In summary, the present results point out that interception of a biradical by N or O_2 can enhance its probability of forming cyclobutane.[10,24] Interception is a viable kinetic probe by which these intermediates can be studied. We underscore the need for a much better understanding of the factors influencing intersystem crossing in biradicals and of the rates for conformational equilibration in such species. Finally, we note the potential synthetic utility of interception in altering product yields in reactions with biradical intermediates.

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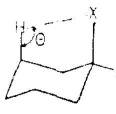
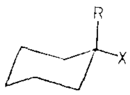
Steric Effects on Carbon-13 Nuclear Magnetic Resonance Shifts in Alkanes[1]

Sir:

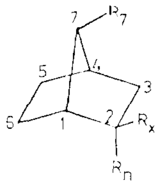
Whereas the gross effects of substituents on α carbon shifts ($\Delta(C_\alpha)$) can be understood in terms of calculated electron densities,[2] the pronounced and stereoselective effects on more remote carbons have led to several conflicting proposals of shielding mechanisms. Most recently, Gorenstein[3] has connected the shielding observed in gauche fragments, as, e.g., in **1**, with increasing bond angles in such arrangements. Introduction of an axial substituent in cyclohexane, however, produces deshielding not only at C_β but in many cases also at C_α (C_γ in **1**, misread in ref 3, is always upfield from the e isomer **2**). Since no reliable and accurate spectroscopical structure determinations are available for heterosubstituted cyclohexanes, we have investigated steric distortions as possible sources of shielding variations using Allinger's molecular mechanics force field (FF).[4] For **1** and **2** ($R = H$ or CH_3; $X = F, Cl, Br, I, OH, CH_3, H$) no correlation of changes of bond length ($\Delta l < 0.3\%$), bond angles ($\Delta\theta < 2\%$) and torsional angles ($\Delta\varphi < 16\%$)[5] with the observed ^{13}C shifts[6] are found. In fact, increasing $XC_\alpha C_\beta$ bond angles correspond to downfield C_α shifts, establishing a regular trend for secondary and tertiary cyclohexyl halides; other angles at C_α change to a significantly lesser degree. Furthermore, variation of the substituent X leads to $XC_\alpha C_\beta C_\gamma$ torsional angle changes, but the $C_{\beta'}C_\alpha C_\beta C_\gamma$ angles change simultaneously in the opposite direction. Only the widening of the $C_\alpha C_\beta C_\gamma$ bond angle in **1** as compared to **2** by up to 2.2° can be related to the smaller deshielding effects of X on C_β in gauche fragments. Hybridization changes for $C_\alpha X$ bonds, as obtained from FF calculated bond angles using Coulson's formula,[7] do not reproduce observed trends in cyclohexane shifts.[5] In the absence of recognizable steric distortions, electrical effects are expected to determine the observed shifts.[8]



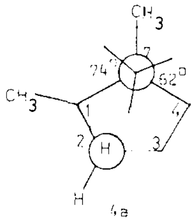
1



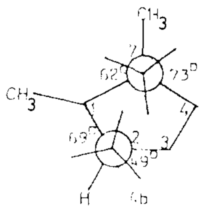
2



3a ($R7=Rx=Rn=H$)
3b ($R7=CH_3$, $Rx=Rn=H$)
3c ($Rx=CH_3$, $R7=Rn=H$)
3d ($Rn=CH_3$, $R7=Rx=H$)



4a



4b

The most clearly defined shielding mechanism by a steric perturbation, proposed by Grant and Cheney,[9] relates the shift at C_i to the force vector exerted on a C_i–H bond. It should apply also to deshielding situations, to interactions with heteroatoms, and to carbon atoms not in γ position. In defining the shielding force vector on the C_i–H bond, an equation is proposed which is derived from a potential[10] for nonbonded interactions:

$$F = 0.6952 \times 10^{-5}(18\epsilon/r^*)[(r^*/r)^{10} - (r^*/r)^7] \cos\theta \quad (1)$$

Equation 1 applies to hydrogen-hydrogen interactions ($\epsilon = 0.004\,109$, $r^* = 3.632$) as well as to carbon-hydrogen interactions ($\epsilon = 0.026\,102$, $r^* = 3.575$);[10] r represents the distance between the hydrogen attached to C_i and the interacting H or C; θ is the angle between the force vector and the C_i–H bond. Since repulsive nonbonded interactions are extremely sensitive to small changes in r, we have applied eq 1 only to fully relaxed molecular structures as obtained by FF energy minimization. An illustrative example is the 1,3 diaxial interaction force in a methyl cyclohexane, which decreases by 80% in going from ideal "standard" to the relaxed geometry. In pioneering their correlation, Grant and Cheney[9] had used nonrelaxed geometries and moreover idealized conformer populations and geometries. The FF calculated geometries of hydrocarbons **1** ($R = H$; $X = CH_3$) and **3a–d**[5] and the observed syn-γ ^{13}C

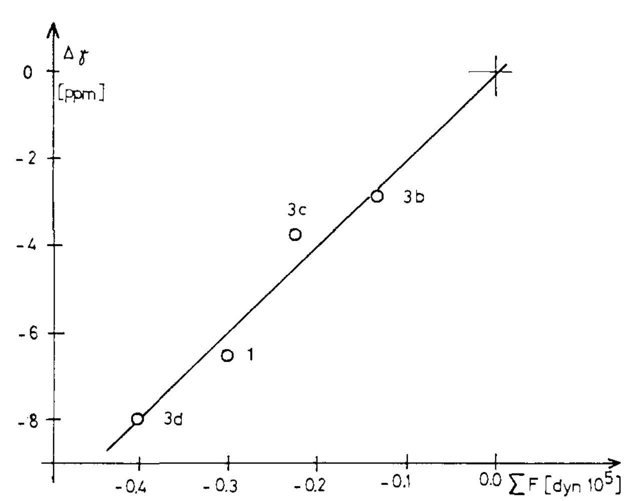


Figure 1. Correlation of $^{13}C_\gamma$ substituent effects $\Delta\gamma$ in compounds **1** (X = CH_3; R = H) and **3b–d** with steric forces ΣF.

shifts[6,11] in these compounds provide a more rigorous test for the steric interaction mechanism (Figure 1). For calculation of the substituent effect, the steric force exerted by the hydrogen, which is to be substituted, has to be subtracted from that exerted by the substituent. It should be noted that the forces as obtained by eq 1 and subsequent summation originate not only in the direct interaction with the substituent, but partially also in secondary carbon skeleton distortions brought about by introduction of the substituent. Thus, replacement of hydrogen by methyl in the 7 position of the rigid norbornane system **3b** generates additional forces by, e.g., C_7 interaction on the syn H atoms at C_2/C_3, which amount to ~40% of the primary interaction by the CH_3 atoms. Consequently, up to 11 interactions have to be taken into account for the F summation of a single compound;[5] the linear function so obtained (correlation coefficient r = 0.976) strongly supports the Grant-Cheney mechanism.[12] The sensitivity obtained from $\Sigma F/\Delta\nu$ plots change from 20 × 10^5 (Figure 1) to ~5 × 10^5 ppm/dyn, if one uses another[4] FF for the ΣF calculation. This is not unexpected in view of the present FF discrepancies regarding nonbonded interactions.

Several cases seemingly contradicting the Grant-Cheney mechanism involve deshielding by steric interaction of δ groups.[13] Since few of these examples include an alicyclic hydrocarbon without polar groups, we have prepared 1,*exo*-2,7,7-tetramethylbicyclo[2.2.1]heptane (**4**, X = CH_3) via the Wittig reaction with camphor. **4** (X = CH_3) indeed shows deshielding at the *syn*-7-methyl carbon by 1.3 ± 0.2 ppm in comparison to **4** (X = H). We note first that the Grant-Cheney mechanism may involve downfield shifts, if $\theta < 90°$ (eq 1). Summation of the forces exerted on *syn*-7-CH_3 by *exo*-2-CH_3 alone, however, would predict a shielding by ca. −18 ppm. Inspection of the geometry obtained by FF calculation for **4** reveals that introduction of the *exo*-2-CH_3 group leads to a more eclipsed torsional angle for the *syn*-7-CH_3 group. This secondary effect generates positive as well as negative forces on the participating C–H bonds. Since a large number of rather small forces change in going from **4** (X = H to X = CH_3), our model is, at the present time, not accurate enough for a safe prediction of the sign for ΣF. It is possible that many substituent induced shifts of methyl groups are partially due to conformational change at this group.

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Supplementary Material Available: Compilations of relevant internal coordinates for **1** and **2** and hybridization calculations and parameters for F evaluation (eq 1) (5 pages). Ordering information is given on any current masthead page.

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Electric Field Effects on Carbon-13 Nuclear Magnetic Resonance Shifts in Heterosubstituted Alkanes

Sir:

Electric effects are expected to play a major role in the screening constants for carbon nuclei in alkanes containing polar groups. The deficiencies of electron densities obtained by MO calculations or of steric effects for the evaluation of ^{13}C shifts[1] have led us to investigate classical approaches to shielding mechanisms in monosubstituted alkanes. Buckirgham et al.[2] expressed the shielding of monovalent nuclei, such as ^1H, as the sum of square electric field effects $\langle E^2\rangle$ and linear field effects E_Z. The deshielding symmetry distortion of a C_i atom electron cloud by a fluctuating C_α–X dipole is given by eq 1, where r_i is the distance from the middle of the C–X bond to C_i, I_X the first ionization potential of X, and P_{CX} the polarizability of the C_α–X bond.

$$\langle E^2\rangle = 3I_XP_{CX}r_i^{-6} \qquad (1)$$

The polarization of electrons at a C_i–Y bond by an intramolecular point charge q can be approximated by

$$\Delta Q_{C,Y} = P_{C,Y}l_{C,Y}^{-1}qr^{-2}\cos\theta \qquad (2)$$

where $\Delta Q_{C,Y}$ is the charge separation induced by a static electric field, $P_{C,Y}$ the polarizability of the C_i–Y bond, $l_{C,Y}$ its length, r its distance from q, θ is angle to the acting electric field vector. Neglecting higher order terms, eq 2 represents E_Z and is expected to be observable over larger intramolecular distances, whereas, owing to the r^{-6} term, the van der Waals effect $\langle E^2\rangle$ falls off sharply, e.g., from 100% at C_β