nediol[7] was synthesized from 2,5-hexanedione by using phenylmagnesium bromide. The NIS was determined to have 98.0–99.5% active iodine and was used as purchased. Irradiation of reaction mixtures was effected with GE Projector Spot 150-W, 130-V tungsten lamps.

Oxidation of 2,5-Dimethyl-2,5-hexanediol with NIS and Irradiation. A 5-mL solution of 0.082 g (0.561 mmol) of 2,5-dimethyl-2,5-hexanediol in benzene was added to 0.258 g (1.147 mmol) of NIS contained in a 10-mL flask. A condenser with a drying tube was attached to the flask. The mixture was stirred and irradiated. Reaction time and percentage yields of acetone (assuming 2 mol of acetone for each mol of diol) were as follows: 10 min (15%), 15 min (49%), 35 min (96%), 55 min (99%), 70 min (99%). Elemental iodine determination gave 0.543 mmol (98%). Succinimide was recovered in 88% yield.

Oxidation of 2,5-Diphenyl-2,5-hexanediol with NIS and Irradiation. A 5-mL solution of 0.152 g (0.538 mmol) of 2,5-diphenyl-2,5-hexanediol in benzene was added to 0.269 g (1.196 mmol) of NIS in a 10-mL flask. A condenser with a drying tube was attached to the flask. The mixture was stirred and irradiated. Reaction times and percentage yields of acetophenone (assuming 2 mol of acetophenone for each mol of diol) were as follows: 1 h 15 min (39%), 2 h (64%), 3 h (83%), 4 h (92%), 6 h (100%), 7 h (99%). Succinimide was recovered in 99% yield (1.070 mmol) and elemental iodine was found at 94% (0.506 mmol). Crude acetophenone was recovered, weight 0.131 g (1.090 mmol, 101%). Preparation of a 2,4-dinitrophenylhydrazone derivative of the acetophenone gave 0.255 g (0.849 mmol, 78%) of product (mp 230–235 °C; lit.[8] mp 238–240 °C).

Oxidation of 2,5-Diphenyl-2,5-hexanediol with NIS in the Dark at Ambient Temperatures. A 5-mL solution of 0.164 g (0.598 mmol) of 2,5-diphenyl-2,5-hexanediol in benzene was added to 0.293 g (1.302 mmol) of NIS contained in a 10-mL flask. The flask was covered with aluminum foil in a dark fume hood. The mixture was stirred. After 23 h of reaction time acetophenone was found in 3% yield as determined by VPC.

Collection of Ethene in the Oxidation of 2,5-Dimethyl-2,5-hexanediol with NIS and Irradiation. The diol (2,5-dimethyl-2,5-hexanediol, 4.185 g, 28.619 mmol) and 30 mL of diphenyl ether were placed in a 50 mL, round-bottomed flask. NIS (6.352 g, 28.232 mmol) was weighed in another flask. Both flasks were placed on a vacuum rack and the system was evacuated. The chemicals were mixed, stirred, and irradiated for 1 h 22 min. Analysis gave an 80% yield of ethene with a molecular weight of 29.0 g/mol. Mass spectrometer analysis of the gas collected indicated 82–83% ethene and 17–18% acetone.

Collection of Ethene in the Oxidation of 2,5-Diphenyl-2,5-hexanediol with NIS and Irradiation. The diol (2,5-diphenyl-2,5-hexanediol, 7.336 g, 32.61 mmol) and 75-mL of diphenyl ether were placed in a 100-mL, round-bottomed flask. NIS (7.336 g, 32.61 mmol) was weighed in another flask. Both flasks were placed on a vacuum rack and the system was evacuated. The chemicals were mixed, stirred, and irradiated for 1 h 20 min. Analyses gave a 57% yield of ethene with a molecular weight of 29.2 g/mol. Mass spectrometer analysis of the ethene indicated a purity of 97–99%.

Iodine Determination. The iodine produced in the oxidation of the 1,4-diols with NIS was determined by adding reaction mixtures to 25 mL of a 1:1 mixture of acetic acid and water. Several drops of concentrated HCl were added, and the iodine was titrated with a standardized solution of thiosulfate. The iodine percentage yield was determined by assuming that 1 mol of iodine is produced from 2 mol of NIS.

Succinimide Determination. Succinimide was recovered from the completed reactions by pouring the reaction mixture into diethyl ether and extracting the ether solution with water. The combined water extracts were washed with fresh ether, and the water solution was evaporated.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this research. We also thank the Department of Chemistry of the University of Kentucky for mass spectrometry data.

Registry No. 1, 110-03-2; 6, 24434-16-0; 8, 91384-70-2; *N*-iodosuccinimide, 516-12-1.

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(8) Rappoport, Z. "Handbook of Tables for Organic Compound Identification", 3rd ed.; The Chemical Rubber Company: Cleveland, 1967.

On the Stereospecifity of Intrinsic ^{2}H/^{1}H NMR Isotope Effects on ^{13}C Chemical Shifts in Cyclohexanes

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The structural dependence of intrinsic ^{2}H/^{1}H NMR isotope effects on ^{13}C chemical shifts, $^{n}\Delta(^{13}\mathrm{C})$, where n is the number of intervening bonds, in organic compounds is of current interest[1] because the determination of these parameters profits from the increasing number of high-field NMR instruments. Another reason is the use of $^{n}\Delta(^{13}\mathrm{C})$ values for assignment purposes in ^{13}C NMR spectra[2] and in this context stereospecific isotope effects are of practical importance. For adamantane, we found $^{n}\Delta_{\mathrm{anti}} > {}^{n}\Delta_{\mathrm{syn}}$ for $n = 3$ and 4.[3] More recently, Jurlina and Stothers[4] have shown that in bicyclic systems $^{3}\Delta$ has its maximum value for an eclipsed arrangement between the respective C–D and C–^{13}C bonds. The authors concluded that these shifts arise from spacial proximity and supporting evidence for such a mechanism was seen in the results of Anet and Dekmezian,[5] who had found large ^{2}H/^{1}H isotope effects on ^{1}H chemical shifts in situations where van der Waals interactions are involved. However, ^{2}H/^{1}H isotope effects on ^{19}F chemical shifts violate this principle, displaying maxima for maximum distances,[6] and further studies of the relationship between stereochemistry and NMR isotope effects are indicated.

Results and Discussion

In the present note we report data on the geometrical dependence of $^{n}\Delta(^{13}\mathrm{C})$ values in cyclohexane derivatives. From low-temperature measurements for cyclohexane-d_1[7] (7), we were able to measure $^{1}\Delta_{\mathrm{ax}}$ and $^{1}\Delta_{\mathrm{eq}}$ separately, but long-range isotope effects could not be resolved. Only the corresponding ^{1}H/^{2}H data for cyclohexane-d_{11}[8] (8) are available. Therefore, we decided to study derivatives substituted in the 4-position by a *tert*-butyl group, known to stabilize the conformation with the alkyl group in the

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(1) (a) "Specialist Periodical Reports", NMR Spectroscopy, Vol. 12, The Royal Society of Chemistry: London, 1983; p 16, and earlier volumes in this series. (b) Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 106.

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(4) Jurlina, J. L.; Stothers, J. B. *J. Am. Chem. Soc.* **1982**, *104*, 4677.

(5) Anet, F. A. L.; Dekmezian, A. H. *J. Am. Chem. Soc.* **1979**, *101*, 5449.

(6) Lambert, J. B.; Greifenstein, L. G. *J. Am. Chem. Soc.* **1973**, *95*, 6150; **1974**, *96*, 5120.

(7) Aydin, R.; Günther, H. *Angew. Chem.* **1981**, *93*, 1000; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 985.

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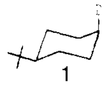
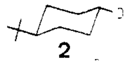
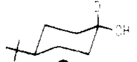
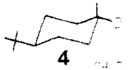
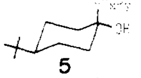
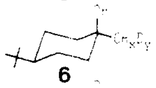
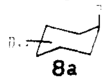
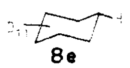
Table I. $^2H/^1H$ Isotope Effects for ^{13}C Chemical Shifts, $^n\Delta$ (ppb), and One-Bond $^{13}C,^2H$ Coupling Constants J (in Hertz) in Cyclohexanes[a]

	x	y		$^1\Delta$	$^2\Delta$	$^3\Delta$	$^4\Delta$	$^5\Delta$	^1J
 **1**				442.2	98.6	14.7	–	–	18.92
 **2**				392.4	106.2	37.7	–	–	19.49
 **3**				483.2	108.1	-6.9	–	–	21.45
 **4**				455.4	134.4	22.4	–	–	22.14
	x	y							
 **5**	2	1		298.2	45.9	13.8	3.2	–	19.19
	1	2		298.2	46.2	14.6	3.3	–	19.14
	0	3		298.4	45.7	14.4	3.2	–	19.09
	x	y							
 **6**	2	1		305.9	47.9	24.7	7.8	-2.6	19.16
	1	2		306.1	48.1	24.3	7.6	-2.2	19.08
	0	3		306.1	48.4	24.1	7.7	-2.1	19.02
 **7a**				444.9 (-80°)	103.7[b]	24.9[b]			18.89
 **7e**				396.4 (-80°)					19.49
 **8a**			(-104°)	-445.9	-102.9	-12.5	(+1.2)	–	122.44
 **8e**			(-104°)	-398.6	-115.7	-33.4	-2.4	–	126.44

[a] ppb = parts per billion; the data for **5** and **6** were divided by the number of deuterons in order to facilitate a comparison of the results; data for **7** and **8** are from ref 7 and 8, respectively; those for **8** are $^1H/^2H$ isotope effects. [b] Average values for **7a** and **7e** at room temperature.

equatorial position to such an extent that the presence of the other conformer (alkyl group *axial*) is negligible.[9] In addition to the monodeuterated hydrocarbons **1** and **2**,[10] the 1-*d* alcohols **3** and **4** as well as the 1-methyl alcohols **5** and **6** (see Table I for formulas) were investigated. Most of the observed isotope effects are positive—a sign convention which corresponds to high-field shifts[16]—but for **3** and **6** negative isotope effects (low-field shifts) are observed over three and five bonds, respectively. The results, together with those for cyclohexane-d_1 (**7**) and cyclohexane-d_{11} (**8**), as well as some one-bond $^{13}C,^2H$ coupling constants, are collected in Table I. Long-range coupling constants for **1**, **2**, and **4** are given in the Experimental Section.

The data for **1** and **2** are in good agreement with the low-temperature results for **7** and **8** and confirm that $^1\Delta_{ax} > {}^1\Delta_{eq}$. For the $^2\Delta$ values, the reverse order holds ($^2\Delta_{ax} < {}^2\Delta_{eq}$). The average value of 102.4 ppb agrees with our room-temperature result for **7**. The difference between the $^2\Delta$ values (7%) is near that for the $^1\Delta$ values (12%). A much larger difference is found for $^3\Delta$, where $^3\Delta_{trans}$ (= $^3\Delta_{eq}$) in **2** is nearly 3 times as large as $^3\Delta_{gauche}$ (= $^3\Delta_{ax}$) in **1**. This is in accord with the adamantane results,[3] where $^3\Delta_{trans}$ is 26 and $^3\Delta_{gauche}$ is 8 ppb and parallels the observations made for $^2H/^1H$ isotope effects on ^{19}F chemical shifts.[6]

Upon introduction of an OH group at C-1, the $^1\Delta$ and $^2\Delta$ values increase, while the $^3\Delta$ values decrease, actually becoming negative for **3**. The relative order observed for the hydrocarbon, however, prevails in all three cases. Long-range isotope effects over four and five bonds were not resolved.

For the deuterated methyl alcohols, **5** and **6**, where the C–D bonds are now in α-position to the cyclohexane ring, measurements made for the mono-, di-, and trideuterated systems are in good agreement. The $^1\Delta$ values are about 25% smaller than those in the deuterated cyclohexanes, and the *equatorial* methyl group now shows the larger effect. However, the difference between *axial* and *equatorial* orientation is rather small. The magnitude of the $^2\Delta$ values as compared to **1** and **2** is reduced by as much as 50%, and the difference between *axial* and *equatorial* shifts is minimal. For the $^3\Delta$ values, which now involve C-2, $^3\Delta_{eq} > {}^3\Delta_{ax}$ is again observed, and the same is true for $^4\Delta$. In both cases the ratio is approximately 2:1. It is noteworthy here that $^3\Delta_{ax}$ for **5** is in accord with the upper limit of 4 ppb estimated by Anet[5] for 2,2,5,5-tetramethyl-1,3-dioxane-d_6. Finally, a $^5\Delta$ value was only resolved for **6**. No explanation for the negative sign of $^5\Delta$ is at hand, but it is interesting to compare this result with our findings for α-deuterated toluenes.[11] Here, C-4 also showed a negative $^5\Delta$ value (−3.9 ppb), which, together with the negative $^3\Delta$ value for C-2,6, was taken as evidence for hyperconjugative interactions. In the present case, there exist no hyperconjugative interactions which could be perturbed by the introduction of deuterium, again demonstrating that a negative long-range $^n\Delta$ value alone does not imply a hyperconjugative mechanism.[12] Since $^3\Delta$ in **6** is large and positive, our interpretation for toluene prevails, even if one were to accept **6** as a model compound for the σ-bond structure of toluene: a rather questionable procedure considering the different geometry and the additional 4-substitution.

Conclusions

The most marked differences between *axial* and *equatorial* $^n\Delta(^{13}C)$ values in **1**–**6** occur for $^3\Delta$ and $^4\Delta$. Usually, $^3\Delta$ can be easily resolved and therefore it seems to be the most reliable indicator of the orientation of a C–D bond or a deuterated methyl group in a cyclohexane ring. The $^2\Delta$ values are larger in magnitude, but their dependence on geometry seems less pronounced. Although $^1\Delta$ is the easiest to measure, its magnitude is determined mainly by the properties of the particular C–D bond and it is presently not known if substituent effects can lead to the reverse order ($^1\Delta_{ax} < {}^1\Delta_{eq}$).

As for the spacial proximity requirements mentioned above, our data do not support a general extension of Anet's findings for $^2H/^1H(^1H)$ effects[5] to $^2H/^1H(^{13}C)$ effects, as suggested by Stothers.[4] In our case, the order for $^3\Delta$ in **1**–**4** and $^4\Delta$ in **5** and **6** should be reversed if spacial proximity were of importance. On the other hand, in the presence of strong steric compression, changes in van der Waals effects that arise from deuterium substitution may also contribute to ^{13}C chemical shift changes. In this respect it is perhaps of interest to note that the effects found for the bicyclic systems[4] are more than twice the largest effects we found in the cyclohexanes.

Keeping in mind the vibrational origin of isotope effects,[13] however, we suggest that in the cases studied here,

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[9] Winstein, S.; Holness, N. J. *J. Am. Chem. Soc.* **1955**, *77*, 5562.

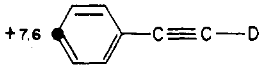
[10] Earlier measurements for **1** and **2** suffered from lower accuracy: Doddrell, D.; Kitching, W.; Adcock, W.; Wiseman, P. A. *J. Org. Chem.* **1976**, *41*, 3036.

[11] Wesener, J. R.; Günther, H. *Tetrahedron Lett.* **1982**, *23*, 2845.

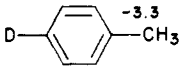
[12] Berger, S.; Künzer, H. *Angew. Chem.* **1983**, *95*, 321; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 321.

[13] Jameson, C. J. *J. Chem. Phys.* **1977**, *66*, 4983.

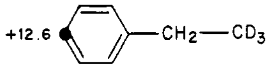
as well as in many others, the efficiency of coupling between certain vibrations of the intervening bond system plays a major role in determining the magnitude of the observed long-range effects. Thus, a more "linear" arrangement as in an *antiperiplanar* conformation is expected to yield the larger $^n\Delta$ values, if C–D and C–C stretching vibrations are considered. Support for this assumption comes from the large long-range isotope effects observed for molecules like **9**,[11] **10**,[12] and **11**.[11] In the present case it allows the rationalization of the results for $^3\Delta$ and $^4\Delta$, where the larger effects are found for those situations in which the intervening bond system can adopt an antiperiplanar conformation or a type of zig-zag arrangement. Spacial proximity of the resonating ^{13}C nucleus and the deuteration site obviously cannot be important here. Since vibrational coupling can also be effective for eclipsed bonds in a vicinal situation, as is well-known, for instance, for the C=O stretching vibration in cyclic α-diketones,[14] the large $^3\Delta$ values in bicyclic systems[4] may also result from vibrational coupling and thus would not be unexpected.



9



10



11

Experimental Section

The synthesis of the compounds followed published procedures (**1**, **2**, **3**, **4**,[15,16] **5**, **6**[17]) using suitably deuterated reagents ($NaBD_4$, CD_3I (Aldrich) and CHD_2I, CH_2DI (Merck, Sharp & Dohme)). ^{13}C NMR spectra were recorded at 100.61 MHz with a Bruker WH 400 spectrometer at 310 K using broad-band ^1H decoupling and a ^2H lock, 10-mm o.d. sample tubes, and $CDCl_3$ as solvent. The concentrations were 1.38 M (**1**, **2**), 2.3 M (**3**), 0.82 M (**4**), and 0.8 M (**5**, **6**), with a ratio of 3:1 for deuterated and non-deuterated material. The digital resolution was 0.037 Hz (**1**–**4**) and 0.01 Hz (**5**, **6**) which results in an experimental error of ca. ±0.5 ppb, if line-broadening is taken into account. Signal assignments were available from the literature (**1**–**4**,[10] **5**, **6**[18]) and the identification of isotope shifts was possible in all cases on the basis of the presence of ^2H, ^{13}C spin–spin coupling and/or the concentration difference for deuterated and nondeuterated material. For **1**, **2**, and **4** the following long-range $^{13}C,^2H$ coupling constants (in hertz) were measured: **1**, $^2J = 0.57$, $^3J = 0.29$; **2**, $^2J = 0.48$, $^3J = 1.25$; **4**, $^3J = 0.73$.

Acknowledgment. We are indebted to Prof. J. B. Stothers for his comments, to Dipl.-Chem. D. Moskau for assistance in some of the experiments, and to the Fonds der Chemischen Industrie for financial support. P.J.-N. thanks the DAAD for a travel grant.

Registry No. **1**, 53042-76-5; **2**, 17553-36-5; **3**, 30461-17-7; **4**, 30461-16-6; **5** (x = 2, y = 1), 91312-20-8; **5** (x = 1, y = 2), 91312-22-0; **5** (x = 0, y = 3), 91312-23-1; **6** (x = 2, y = 1), 91312-21-9; **6** (x = 1, y = 2), 91312-24-2; **6** (x = 0, y = 3), 91312-25-3; **7a**, 26168-37-6; **8a**, 1520-59-8; ^{13}C, 14762-74-4; D_2, 7782-39-0.

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[17] DePuy, C. H.; King, R. W. *J. Am. Chem. Soc.* **1961**, *83*, 2743.

[18] Senda, Y.; Ishiyama, J.; Imaizumi, S. *Tetrahedron* **1975**, *31*, 1601; cited from Breitmaier E., Haas, G. Voelter, W. "Atlas of ^{13}C NMR Data", Vol. 2, Heyden: London 1976.

3-Fluorocyclopropene

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As an extension of the use of 3,3-difluorocyclopropene and 1,3,3-trifluorocyclopropene as precursors of the monofluoro- and difluorocyclopropenyl cations,[1,2] we sought 3-fluorocyclopropene (**1**) as a source of the cyclopropenyl cation itself. However, when finally made, **1** proved to be too labile for use in most chemistry, including preparation of colorless cation solutions in sulfur dioxide at low temperature for use in Raman spectroscopy.

Dehydrohalogenation of halocyclopropanes has been a useful way to prepare other fluorocyclopropenes, including 3,3-difluorocyclopropene,[3] 1,3,3-trifluorocyclopropene,[2] and perfluorocyclopropene.[4] Accordingly, the cis and trans isomers of 1-chloro-2-fluorocyclopropane were synthesized and treated with a variety of strong bases, including Ascarite (sodium hydroxide on asbestos) coated with a crown ether, in unsuccessful attempts to prepare **1**.

Ultimately, 3-chlorocyclopropene (**2**), which was prepared by the method of Breslow and co-workers,[5] was converted into **1** by passing gaseous **2** through a column containing a rigorously dry mixture of silver difluoride and potassium fluoride.[6] This fluorination reaction, which is presumed to go through a cation intermediate under mild conditions, goes in high yield in the cyclopropene system. The purity of the **1** product, which is too labile for chemical or gas chromatographic purification, depends on careful prior purification of **2**. **1** does not survive passage through an Ascarite-packed column, which explains the failure of the dehydrohalogenation method of preparation. Even in the gas phase **1** has a limited lifetime in an infrared cell. Localized dark deposits formed in a decomposition process. Hydrogen fluoride, silicon tetrafluoride, and acetylene were volatile products of this composition in glass cells. Good-purity samples of **1** sealed in melting point capillaries made of borosilicate glass could be studied in Raman experiments for hours at −50 °C. Such samples could be stored for months at liquid nitrogen temperature.

Proton and ^{19}F NMR spectra at −50 °C confirmed the identity of **1**. The proton spectrum consisted of a doublet of doublets ($J_{HF} = 3.2$ Hz, $J_{HH} = 1.5$ Hz) at 7.7 ppm relative to Me_4Si due to the HC=CH protons and a doublet of triplets ($J_{HF}{}^{gem} = 110$ Hz, $J_{HH} = 1.5$ Hz) at 5.0 ppm due to the CFH proton. The ^{19}F spectrum was a doublet of triplets ($J_{HF}{}^{gem} = 110$ Hz, $J_{HF} = 3.2$ Hz) at a chemical shift of −145 ppm (upfield) relative to $CFCl_3$. At temperatures above −20 °C most of the fine structure had collapsed. The geminal HF coupling constant of 110 Hz is exceptionally large. In 1-fluoroethylene $J_{HF}{}^{gem} \approx 80$ Hz.[7] In 1-fluoro-

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