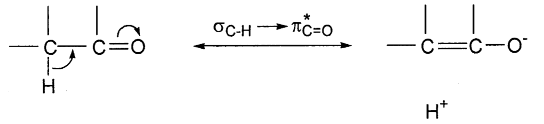
in principle act as electron donors to adjacent π double bonds or carbonyl groups as depicted in eq 6.[21]



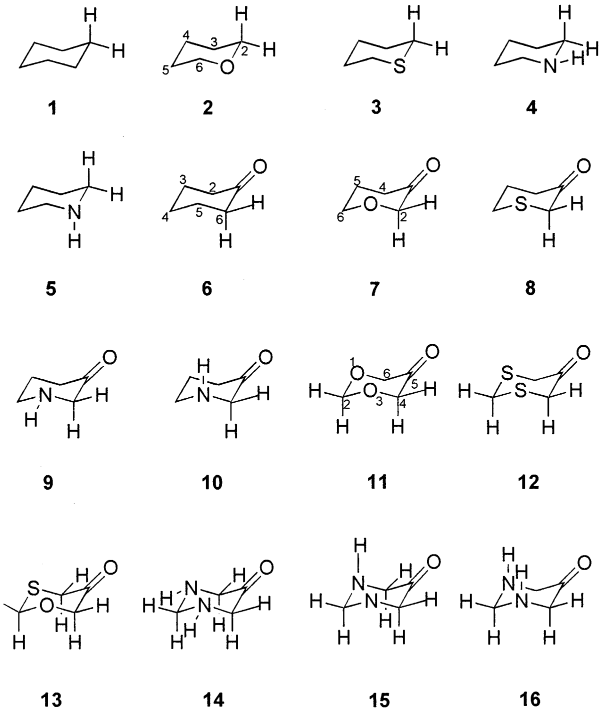
(6)

In this paper, we describe a computational study aimed at determining the relative importance of hyperconjugative interactions involving sigma C−H donor bonds and the carbonyl π system as the acceptor orbital. Specifically, we sought manifestation of $\sigma_{C-H} \rightarrow \pi^*_{C=O}$ stereoelectronic interaction upon the magnitude of calculated $^1J_{C-H}$ coupling constants. An additional question of interest is whether stereoelectronic effects are additive in systems where a sigma C−H bond can participate both as an acceptor σ^*_{C-H} orbital (in particular, $n_X \rightarrow \sigma^*_{C-H}$ hyperconjugation, X = O, N) and as a donor σ_{C-H} orbital (in particular, $\sigma_{C-H} \rightarrow \pi^*_{C=O}$ hyperconjugation).

Results and Discussion

A. General Remarks. Chart 2 presents the 16 molecular structures that were examined in this work. Cyclohexane **1** serves as the parent, reference compound, whereas heterocycles **2**−**5** provide the fundamental information on the consequences of replacing a methylene group in cyclohexane for oxygen (**1** → **2**), sulfur (**1** → **3**), equatorial N−H (**1** → **4**), and axial N−H (**1** → **5**). Specifically, all C−H bond lengths in **2**-**5** are compared with the reference C−H$_{ax}$ and C−H$_{eq}$ bond lengths in cyclohexane: any C−H bond lengthening observed in **2**−**5** might reflect stereoelectronic interactions, where σ^*_{C-H} is the acceptor orbital. (Nevertheless, interactions where σ_{C-H} is a donor orbital, as in $\sigma_{C-Hax} \rightarrow \sigma^*_{C-Hax}$ hyperconjugation, should also result in C−H bond lengthening since electron density is removed from a bonding orbital). Furthermore, although longer C−H bonds are *not* always associated with larger one-bond C−H coupling constants,[13,17c] weaker C−H bonds are expected to be associated with smaller $^1J_{C-H}$ coupling constants.[8−17]

Chart 2



Cyclohexanone **6** allows determination of any effect that the presence of the carbonyl group has on the C−H bond strength for the ring methylenes. In particular, as indicated in the Introduction, axial C−H$_{ax}$ bonds adjacent to the carbonyl π-system should hyperconjugate, leading to weaker bonds. By contrast, equatorial C−H$_{eq}$ bonds adjacent to the carbonyl are essentially orthogonal to the π orbital, so that hyperconjugation $\sigma_{C-Heq} \rightarrow \pi^*_{C=O}$ will be negligible. Thus, it is anticipated that for the methylenic groups adjacent to the carbonyl, $^1J_{C-Hax} < {}^1J_{C-Heq}$ (see below).

1-Heterocyclohexan-3-ones **7**−**10** present four distinct pairs of methylenic C−H bonds. Most interestingly, the axial C−H bond at C(2) can participate in *two* stereoelectronic interactions: as acceptor orbital in $n_X \rightarrow \sigma^*_{C-Happ}$ "anomeric-type" hyperconjugation, and as donor in a $\sigma_{C-Hax} \rightarrow \pi^*_{C=O}$ interaction. Neither of these interactions should be relevant in C(2)−H$_{eq}$, so that the difference $^1J_{C(2)-Heq} - {}^1J_{C(2)-Hax}$ should be a measure on the degree of additivity of hyperconjugative mechanisms, which are best evaluated by examination of C−H$_{ax}$ and C−H$_{eq}$ at C(4), where only the $\sigma_{C-Hax} \rightarrow \pi^*_{C=O}$ interaction is revelant, and at C(6), where $n_X \rightarrow \sigma^*_{C-Hax}$ must be the dominant stereoelectronic interaction relative to $\sigma_{C-Heq} \rightarrow \sigma^*_{C-C}$ or $\sigma_{C-Heq} \rightarrow \sigma^*_{X-C}$ alternative interaction that weaken the equatorial C(6)−H bond.[23]

Finally, the question of additivity of stereoelectronic effects on C−H bond length and $^1J_{C-H}$ coupling constants can be answered by examination of 1,3-diheterocyclohexan-5-ones **11**−**16**. Indeed, the methylenic axial and equatorial C−H bonds at C(2) in these compounds are adjacent to *two* heteroatoms, so that two $n_X \rightarrow \sigma^*_{C-Happ}$ interactions are possible. In contrast, the methylenic C−H bonds at C(4,6) in heterocycles **11**−**16** are both adjacent to one heteroatom possessing one or two lone pairs of electrons and to the carbonyl group.

B. Computational Methods. Full geometry optimizations (no symmetry constraints) of all compounds were performed using the hybrid functional B3LYP with a 6-31G(*d*,p) basis set. For compounds **6** and **11**−**16**, six *d* orbital functions were used instead of the usual five *d* functions, and for compounds **2**−**5** and **7**−**10** six *d* and 10 *f* orbital functions were used. These calculations were carried out with the Gaussian 92 Program (G92).[24] As it is reported, in this protocol electron exchange is taken into account by a combined local and gradient-corrected correlation functional, $C^*E_C^{LYP} + (1 - C)^*E_C^{VWN}$, where LYP is the correlation functional of Lee, Yang, and Parr,[25] including

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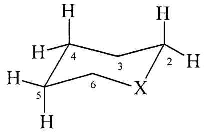
both local and gradient corrected terms, and VWN is the Vosco, Wilk, and Nusair 1980 correlation functional fitting the RPA solution to the uniform gas, often referred to as Local Spin Density (LSD) correlation.[26] VWN is used to provide the excess local correlation required, since LYP contains a local term essentially equivalent to VWN.[25] For compounds **2** to **10**, 6*d* and 10*f* keywords were included, whereas for compounds **11** to **16** only the 6*d* keyword was used.

The density functional calculation of ^{1}H and ^{13}C NMR coupling constants was done using the recently proposed approach of Malkin, Malkina, and Salahub.[27−29] Within this methodology, three contributions to the NMR coupling constants are considered, namely, the Fermi contact (FC), the paramagnetic spin−orbit (PSO) and the diamagnetic spin−orbit (DSO). The spin-dipolar (SD) and cross terms such as FC−SD are neglected. The FC term is calculated by finite perturbation theory (FPT), the PSO contribution is obtained using the sum-over-states density functional perturbation theory (SOS-DFPT)[27a] and the DSO term by numerical integration.[28,29] These spin−spin coupling constant calculations were carried out with a modified version of the deMon-KS program[30,31] together with the deMon-NMR program.[28−30] Following the suggestions made by the authors of this latter code, the NMR spin−spin coupling constants were calculated using the semilocal exchange of Perdew and Wang[32] and the correlation functional of Perdew,[33] a combination that will be denoted as PP. A value of 0.001 was used for the perturbation parameter in the FPT calculation of the FC term and the lighter nucleus is selected as the perturbation center. The PSO contribution was obtained with the local 1 approximation.[27] A fine grid (with 32 radial points) with an extra iteration was used, and the basis set employed in the coupling constant calculations was the IGLO−III of Kulzelnigg.[34] Thus, following the usual notation, the level of theory for the determination of coupling constants used in this work is PP/IGLO−III//B3LYP/6-31G(*d*,*p*).

C. Cyclohexane 1 and Monoheterocyclohexanes 2−5. Table 1 collects the structural data for cyclohexane **1**, oxane **2**, thiane **3**, and azanes **4** and **5**, where the N−H bond is oriented equatorial or axial, respectively. In the 4-31G calculations of Wiberg et al.[35] the axial and equatorial C−H bond lengths of cyclohexane **1** are 1.088 and 1.086 Å, respectively. Our values (ref 17d and this work) also predict that the axial C−H bond of cyclohexane is longer (and thus weaker) than the equatorial C−H bond: $C{-}H_{ax} = 1.100$ Å and $C{-}H_{eq} = 1.098$ Å. In the Cieplak language,[4a,20] the longer and weaker axial C−H bonds are the result of $\sigma_{C-Hax} \rightarrow \sigma^{*}_{C-Hax}$ hyperconjugation between antiperiplanar bonds.[12,36]

Table 1. Optimized Geometries at the B3LYP/6-31G(d,p) Level (distances in Å, angles in deg) for Cyclohexane (**1**), Oxane (**2**), Thiane (**3**), Equatorial Azane (**4**), and Axial Azane (**5**)



1, X = CH_2
2, X = O
3, X = S
4, X = equat. N–H
5, X = axial N–H

	1	**2**	**3**	**4**	**5**
X−C(2)	1.537	1.423	1.838	1.465	1.467
C(2)−C(3)	1.532	1.531	1.531	1.533	1.540
C(3)−C(4)	1.532	1.537	1.537	1.537	1.537
$C(2){-}H_{ax}$	1.100	1.105	1.097	1.109	1.100
$C(2){-}H_{eq}$	1.098	1.094	1.094	1.096	1.096
$C(3){-}H_{ax}$	1.108	1.097	1.097	1.097	1.100
$C(3){-}H_{eq}$	1.098	1.097	1.098	1.097	1.098
$C(4){-}H_{ax}$	1.100	1.099	1.100	1.100	1.100
$C(4){-}H_{eq}$	1.106	1.096	1.096	1.096	1.096
X−C(2)−C(3)	111.5	111.8	112.9	109.6	114.2
C(2)−C(3)−C(4)	111.5	110.2	112.9	110.7	110.7
C(3)−C(4)−C(5)	111.5	110.1	113.3	110.8	110.8
C(6)-X−C(2)	111.5	112.1	98.0	112.1	112.0
X−C(2)−C(3)−C(4)	54.9	55.7	60.1	56.4	53.2
C(2)−C(3)-C(4)−C(5)	54.9	51.5	59.3	52.6	52.6
C(6)-X−C(2)−C(3)	54.9	60.3	53.4	62.1	52.7
$X{-}H_{ax}$	- - - -	- - - -	- - - -	- - - -	1.019
$X{-}H_{eq}$	- - - -	- - - -	- - - -	1.016	- - - -

Although the bond length difference between axial and equatorial C−H bonds in cyclohexane is small ($r_{C-Hax} - r_{C-Heq} = 0.002$ Å), it becomes quite large for methylenes adjacent to oxygen and nitrogen (Table 1). For example, in oxane **2** ($r_{C(2)-Hax} - r_{C-Heq} = 0.011$ Å) and azane **4** (equatorial N−H bond, thus axial lone pair at nitrogen, $r_{C(2)-Hax} - r_{C-Heq} = 0.013$ Å). This larger $C{-}H_{ax/eq}$ bond length difference can of course be ascribed to the stereoelectronic effect $n_X \rightarrow \sigma^{*}_{C-Happ}$ present in **2** and **4**.[5,8,11−17]

Recently, Freeman and co-workers[37] reported the calculated optimized geometries for oxane (**2**) at various levels of theory, including higher levels of theory than those reported in this work. Nevertheless, it was found that HF 6-31G* basis sets afforded data that were generally reproduced at MP2 levels.[37] Most relevant to the present discussion, the structural data reported by Freeman also indicate that axial C−H bonds adjacent to oxygen are 0.009 to 0.014 Å longer than the equatorial C−H bonds. The lengthening of the C(2,6)-H_{ax} bonds in the chair conformation of oxane **2** is also ascribed by Freeman, Hehre, and co-workers to $n_O \rightarrow \sigma^{*}_{C-Hax}$ hyperconjugation.[37]

An interesting observation printed out by one of the reviewers is that, except for azane **5** (axial N−H), the C(2)−C(3) bonds in **2**, **3**, and **4** are shorter than the C(3)−C(4) bonds. Although the shorter C(2)−C(3) bonds in **2**−**4** may arise from the electronegativity effect by the heteroatom[38] (increased s-character at C(2)), it can be appreciated that the longer C(2)−C(3) bond is present in the only heterocycle in the series where the equatorial orientation of the lone pair at nitrogen prevents

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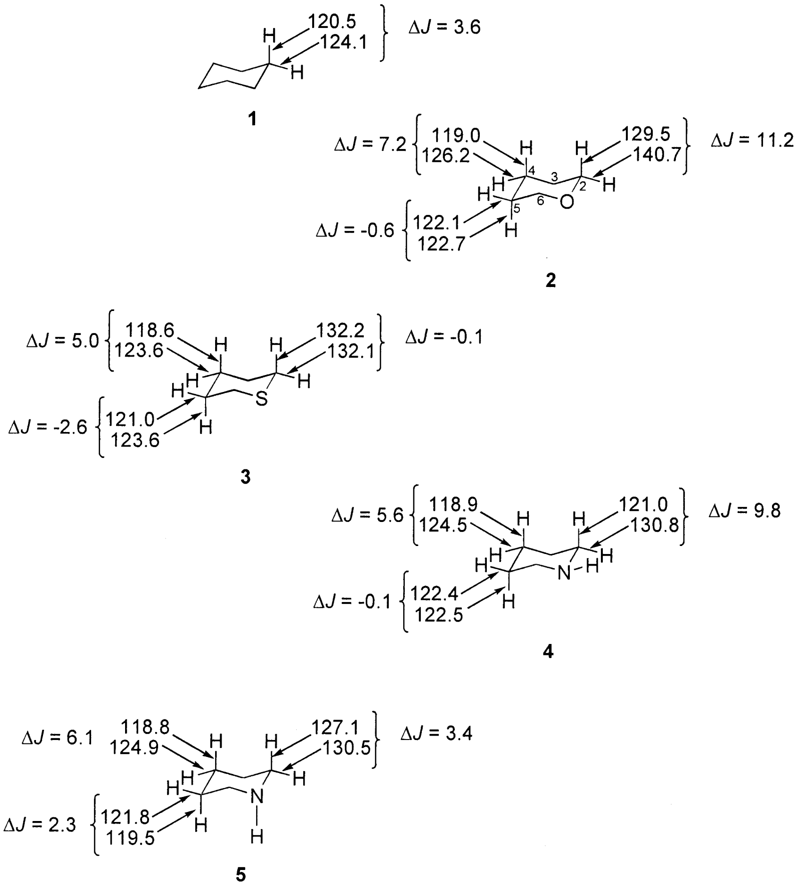
Chart 3



anomeric $n_{\mathrm{N}} \rightarrow \sigma^*_{\mathrm{C-H}ax}$ interaction. It can be argued that the s-character at C(2) in azane **5** is therefore lower, resulting in a longer C(2)−C(3) bond.

Thiane **3** has previously been studied computationally by the Freeman group.[39] The agreement between their structural parameters calculated at the B3LYP/6−31G(d) level and the data reported in Table 1 at the B3LYP/6-31G(d,p) level is almost perfect.

It should be noted that the small bond length difference, $r_{\mathrm{C(2)-H}ax} - r_{\mathrm{C(2)-H}eq} = 0.003$ Å) encountered in thiane **3** is in line with the poor ability by sulfur to participate as donor in $n_{\mathrm{S}} \rightarrow \sigma^*_{\mathrm{C-H}app}$ hyperconjugation.[12,13,15−18] As anticipated, $\Delta r_{\mathrm{C(2)-H}ax/eq}$ in azane **5** is also comparable to that in cyclohexane itself, because an axial N−H bond in azane presents necessarily an equatorial nitrogen lone pair, that is essentially orthogonal to the vicinal C−H bonds.

Finally, $r_{\mathrm{C(3)-H}ax} = r_{\mathrm{C(3)-H}eq} = 1.097$ Å in oxane **2**; thus, $\Delta r_{\mathrm{C(3)-H}ax/eq} = 0$. This finding can be explained in terms of competition between the normal $\sigma_{\mathrm{C-H}} \rightarrow \sigma^*_{\mathrm{C-H}app}$, which weakens the axial C(3)−H bond, and an opposing effect that weakens the equatorial C(3)−H bond. Alabugin[13] has suggested a stereoelectronic interaction between a pseudoaxial nonbonding electron pair on a β-oxygen and the equatorial C−H bond (eq 5) as responsible for the weakening of this bond, $\beta\text{-}n_{\mathrm{O}ax} \rightarrow \sigma^*_{\mathrm{C-H}eq}$.

Many more data in Table 1 are valuable for the evaluation of stereoelectronic interactions in six-membered rings. A particularly interesting observation is the significant difference in the axial C(2)−H bond lengths in isomeric azanes **4** and **5**. Only compound **4** should show the "anomeric" $n_{\mathrm{N}} \rightarrow \sigma^*_{\mathrm{C(2)-H}ax}$ effect, and indeed $r_{\mathrm{C(2)-H}ax} = 1.109$ Å for **4**, whereas $r_{\mathrm{C(2)-H}ax} = 1.100$ Å for **5**.

Chart 3 presents the calculated one bond $^{13}\mathrm{C}-^{1}\mathrm{H}$ coupling constants (Hz) for cyclohexane (**1**) and monoheterocyclohexanes **2**−**5**. To facilitate the analysis of the collected data, Chart 3 also includes the difference $\Delta J_{ax/eq} = J_{\mathrm{C-H}eq} - J_{\mathrm{C-H}ax}$ for each distinct methylene in the molecule. Positive ΔJ values reflect then normal "Perlin effects"; that is, typical situations where $\sigma_{\mathrm{C-H}ax} \rightarrow \sigma^*_{\mathrm{C-H}app}$ and/or $n_{\mathrm{X}} \rightarrow \sigma^*_{\mathrm{C-H}app}$ stereoelectronic interactions lead to weaker axial C−H bonds and smaller $^{1}J_{\mathrm{C-H}ax}$ coupling constants, relative to $^{1}J_{\mathrm{C-H}eq}$.[8−17.37,40]

With respect to our parent, reference cyclohexane (**1**) molecule, calculations reproduce the relative magnitude of both the C−H$_{ax}$ and C−H$_{eq}$ coupling constants, that is, the normal "Perlin effect" observed in cyclohexane,[41] as well as the absolute values, within reasonable limits (±2−3 Hz). Indeed, the calculated values $^{1}J_{\mathrm{C-H}ax}$= 120.5 Hz and $^{1}J_{\mathrm{C-H}eq} = 124.1$ Hz are to be compared with the corresponding experimental values, 122.4 and 126.4 Hz, respectively.[41]

There exist three distinct methylenic pairs of C−H bonds in oxane **2**. As anticipated, $n_{\mathrm{O}} \rightarrow \sigma^*_{\mathrm{C-H}app}$ hyperconjugation weakens the axial C−H bonds at C(2,6), so that $^{1}J_{\mathrm{C(2,6)-H}ax} =$

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(40) The dissection of the NMR coupling constanst into the Fermi Contact (FC) and diamagnetic and paramagnetic spin−orbit contributions (DSO and PSO, respectively) shows that the FC term plays the decisive role: see Table 3 in ref 17e.

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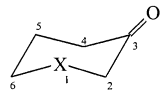
129.5 Hz is significantly smaller than $^{1}J_{\mathrm{C(2,6)-H}eq} = 140.7$ Hz; thus, the calculated $\Delta^{1}J_{ax/eq}$ is 11.2 Hz. In strong contrast, $^{1}J_{\mathrm{C(3,5)-H}ax} = 122.7$ Hz $>$ $^{1}J_{\mathrm{C(3,5)-H}eq} = 122.1$ Hz, and $\Delta^{1}J_{\mathrm{ax/eq}} = -0.6$ Hz. This *reverse* correlation of ^{1}J-values relative to cyclohexane[42] is in agreement with the proposal advanced by Anderson et al.[19] and Alabugin,[13] that a stereoelectronic "homoanomeric" interaction between a lone pair on a β−oxygen and the equatorial C−H bond, as depicted in eqs 4 and 5, weakens this bond. The difference between the Anderson[19] and the Alabugin[13] proposals consists of that the former invokes the participation of the pseudoequatorial oxygen lone pair ($\beta - n_{\mathrm{O}eq} \rightarrow \sigma^{*}_{\mathrm{C-H}eq}$, eq 4), whereas the latter supports the involment of the pseudoaxial lone pair ($\beta - n_{\mathrm{O}ax} \rightarrow \sigma^{*}_{\mathrm{C-H}eq}$, eq 5). Finally, the calculated coupling constants for the methylenic C−H bonds at C(4) [$^{1}J_{\mathrm{C(4)-H}ax} = 119.0$ Hz $<$ $^{1}J_{\mathrm{C(4)-H}eq} = 126.2$ Hz; $\Delta^{1}J_{ax/eq} = 7.2$ Hz] are those expected for a "cyclohexane-like" methylenic segment.

The one bond C−H coupling constants calculated for thiane **3** (Chart 3) reveal two "reverse" Perlin effects:[42] at C(2), where $n_{\mathrm{S}} \rightarrow \sigma^{*}_{\mathrm{C(2)-H}ax}$ hyperconjugation is not relevant[13,18] (see above) and the expected $\sigma_{\mathrm{C(3)-H}} \rightarrow \sigma^{*}_{\mathrm{C(2)-H}ax}$ interaction is offset by a dominant $\sigma_{\mathrm{C(6)-S}} \rightarrow \sigma^{*}_{\mathrm{C(2)-H}eq}$ stereoelectronic effect.[12,17] By the same token, at C(3) $^{1}J_{\mathrm{C-H}eq} < {}^{1}J_{\mathrm{C-H}ax}$ (121.0 and 123.6 Hz, respectively). This observation is best interpreted in terms $\sigma_{\mathrm{S-C(2)}} \rightarrow \sigma^{*}_{\mathrm{C(3)-H}eq}$ electron transfer that is apparently more important than two $\sigma_{\mathrm{C-H}} \rightarrow \sigma^{*}_{\mathrm{C(3)-H}ax}$ and *two* $\sigma_{\mathrm{C(3)-H}ax} \rightarrow \sigma^{*}_{\mathrm{C-H}}$ hyperconjugative interactions. Other stereoelectronic interactions that weaken the equatorial C(3)−H bond are, $\sigma_{\mathrm{C(3)-H}eq} \rightarrow \sigma^{*}_{\mathrm{S-C(2)}}$, $\sigma_{\mathrm{C(3)-H}eq} \rightarrow \sigma^{*}_{\mathrm{C(4)-C(5)}}$, and $\sigma_{\mathrm{C(4)-C(5)}} \rightarrow \sigma^{*}_{\mathrm{C(3)-H}eq}$, although these contributions are anticipated to be less important in view of the poor acceptor ability of the $\sigma^{*}_{\mathrm{S-C}}$ and $\sigma^{*}_{\mathrm{C-C}}$ orbitals, as well as the poor donor ability of the $\sigma_{\mathrm{C-C}}$ orbital.[13,17]

Most interestingly, from the relative magnitude of the "reverse Perlin effects" observed at C(2) and C(3) in thiane **3**, it can be inferred that electron transfer from an antiperiplanar S−C bond orbital is more efficient than from a C−S donor orbital. That is, as suggested in ref 17a,c, although the energy of the $\sigma_{\mathrm{S-C}}$ and $\sigma_{\mathrm{C-S}}$ orbitals is expected to be the same, bond polarities are actually opposite and this may lead to a more efficient $\sigma_{\mathrm{S-C}} \rightarrow \sigma^{*}_{\mathrm{C-H}app}$ interaction relative to $\sigma_{\mathrm{C-S}} \rightarrow \sigma^{*}_{\mathrm{C-H}app}$. Different acceptor abilities of S−C orbitals have also been observed by Alabugin and Zeidan,[43] who suggest that the difference in orbitals overlap is responsible for the contrasting behavior. Again, additional hyperconjugative effects weakening the axial and equatorial C(3)−H bonds in thiane **3** should modulate the final values for $\Delta^{1}J_{ax/eq}$ collected in Chart 3.

Finally, a normal Perlin effect is found at C(4): $^{1}J_{\mathrm{C-H}ax} = 118.6$ Hz $<$ $^{1}J_{\mathrm{C-H}eq} = 123.6$ Hz; $\Delta^{1}J_{ax/eq} = 5.0$ Hz. Analysis of the $^{1}J_{\mathrm{C-H}}$ coupling constants in azanes **4** and **5** is particularly interesting because of the possible consequences of the pseudoaxial and pseudoequatorial orientation of the nitrogen lone pair in these models. Indeed, in azane **4** (equatorial N−H), a substantial Perlin effect is appreciated at C(2): $^{1}J_{\mathrm{C-H}ax} = 121.0$ Hz $<$ $^{1}J_{\mathrm{C-H}eq} = 130.8$ Hz; $\Delta^{1}J_{ax/eq} = 9.8$ Hz. By contrast, in azane **5**, where the nitrogen lone pair is gauche to both C(2)−H bonds, a much diminished normal Perlin effect is found: $\Delta^{1}J_{ax/eq} = 3.4$ Hz. Importantly, in azane **4** $^{1}J_{\mathrm{C(3)-H}ax} \approx {}^{1}J_{\mathrm{C(3)-H}eq} \approx 122.5$ Hz, whereas in epimeric azane **5** the normal trend is observed: $^{1}J_{\mathrm{C(3)-H}ax} = 119.5$ Hz $<$ $^{1}J_{\mathrm{C(3)-H}eq} = 121.8$ Hz. This result indicates that, contrary to the findings reported in 1,3-dioxanes and 1,2,4-trioxanes,[19a−c] W-type stereoelectronic interaction involving the β−nitrogen (β-$n_{\mathrm{N}eq} \rightarrow \sigma^{*}_{\mathrm{C(3)-H}eq}$) is not relevant. On the other hand, this result does fit expectation in terms β-$n_{\mathrm{N}ax} \rightarrow \sigma^{*}_{\mathrm{C(3)-H}eq}$ hyperconjugation (cf. eq 5), as advanced by Alabugin.[13] That a W-type stereoelectronic interaction is not relevant in azanes, has already been suggested on the basis of experimental observations by Anderson, Cai, and Davies.[19d] Finally, normal Perlin effects ($^{1}J_{\mathrm{C-H}ax} < {}^{1}J_{\mathrm{C-H}eq}$) are seen at C(4), both in **4** and **5**.

Table 2. Optimized Geometries (distances in Å, angles in deg) for Cyclohexanone (**6**), and 3-Keto-monoheterocyclohexanes **7**−**10**. B3LYP/6-31G(*d*,*p*)



6, X = CH_2
7, X = O
8, X = S
9, X = equat. N−H
10, X = axial N−H

	6	**7**	**8**	**9**	**10**
X−C(2)	1.543	1.420	1.843	1.464	1.470
C(2)−C(3)	1.542	1.531	1.524	1.529	1.531
C(3)−C(4)	1.542	1.522	1.523	1.523	1.524
C(4)−C(5)	1.543	1.539	1.534	1.540	1.543
C(5)−C(6)	1.535	1.528	1.530	1.530	1.537
C(6)-X	1.535	1.423	1.836	1.462	1.466
X−H_{ax}	1.098				1.018
X−H_{eq}	1.096			1.016	
C(2)−H_{ax}	1.100	1.107	1.097	1.111	1.101
C(2)−H_{eq}	1.093	1.092	1.100	1.093	1.093
C(3)=O	1.217	1.215	1.215	1.215	1.217
C(4)−H_{ax}	1.100	1.101	1.100	1.101	1.101
C(4)−H_{eq}	1.093	1.093	1.093	1.093	1.093
C(5)−H_{ax}	1.098	1.096	1.095	1.095	1.098
C(5)−H_{eq}	1.096	1.096	1.098	1.096	1.097
C(6)−H_{ax}	1.099	1.104	1.097	1.109	1.099
C(6)−H_{eq}	1.096	1.093	1.094	1.095	1.095
X−C(2)−C(3)	112.0	113.7	111.1	110.7	114.1
C(2)−C(3)−C(4)	115.2	115.7	116.1	115.4	114.7
C(3)−C(4)−C(5)	112.0	112.7	113.6	113.0	112.2
C(4)−C(5)−C(6)	111.6	110.4	112.9	110.8	110.9
C(5)−C(6)-X	111.2	110.7	112.5	108.8	113.6
O−C(3)−C(2)	122.3	121.3	121.4	121.8	122.3
O−C(3)−C(4)	122.3	123.0	122.5	122.7	122.8
C(6)-X−C(2)	111.6	112.8	97.7	112.7	112.5
X−C(2)−C(3)−C(4)	48.3	39.7	59.1	45.0	45.5
C(2)−C(3)−C(4)−C(5)	48.3	35.8	56.0	40.5	44.1
C(3)−C(4)−C(5)−C(6)	51.7	44.4	55.6	46.5	47.7
C(4)−C(5)−C(6)−X	56.5	58.8	60.9	58.1	54.7
C(5)−C(6)−X−C(2)	56.5	64.6	56.7	65.6	56.1
C(6)−X−C(2)−C(3)	51.7	54.1	54.3	58.1	50.5
X−C(2)−C(3)-O	132.1	143.8	120.9	138.5	134.9

D. Cyclohexanone 6 and 1-Heterocyclohexan-3-ones 7−10. Table 2 collects the calculated structural data for ketones **6**−**10**, where the axial and equatorial C−H bonds adjacent to the carbonyl group provide convenient probes for potential $\sigma_{\mathrm{C-H}ax} \rightarrow \pi^{*}_{\mathrm{C=O}}$ hyperconjugation.

Most interestingly, a quite large difference in bond lengths (r) is calculated for the axial vis-à-vis equatorial C−H bonds adjacent to the carbonyl group in **6**−**10** (Table 2). Indeed, the axial C−H bonds at C(2) and C(4) in cyclohexanone **6** are substantially longer ($r_{\mathrm{C(2,4)-H}ax} = 1.100$ Å) than the equatorial C−H bonds ($r_{\mathrm{C(2,4)-H}eq} = 1.093$ Å); thus, $\Delta r_{ax/eq} = 0.007$ Å. It is recalled that $\Delta r_{ax/eq}$ in cyclohexane itself is only 0.002 Å. This contrasting behavior supports the participation of

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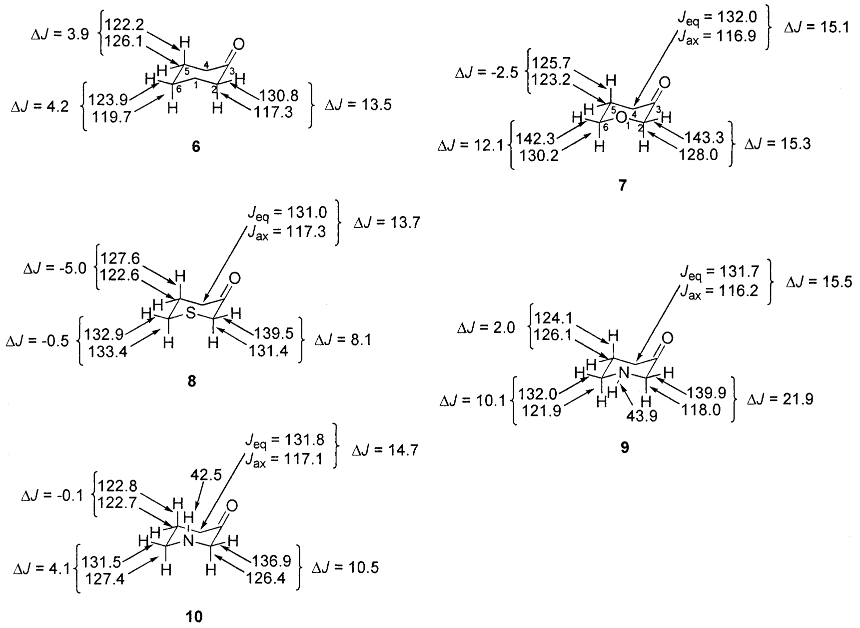
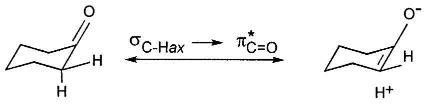
(42) The term "reverse Perlin effect" has been introduced in describing such unusual spectroscopic trend.[17,19] It should be stressed, however, that this term refers to an empirical observation rather than to the underlying fundaments of the effect. See also ref 13.

(43) Alabugin, I. V.; Zeidan, T. A. *J. Am. Chem. Soc.* **2002**, *124*, 3175−3185.

Chart 4



$\sigma_{\mathrm{C-H}ax} \rightarrow \pi^*_{\mathrm{C=O}}$ hyperconjugation in cyclohexanone **6**, as it was discussed in the Introduction (eq 7).



(7)

Even larger is the difference in bond lengths between the axial and equatorial C−H bonds at C(2) in heterocyclohexan-3-ones **7** (X = O) and **9** (equatorial N−H), $\Delta r_{ax/eq}$ (**7**) = 0.015 Å and $\Delta r_{ax/eq}$ (**9**) = 0.018 Å. The almost double $\Delta r_{ax/eq}$ value in the latter compounds relative to **6** arises, of course, from a second stereoelectronic effect with heteroatom participation, $n_{\mathrm{X}} \rightarrow \sigma^*_{\mathrm{C(2)-H}ax}$, where X = O or equatorial N−H. Therefore, the results show additivity of the two stereoelectronic interactions where C(2)−H$_{ax}$ participates in **7** and **9**: $\sigma_{\mathrm{C-H}ax} \rightarrow \pi^*_{\mathrm{C=O}}$ and $\mathrm{n_X} \rightarrow \sigma^*_{\mathrm{C-H}ax}$. Interestingly, $\Delta r_{ax/eq}$ is only worth 0.008 Å in **10** (X = axial N−H), where the nitrogen lone pair is not antiperiplanar to any of the C(2)−H bonds. Finally, an opposite trend in $\Delta r_{ax/eq}$ is found for C(2) in sulfur-containing **8**, where the equatorial C(2)−H$_{eq}$ bond is actually longer by 0.003 Å than C(2)−H$_{ax}$ (Table 2). This result suggests that $n_{\mathrm{S}} \rightarrow \sigma^*_{\mathrm{C(2)-H}ax}$ is not operative, and the additional loss of $\sigma_{\mathrm{C-H}ax} \rightarrow \sigma^*_{\mathrm{C-H}ax}$ hyperconjugation leads to the observation that C(2)-H$_{ax}$ in **8** is shortened (Table 2), despite the anticipated $\sigma_{\mathrm{C(2)-H}ax} \rightarrow \pi^*_{\mathrm{C=O}}$ interaction.

On the other hand, the observation (Table 2) that $r_{\mathrm{C(5)-H}eq} \geq r_{\mathrm{C(5)-H}ax}$ in **7**−**10** is in line with the importance of β-$n_{\mathrm{O}} \rightarrow \sigma^*_{\mathrm{C-H}eq}$ in **7** and $\sigma_{\mathrm{X-C}} \rightarrow \sigma^*_{\mathrm{C-H}eq}$ in **8**−**10**. As previously discussed above, experimentally observed[17] upfield shifts for the equatorial C−H NMR proton signals in heterocycles related to **7** and **8**, indicate that the alternative $\sigma_{\mathrm{C(5)-H}eq} \rightarrow \sigma^*_{\mathrm{X-C}}$ interaction is of minor importance relative to $\sigma_{\mathrm{X-C}} \rightarrow \sigma^*_{\mathrm{C-H}eq}$ hyperconjugation.

Chart 4 collects the calculated one bond ^{13}C−^{1}H coupling constants (in Hz) for cyclohexanone **6** and 3-keto-heterocyclohexanones **7**−**10**. Chart 4 includes the corresponding difference $\Delta^1 J_{ax/eq} = {}^1J_{\mathrm{C-H}eq} - {}^1J_{\mathrm{C-H}ax}$ for each distinct methylenic pair of C−H bonds in the molecule. According to the arguments advanced in this paper, positive $\Delta^1 J_{ax/eq}$ values reflect *normal* trends in Perlin effects, where $\sigma_{\mathrm{C-H}} \rightarrow \sigma^*_{\mathrm{C-H}app}$, $n_{\mathrm{X}} \rightarrow \sigma^*_{\mathrm{C-H}app}$, and $\sigma_{\mathrm{C-H}ax} \rightarrow \pi^*_{\mathrm{C=O}}$ stereoelectronic interactions originate longer and weaker axial C−H bonds, and therefore smaller $^1J_{\mathrm{C-H}ax}$ coupling constants, relative to $^1J_{\mathrm{C-H}eq}$.

As expected, normal and moderate Perlin effects are found at C(1), C(5), and C(6) of cyclohexanone **6** ($^1J_{\mathrm{C-H}eq} - {}^1J_{\mathrm{C-H}ax}$ = 3.9 anf 4.2 Hz, Chart 4). The "reverse Perlin effects"[42] observed at C(5) in keto-oxane **7**, and C(5) keto-thiane **8** (Chart 4) are in line with competing β-$\mathrm{n_{O}}_{ax} \rightarrow \sigma^*_{\mathrm{C(5)-H}eq}$ or $\sigma_{\mathrm{S-C}} \rightarrow \sigma^*_{\mathrm{C(5)-H}eq}$ (see above).

Evidence supporting the additivity of stereoelectronic effects on the magnitude of $^1J_{\mathrm{C-H}}$ coupling constants is manyfold. For instance, the difference $^1J_{\mathrm{C(6)-H}eq} - {}^1J_{\mathrm{C(6)-H}ax}$ = 10.1 Hz for the methylenic C−H bonds vicinal to the equatorial N−H group in azane **9** arises mainly from the $\mathrm{n_N} \rightarrow \sigma^*_{\mathrm{C(6)-H}ax}$ interaction, whereas $\Delta J_{ax/eq}$ at C(4) amounts to 15.5 Hz ($\sigma_{\mathrm{C(4)-H}ax} \rightarrow \pi^*_{\mathrm{C=O}}$); these two values are to be compared with $\Delta^1 J_{ax/eq}$ at C(2) = 21.9 Hz, where both hyperconjugative effects are operative. (Chart 4). By contrast, $\Delta^1 J_{ax/eq}$ at C(6), C(4), and C(2) for azane **10** (axial N−H) are 4.1, 14.7, and 10.5 Hz, respectively. Thus, whereas the value of $\Delta^1 J_{ax/eq}$ is essentially unchanged at C(4), those at C(6) and C(2) are significantly smaller owing to the missing $\mathrm{n_N} \rightarrow \sigma^*_{\mathrm{C-H}ax}$ interaction.

E. 1,3-Diheterocyclohexan-5-ones 11−**16.** Table 3 presents the calculated structural data for compounds **11**−**16**, where each methylenic pair of C−H bonds is adjacent to *two* heteroatoms, or one heteroatom and one carbonyl group. Examination of these compounds was deemed relevant in order to gain additional information regarding the additivity of stereoelectronic effects on the magnitude of one bond $^1J_{\mathrm{C-H}}$ coupling constants.

Most remarkable is the very long bond calculated for the axial carbon−hydrogen bond at C(2) in keto-diazane **14**: $r_{\mathrm{C(2)-H}ax}$ = 1.118 Å! By comparison, $r_{\mathrm{C(2)-H}ax}$ is equal to 1.107 Å in epimer **15**, and $r_{\mathrm{C(2)-H}ax}$ is normal (1.098 Å) in keto-diazane **16**, where both N−H bonds are axial. This trend is, of course, in full agreement with an additive effect of $n_{\mathrm{N}} \rightarrow \sigma^*_{\mathrm{C-H}app}$

Chart 5

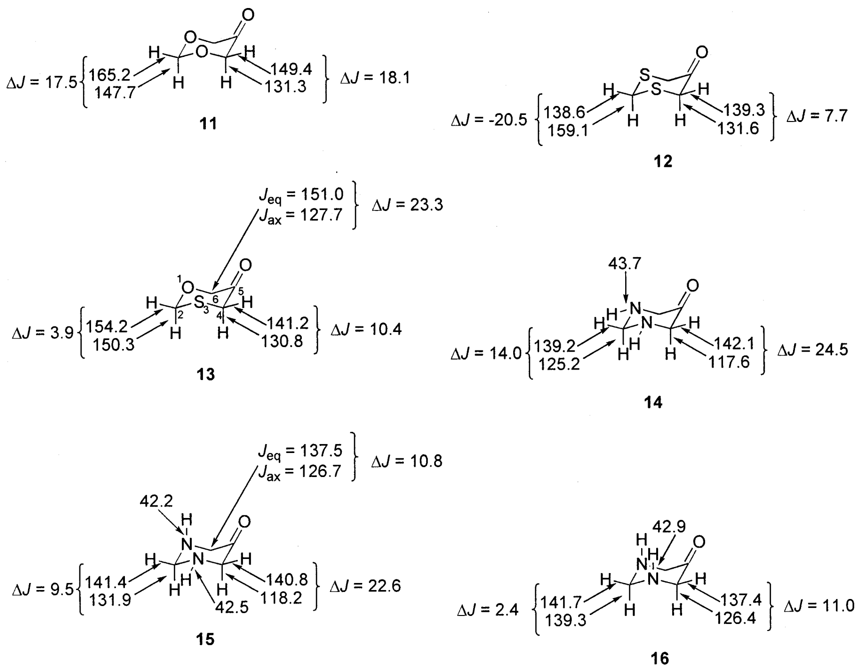
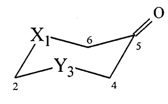


Table 3. Optimized Geometries (distances in Å, angles in deg) for 1,3-Diheterocyclohexan-5-ones **11**−**16**, at the B3LYP/6-31G(d,p) Level of Theory



11, X = Y = O
12, X = Y = S
13, X = O; Y = S
14, X = Y = equat. N–H
15, X = equat. N–H; Y = axial N–H
16, X = Y = axial N–H

	11	**12**	**13**	**14**	**15**	**16**
X(2)	1.406	1.829	1.403	1.457	1.465	1.463
C(2)−Y	1.406	1.829	1.839	1.457	1.453	1.463
Y−C(4)	1.422	1.844	1.841	1.463	1.469	1.471
C(4)−C(5)	1.527	1.524	1.522	1.527	1.530	1.531
C(5)−C(6)	1.527	1.524	1.533	1.527	1.529	1.531
C(6)-X	1.422	1.844	1.423	1.463	1.466	1.471
C(2)−H_{ax}	1.107	1.094	1.101	1.118	1.107	1.098
C(2)−H_{eq}	1.090	1.092	1.091	1.094	1.094	1.094
C(4)−H_{ax}	1.105	1.097	1.098	1.111	1.101	1.101
C(4)−H_{eq}	1.092	1.091	1.091	1.093	1.093	1.093
C(6)−H_{ax}	1.105	1.097	1.106	1.111	1.111	1.101
C(6)−H_{eq}	1.092	1.091	1.091	1.093	1.093	1.093
C=O	1.213	1.214	1.214	1.214	1.215	1.216
X−C(2)−Y	112.1	115.3	112.8	108.1	111.2	116.6
C(2)−Y-C(4)	111.9	98.1	95.1	112.0	111.2	111.8
Y−C(4)−C(5)	113.8	112.7	112.1	111.3	114.9	114.4
C(4)−C(5)−C(6)	116.3	116.6	117.5	115.7	115.4	114.7
C(5)−C(6)−X	113.8	112.7	115.4	111.2	111.0	114.4
O−C(5)−C(4)	121.7	121.7	121.7	122.0	122.5	122.6
C(6)-X−C(2)	111.9	98.1	113.8	111.9	111.8	111.8
O−C(5)−C(6)	121.7	121.7	120.6	122.0	121.9	122.6
X−C(2)−Y−C(4)	65.1	61.2	60.5	65.5	59.8	54.2
C(2)−Y−C(4)−C(5)	43.9	57.5	48.9	51.9	45.2	45.4
Y−C(4)−C(5)-C(6)	26.1	66.6	48.1	39.0	35.8	39.8
Y−C(4)−C(5)−O	159.0	114.9	136.7	146.9	145.0	142.0
C(4)−C(5)−C(6)−X	26.3	66.3	46.7	39.2	38.8	39.9
C(5)−C(6)-X−C(2)	43.9	57.5	56.3	52.3	52.8	45.4
C(6)−X−C(2)−Y	65.1	61.2	68.7	65.7	65.2	54.2
X−C(6)−C(5)−0	159.0	114.9	138.0	146.9	148.0	142.0
X−H_{ax}					1.019	1.109
X−H_{eq}				1.016	1.016	

hyperconjugation on bond length. Furthermore, as expected from this "anomeric " interaction,[3] C−N bonds are shorter in **14** ($r_{C(4,6)-N} = 1.463$ Å) than in **16** ($r_{C(4,6)-N} = 1.471$ Å). For **15**, the carbon bond to equatorial N−H is shorter (1.466 Å) than the bond to axial N−H (1.469 Å). Finally, the torsional angles provide information on the consequences of lone pair orientation on geometry. For example, using again diazane derivatives **14**−**16**, it is appreciated (Table 3) that dihedral angle NH−C(4)−C(5)-O is substantially larger in **14** (equatorial N−H, double bond-no bond hyperconjugation leads to a flattening of the ring) relative to **16**: 146.9° and 142.0°, respectively.

Additivity of stereoelectronic $\sigma_{C-S} \rightarrow \sigma^*_{C(2)-Heq}$ hyperconjugation is also apparent in the series dioxanone **11**/oxathianone **13**/dithianone **12**, with *increasing* $r_{C(2)-Heq}$: 1.090, 1.091, and 1.092 Å, respectively. Furthermore, the parameter $r_{C(2)-Hax}$ *decreases* in the same series of compounds: 1.107, 1.101, and 1.094 Å for **11**, **13**, and **12**, respectively. (Table 3). This trend is congruent with a manifestation of two $n_O \rightarrow \sigma^*_{C(2)-Hax}$ interactions in **11**, only one in **13**, and none in **12**.

Other structural data available in Table 3 are also in line with the additive nature of the stereoelectronic effects operative in heterocycles **11**−**16**, including their impact on the magnitude of the $^1J_{C-H}$ coupling constants (Hz) presented in Chart 5. To facilitate the analysis of the coupling patterns, Chart 5 includes also the differences $\Delta^1J_{ax/eq}$ between methylenic C−H bonds.

The largest difference in one bond coupling constants for a methylenic pair of C−H bonds is found at C(4,6) in keto-diazane **14**, where both N−H bonds are equatorial. Thus, the combined influence of one $n_N \rightarrow \sigma^*_{C(4,6)-Hax}$ stereoelectronic effect, as well as $\sigma_{C(4,6)-Hax} \rightarrow \pi^*_{C=O}$ hyperconjugation, is reflected in a rather large $\Delta^1J_{ax/eq} = 24.5$ Hz. A similar situation is present at C(6) in oxathianone **13**, where $\Delta^1J_{ax/eq} = 23.3$ Hz. Here again, the axial carbon−hydrogen bond experiences $n_O \rightarrow \sigma^*_{C(6)-Hax}$ *and* $\sigma_{C(6)-Hax} \rightarrow \pi^*_{C=O}$ hyperconjugative interactions. Interestingly, $\Delta^1J_{ax/eq}$ for C(4,6) in keto-diazane **16** (both N−H bonds axial) is only worth 11.0 Hz. In this case, no $n_N \rightarrow \sigma^*_{C(4,6)-Hax}$ is feasible, so that the $\Delta^1J_{ax/eq}$ value originates almost exclusively from $\sigma_{C(4,6)-Hax} \rightarrow \pi^*_{C=O}$ hyperconjugation. Keto-diazane **15** presents a methylene at C(4) that shows a behavior similar to that exhibited by **14**, and then another methylene at C(6) that mirrors **16** (Chart 5).

With regard $\Delta^1 J_{ax/eq}$ values at C(2) in the **11**−**16** series, a whole range is registered: from a largest positive $\Delta^1 J_{ax/eq} = 17.5$ Hz for dioxanone **11** (two $n_O \rightarrow \sigma^*_{C(2)-Hax}$), to a medium size $\Delta^1 J_{ax/eq} = 9.5$ Hz in keto-diazane **15** (one $n_N \rightarrow \sigma^*_{C(2)-Hax}$), to a small $\Delta^1 J_{ax/eq} = 3.9$ Hz in oxathianone **13** (one $n_O \rightarrow \sigma^*_{C(2)-Hax}$ interaction counterbalanced by one $\sigma_{C-S} \rightarrow \sigma^*_{C(2)-Heq}$ effect), to a large *reversed* $\Delta^1 J_{ax/eq} = -20.5$ Hz (two $\sigma_{C-S} \rightarrow \sigma^*_{C(2)-Heq}$ interactions) in dithianone **12**.

Conclusions

Theoretical evaluation of the molecular geometry [B3LYP/6-31G(*d*,*p*) level] and the associated one bond $^1J_{C-H}$ NMR coupling constants [PP/IGLO−III//B3LYP/6-31G(*d*,*p*) theory] for a series of 16 six-membered cyclic compounds, including cyclohexane as reference model and derivatives containing one or two heteroatoms as well as a carbonyl group, afforded a wealth of relevant information. In particular, both C−H bond lengths and differences in $^1J_{C-H}$ coupling constants seem to confirm the validity of models based on stereoelectronic effects, $n_X \rightarrow \sigma^*_{C-Happ}$, $\sigma_{C-S} \rightarrow \sigma^*_{C-Happ}$, $\sigma_{S-C} \rightarrow \sigma^*_{C-Happ}$, $\sigma_{C-H} \rightarrow \sigma^*_{C-Happ}$, and β-$n_{Oax} \rightarrow \sigma^*_{C-Heq}$, among the most relevant.

Furthermore, for C−H bonds participating as donor and/or acceptor orbital in more than one stereoelectronic interaction, the calculated structural (r_{C-H} bond length) and spectroscopic ($^1J_{C-H}$ coupling constant) indicate additivity of the corresponding effects.

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Supporting Information Available: Calculated geometries for **1**−**16** and their calculated energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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