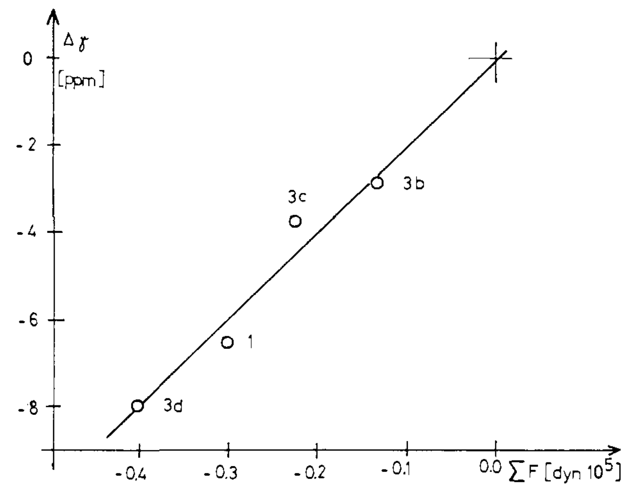

Figure 1. Correlation of $^{13}C_\gamma$ substituent effects $\Delta\gamma$ in compounds **1** ($X = CH_3$; $R = H$) and **3b–d** with steric forces ΣF.

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 $\sim 5 \times 10^5$ 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.

Acknowledgments. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We sincerely thank Professor N. L. Allinger for allowing us to use his FF program and for helpful discussions.

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.

References and Notes

(1) Part 17 of Carbon-13 Nuclear Magnetic Resonance Spectroscopical and Stereochemical Investigations. Part 16: H.-J. Schneider, W. Gschwendtner, D. Heiske, V. Hoppen, and F. Thomas, *Tetrahedron*, **33**, 1769 (1977).

(2) (a) G. E. Maciel, *Top. Carbon-13 NMR Spectrosc.*, **1**, 53–78 (1974); (b) K. Seidman and G. E. Maciel, *J. Am. Chem. Soc.*, **99**, 659 (1977).

(3) D. G. Gorenstein, *J. Am. Chem. Soc.*, **99**, 2254 (1977). In contrast to ref 3, we obtain a monotonous decrease of ΔJ with increasing bond angle distortion.[5]

(4) For a recent discussion, see N. L. Allinger, C. Hindman, and H. Hönig, *J. Am. Chem. Soc.*, **99**, 3282 (1977). We are aware of the ambiguities of presently available force fields, particularly regarding nonbonded interactions, but nevertheless expect to obtain correct trends for different substituents in similar carbon frameworks.

(5) For data, see paragraph at the end of paper regarding supplementary material.

(6) H.-J. Schneider and V. Hoppen, *Tetrahedron Lett.*, 579 (1974), and unpublished results.

(7) C. A. Coulson, "Valence", Oxford University Press, London, 1953, pp 194, 195.

(8) See H.-J. Schneider and W. Freitag, *J. Am. Chem. Soc.*, following paper in this issue.

(9) D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, **89**, 5315 (1967).

(10) (a) A. Warshel and S. Lifson, *J. Chem. Phys.*, **53**, 582 (1970); (b) O. Ermer and S. Lifson, *J. Am. Chem. Soc.*, **94**, 4121 (1973).

(11) E. Lippmaa, T. Pehk, N. A. Belikova, A. A. Bobyleva, A. N. Kalinichenko, M. D. Ordubadi, and A. F. Platé, *Org. Magn. Reson.*, **8**, 74 (1976).

(12) Cf. E. Lippmaa, T. Pehk, and J. Paasivirta, *Org. Magn. Reson.*, **5**, 277 (1973). The failure to observe the correlation to Grant–Cheney effects in ref 11 is probably due to the use of the too simplified original equation[9] and of nonreal molecular structures.

(13) (a) A. J. Jones, P. D. Gardner, D. M. Grant, W. M. Litchman, and V. Boekelheide, *J. Am. Chem. Soc.*, **92**, 2386 (1970); (b) J. B. Stothers and C. T. Tan, *Can. J. Chem.*, **54**, 917 (1976).

Hans-Jörg Schneider,* Eckehard F. Weigand
Fachrichtung OrganischeChemie
Universität des Saarlandes
D 6600 Saarbrücken 11, Germany

Received August 17, 1977

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. Buckingham 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.

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

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

$$\Delta Q_{C_iY} = P_{C_iY} l_{C_iY}^{-1} q r^{-2} \cos\theta \qquad (2)$$

where ΔQ_{C_iY} is the charge separation induced by a static electric field, P_{C_iY} the polarizability of the C_i–Y bond, l_{C_iY} 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

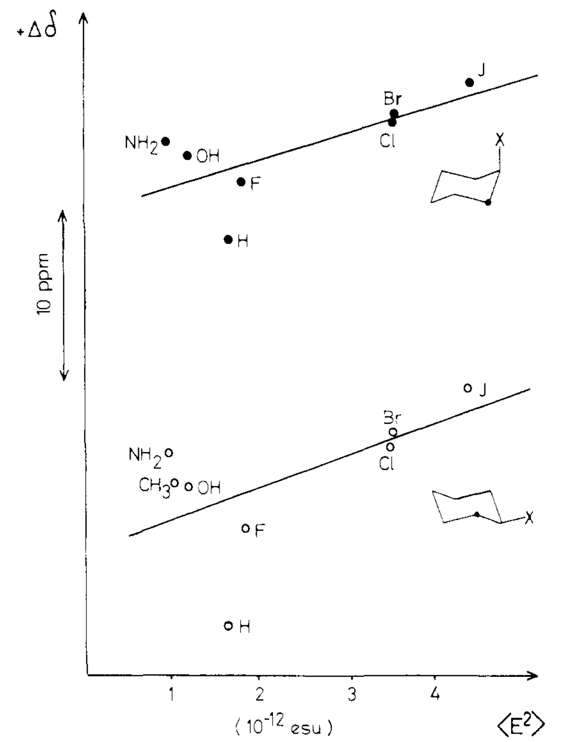

Figure 1. Correlation of substituent induced shifts on C_β in cyclohexanes with square electric field effects.

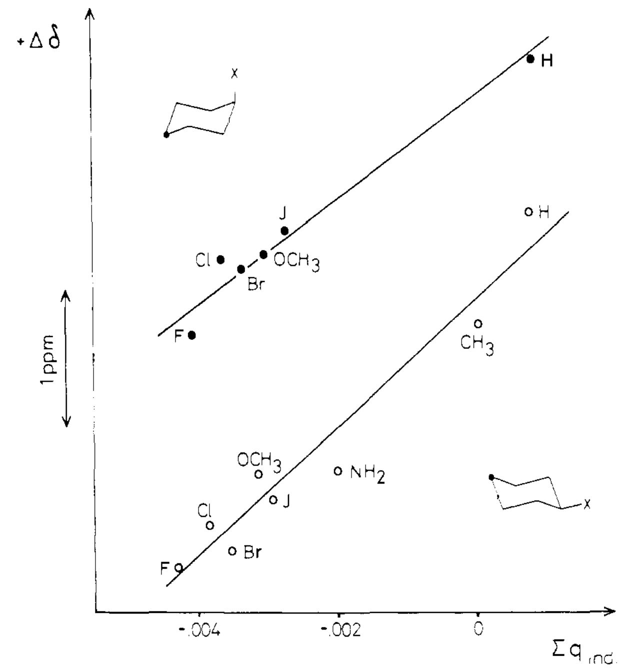

Figure 2. Correlation of substituent induced shifts on C_δ in cyclohexanes with linear electric field effects.

to 5% at C_γ and 2% at C_δ in a normal alkane chain.

Feeney, Sutcliffe, and Walker[3] were the first to describe C_β carbon shifts by eq 1. Application to geometrically well-defined cyclohexanes leads to fairly linear relations for halides (Figure 1); the absolute shift difference observed for e (equatorial) and a (axial) substituents[4] can be ascribed to bond angle widening in axial conformations.[1] The deviations observed for substituents, such as CH_3, OH, NH_2, are most likely not due to steric effects,[1] but to additional field effects of these less symmetrical groups.

Linear electric field interactions (eq 2) have been used to rationalize, e.g., protonation ^{13}C shifts in amino compounds.[5,6] Heterosubstituted alkanes pose the additional problem of defining location and charge at the polar bond. We have used C-X dipole moments and some CNDO calculated electron densities[7] for locating point charges at C_α and at X with a subsequent ΔQ_{C_iY} summation over all bonds attached to the observed carbon C_i. Calculations were based on molecular structures obtained individually for different e- or a-substituted cyclohexanes by a suitable force field;[1] the middle of the C_i-Y bonds was taken for the longitudinal action only of the field vector, assuming a homogeneous field along the bond. Although the field-induced electron flow in saturated compounds is expected to be substantially smaller than in compounds with multiple, more polarizable bonds,[8,9] satisfactory correlations of C_δ shielding in cyclohexanes are observed (Figure 2). The sensitivity of 400 ppm/e is in the expected range (errors of 10% in q, P, and θ and 2.5% in r will give deviations in $\Sigma\Delta Q_i$ of 35%).

Comparison of C_γ shifts in cyclohexanes with $\Sigma\Delta Q_i$ generated by the C_α and X point charges gives poor correlations with +1900 and −1200 ppm/e for e and a substituents, respectively. However, in contrast to the electric field effect on more remote carbon atoms, the polarization at C_γ markedly depends on the small secondary charge alternations induced at C_β by varying X. Thus, allowing for an electron density accumulation at C_β increasing from 0 to only 2% going from X = H to X = F, one arrives at fairly linear correlations of the tripole (X, C_α, C_β) effect on C_γ with 150 ppm/e for e- and 500 ppm/e for a-substituted cyclohexanes. The same set of point charges leaves the correlation of C_δ shifts to $\Sigma\Delta Q$ (Figure 2) undistorted. Although no theoretical model presently available can be expected to reproduce the very small charge alternations quantitatively, it is noteworthy that the charge accumulation effect at C_β by back-donation from heteroatom lone electron pairs is found in MO-calculated Mulliken populations, particularly with fluoroalkanes.[10] Thus both syn- and anti-γ ^{13}C substituent-induced shifts can originate in classical field effects.

Acknowledgments. This work was supported by the Deutsche Forschungsgemeinschaft. In addition, we wish thank the Fonds der Chemischen Industrie for a stipend for one of us (W.F.).

Supplementary Material Available: Tables of numerical values used for the calculation of $\langle E^2\rangle$ and ΔQ (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) H.-J. Schneider and E. F. Weigand, *J. Am. Chem. Soc.*, preceding paper in this issue and references cited therein. This is paper 18 of our series.
(2) W. T. Raynes, A. D. Buckingham, and H. J. Bernstein, *J. Chem. Phys.*, **36**, 3481 (1962).
(3) J. Feeney, L. H., Sutcliffe, and S. Walker, *Mol. Phys.*, **11**, 117 (1966).
(4) H.-J. Schneider and V. Hoppen, *Tetrahedron Lett.*, 579 (1974).
(5) W. J. Horsley and H. Sternlicht, *J. Am. Chem. Soc.*, **90**, 3738 (1968).
(6) J. G. Batchelor, *J. Am. Chem. Soc.*, **97**, 3410 (1975), and references cited therein. The use of group coefficients as proposed by Batchelor requires symmetry restrictions, which usually do not hold in geometries of real molecules as obtained by spectroscopic methods or by force field minimizations.[1] Furthermore the symmetry restrictions and the claimed zero sensitivity of quaternary carbon atoms to E_Z neglect distance differences from q for the bonds participating in one group (H.-J. Schneider and M. Lonsdorfer, unpublished results).
(7) V. I. Minkin, O. A. Osipov and Y. A. Zhdanov, "Dipole Moments in Organic Chemistry", Plenum Press, New York/London, 1970, pp 88, 196.
(8) K. Seidman and G. E. Maciel, *J. Am. Chem. Soc.*, **99**, 3254 (1977).
(9) H.-J. Schneider, W. Gschwendtner, and K. Buchheit, *J. Magn. Reson.*, **26**, 175 (1977).
(10) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4523 (1967).

Hans-Jörg Schneider,* Wolfgang Freitag
Fachrichtung Organische Chemie
Universität des Saarlandes
D 6600 Saarbrücken 11, Germany
Received August 17, 1977