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Temperature Effects on ^{13}C n.m.r. Chemical Shifts of Normal Alkanes and some Linear and Branched 1-Alkenes

J. W. de Haan,* L. J. M. van de Ven, A. R. N. Wilson, and Mrs A. E. van der Hout-Lodder

Laboratories of Instrumental Analysis and Organic Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands

C. Altona and D. H. Faber

Chemical Laboratories of the University, P.O. Box 75, Leiden, The Netherlands

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Abstract— ^{13}C n.m.r. chemical shifts of a number of 1,1-disubstituted ethylenes are presented. Moreover, effects of changing temperatures on the ^{13}C n.m.r. chemical shifts of some of these compounds as well as of three normal alkanes are given. These variations in chemical shifts are attributed to varying amounts of sterically induced shifts in the different conformational equilibria. In addition to the well-known 1,4 interaction between two alkyl groups shielding effects on the carbon atoms of the connecting bonds are also proposed. No definite explanation of this effect is presented at this time. It is further shown that no simple correlations exist between ^{13}C n.m.r. chemical shifts and calculated total charge densities at this level. Instead, the experimental results in 1-alkenes are rationalized by assuming a linear dependence of the ^{13}C n.m.r. chemical shifts of C-1 and C-2 via rehybridizations on changes in bond angles for small skeletal deformations caused by steric interactions. These changes in geometries, as well as conformational energies in three 1-alkenes, were calculated by means of VFF calculations. Finally, upfield shifts for both C-2 and C-4 are proposed for those conformations of 1-alkenes in which the C-3—C-4 group interacts with the p_z -orbital of C-2.

INTRODUCTION

SOME time ago we published ^{13}C n.m.r. chemical shifts at ambient temperatures of a number of (*Z*)- and (*E*)-1,2-disubstituted and 1,1,2-trisubstituted ethylenes.¹ Conclusions concerning conformational equilibria in trisubstituted ethylenes were hampered at that time by lack of suitable shift data for 1,1-disubstituted ethylenes. Moreover, interactions other than the well documented 1,4 type are involved in such a study. Recently, both Grant *et al.*² and Stothers *et al.*³ showed that 1,5 interactions in particular may well yield downfield chemical shift effects.

Since our previous study¹ appeared, a number of calculations concerning conformational equilibria in hydrocarbons have been published, some based on MO principles,⁴ others on VFF methods.⁵ The intention of the present paper is twofold. First, chemical shifts of a number of 1,1-disubstituted ethylenes will be presented. Second, the effects of changing temperature on ^{13}C n.m.r. chemical shifts of some normal alkanes and linear 1-alkenes are combined with VFF calculated conformational energies in order to postulate some additional types of sterically induced ^{13}C n.m.r. chemical shifts. Finally, a tentative rationalization of these effects is offered.

* Author to whom correspondence should be addressed.

EXPERIMENTAL

Samples were purchased from API (Project 44) and Chemical Samples Co. and were used without further purification. Spectra were run at +20 and -60 °C, as well as at some intermediate temperatures, in 5 mm sample tubes on a Varian HA-100 spectrometer interfaced with a Digilab FTS-NMR-3 Pulsing and Data System. 1,2-Dibromo-1,1,2,2-tetrafluoroethane was used as an external ^{19}F lock and TMS dissolved in the lock substance served as a reference.

In order to avoid, as far as possible, intrinsic solvent effect differences⁶ interfering with our results, we dissolved all samples in normal hexane (c. 10 mol percent). The solvent effect of the lock substance on TMS was checked by measuring with respect to pure TMS and TMS in normal hexane.⁷ These measurements were carried out with the lock substance in an internal capillary and the sample in the outer 5 mm tube and vice versa. The variation of the solvent effect of the lock substance with temperature remains unknown. In order to estimate this dependence in the present case, we measured the shifts of cyclopentane, cyclohexane and norbornadiene dissolved in normal hexane with respect to TMS dissolved in the lock substance over the same temperature region. In these compounds conformational changes with temperature are unlikely. The apparent thermal shifts contain contributions from TMS (*vide supra*) and also from the changing solvent effects of normal hexane on the solutes. The numerical values of these shifts were: cyclopentane, -0.24 ppm; cyclohexane, -0.34 ppm and norbornadiene, -0.31 ppm (C-2, C-3, C-5, C-6) -0.26 ppm (C-1, C-4) and -0.31 ppm (C-7). The average of these numbers was used to correct our other experimental thermally induced shifts. This includes the assumption that the variation of solvent effects with temperature will not differ very much for different carbon atoms within a given molecule, and also that the variation between analogous compounds will be small. The total uncertainty introduced in this manner is estimated not to exceed 0.1 ppm.

RESULTS AND DISCUSSION

The experimental chemical shifts of a number of linear and branched 1-alkenes are given in Table 1. Table 2 contains the effects of changing temperatures on the chemical shifts of three normal alkanes and a number of 1-alkenes after application of the appropriate corrections (see Experimental).

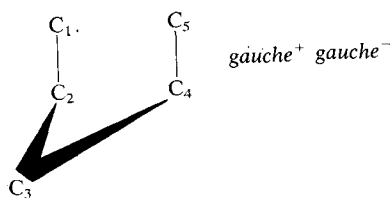
Non-bonded 1,4 and 1,5 interactions between polarizable C—H bonds leading to sterically induced shifts in ^{13}C n.m.r. spectra are relatively well-documented. The 1,4 (γ') effects are all upfield,⁸ and 1,5 (δ') effects may be of either sign.^{2,3,9} In normal alkanes these interactions occur more strongly in the energetically unfavourable 1,4 *gauche* conformations.

TABLE 1. ^{13}C n.m.r. CHEMICAL SHIFTS IN PPM DOWNFIELD FROM TMS OF SOME LINEAR AND SUBSTITUTED 1-ALKENES

| | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | C-s ^a | C-s' ^a |
|-----------------------|--------|--------|-------|-------|-------|-------|------------------|-------------------|
| Propene | 115.95 | 133.61 | 19.41 | | | | | |
| 1-Butene | 113.49 | 140.49 | 27.39 | 13.43 | | | | |
| 1-Pentene | 114.66 | 138.91 | 36.68 | 22.81 | 13.75 | | | |
| 1-Hexene | 114.17 | 138.83 | 33.86 | 31.64 | 22.49 | 13.73 | | |
| 4-Me-1-pentene | 115.39 | 137.53 | 43.72 | 28.50 | 22.22 | | 22.22 | |
| 4-Me-1-hexene | 115.57 | 137.56 | 41.58 | 35.08 | 29.56 | 11.51 | 19.10 | |
| 4,4-diMe-1-pentene | 116.79 | 135.93 | 49.11 | 30.93 | 29.53 | | 29.53 | 29.53 |
| 2-Me-propene | 111.26 | 141.79 | 24.20 | | | | 24.20 | |
| 2-Me-1-butene | 109.06 | 146.98 | 31.09 | 12.55 | | | 22.55 | |
| 2-Me-1-pentene | 110.16 | 145.25 | 40.46 | 21.19 | 13.63 | | 22.08 | |
| 2-Me-1-hexene | 110.07 | 145.43 | 38.01 | 30.43 | 22.83 | 13.95 | 22.26 | |
| 2-Et-1-butene | 106.73 | 152.65 | 28.14 | 12.42 | | | 28.14 | 12.42 |
| 2-Et-1-pentene | 108.08 | 150.94 | 38.92 | 21.46 | 13.86 | | 29.16 | 12.50 |
| 3-Me-1-butene | 111.41 | 145.94 | 32.70 | 22.30 | | | 22.30 | |
| 3-Me-1-pentene | 112.59 | 144.48 | 40.01 | 29.79 | 11.56 | | 19.85 | |
| 3-Me-1-hexene | 112.52 | 144.85 | 38.14 | 39.62 | 20.74 | 14.23 | 20.40 | |
| 3-Et-1-pentene | 114.48 | 143.00 | 48.29 | 23.85 | 11.67 | | 23.85 | 11.67 |
| 3,3-diMe-1-pentene | 110.68 | 148.31 | 36.90 | 35.56 | 8.96 | | 26.58 | 26.58 |
| 3,3-diMe-1-butene | 108.50 | 149.27 | 33.78 | 29.41 | | | 29.41 | 29.41 |
| 2,3-diMe-1-butene | 108.04 | 151.06 | 35.68 | 21.56 | | | 19.85 | 21.56 |
| 2,3-diMe-1-pentene | 109.83 | 149.44 | 43.52 | 28.26 | 11.59 | | 18.98 | 19.47 |
| 2,3-diMe-1-hexene | 109.79 | 149.75 | 41.52 | 38.04 | 21.11 | 14.36 | 18.99 | 19.99 |
| 3-Et-2-Me-1-pentene | 111.86 | 147.10 | 51.84 | 26.60 | 12.07 | | 18.25 | 26.60 |
| 2,3,3-triMe-1-butene | 108.31 | 153.41 | 35.97 | 29.39 | | | 19.58 | 29.39 |
| 2,3,3-triMe-1-pentene | 108.50 | 151.53 | 39.33 | 33.74 | 9.15 | | 19.60 | 27.16 |
| 2,4-diMe-1-pentene | 111.60 | 144.34 | 48.23 | 26.43 | 22.56 | | 22.24 | 22.56 |
| 2,4,4-triMe-1-pentene | 114.41 | 143.55 | 52.29 | 31.65 | 30.43 | | 25.47 | 30.43 |
| 3,4-diMe-1-pentene | 113.59 | 143.09 | 44.83 | 33.29 | 19.91 | | 17.24 | 19.91 |

^a C-s denotes the carbon in α -position to the main chain of the molecule, C-s' the carbon in β -position. In multiply substituted compounds C-s and C-s' denote the α -carbons in numerical order of the substitution positions.

For given conformational energies, conformational populations may be calculated using the Boltzmann equation. No accurate conformational energies for alkanes seem to be known at present; usually the average energy difference between *gauche* and *anti* conformations is taken to be *c.* 700 cal mol⁻¹.¹⁰ Only *gauche*⁺ *gauche*⁻ conformations which are of relatively high energy lead to appreciable 1,5 interactions.



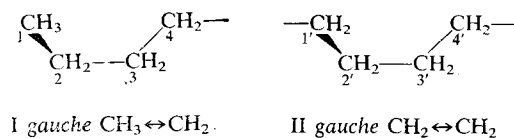
The populations and hence also the changes in populations upon changing temperatures are considered to be too small to be noticeable in our experiments. Our experimental results for pentane, hexane and heptane show rather constant induced chemical shift differences for C-1 and C-2 in all three compounds and for C-3 in the latter two. This suggests that conformational changes are confined mainly to the C-1—C-2—C-3—C-4 part of these molecules, i.e. to fragment I and its *anti* counterpart. This, in turn, indicates that *gauche* CH₂—CH₂ interactions in normal alkanes (fragment II) introduce significantly larger energies than interactions of type I. Thus, the relative populations of *anti-gauche-anti* conformations in heptane and *anti-gauche-anti* conformations in hexane are very low over the entire temperature region investigated in this study. The problem

TABLE 2. DIFFERENTIAL CHEMICAL SHIFTS IN PPM IN ^{13}C n.m.r. SPECTRA UPON COOLING FROM +20 TO -60 °C^a

| | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | C-s ^b | C-s' ^b |
|----------------|-------|-------|-------|-------|-------|-------|------------------|-------------------|
| Normal pentane | +0.42 | +0.46 | +0.23 | +0.46 | +0.42 | | | |
| Normal hexane | +0.44 | +0.38 | +0.47 | +0.47 | +0.38 | +0.44 | | |
| Normal heptane | +0.44 | +0.36 | +0.41 | +0.73 | | | | |
| 1-Butene | +0.26 | -0.10 | +0.25 | +0.14 | | | | |
| 1-Pentene | +0.21 | -0.15 | +0.24 | +0.03 | +0.32 | | | |
| 1-Hexene | +0.20 | -0.17 | +0.48 | +0.01 | +0.30 | +0.42 | | |
| 4-Me-1-pentene | +0.26 | +0.10 | +0.20 | +0.01 | +0.22 | | +0.22 | |
| 4-Me-1-hexene | +0.34 | -0.01 | +0.35 | -0.16 | +0.07 | +0.45 | +0.07 | |
| 2-Me-1-butene | -0.13 | -0.40 | -0.30 | -0.17 | | | +0.69 | |
| 2-Me-1-pentene | +0.11 | -0.30 | -0.18 | -0.22 | +0.32 | | +0.29 | |
| 2-Me-1-hexene | +0.07 | -0.34 | +0.07 | -0.24 | +0.20 | +0.45 | +0.30 | |
| 2-Et-1-butene | -0.53 | -0.65 | -0.03 | -0.25 | | | -0.03 | -0.25 |
| 2-Et-1-pentene | -0.32 | -0.78 | +0.08 | -0.35 | +0.25 | | -0.39 | -0.29 |
| 3-Me-1-butene | +0.16 | -0.26 | +0.24 | +0.04 | | | +0.04 | |
| 3-Me-1-pentene | +0.52 | -0.20 | +0.65 | +0.12 | +0.59 | | +0.67 | |
| 3-Et-1-pentene | +0.86 | -0.28 | +0.35 | +0.51 | +0.59 | | +0.51 | +0.59 |

^a Positive values refer to downfield chemical shifts upon cooling.

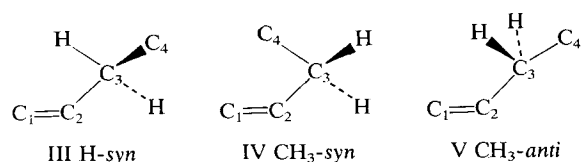
^b C-s denotes the substituent in α -position to the main chain, C-s' denotes the substituent in β -position



of determining unique differential shieldings for all individual carbon atoms in the normal alkanes is mathematically undetermined. It can be deduced, however, that in I the induced shift on C-1 is larger than for C-4, (c. 0.2 ppm of the thermally induced shift of C-4 is to be ascribed to conformations in which C-4 is in an internal position, like C-2 and C-3). Also noteworthy is the downfield shift found for C-3 in pentane upon cooling. This carbon atom is not involved in any 1,4 interaction.

Apparently an upfield shift is also induced on C-2 and C-3 when C-1 and C-4 are subject to a *gauche* steric interaction. This result is rather important; part of the downfield thermally induced shifts for C-2—C-5 in hexane and C-2—C-6 in heptane should also be ascribed to this phenomenon.

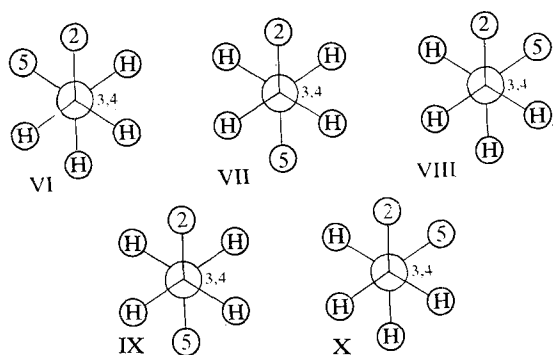
Conformational energies of three linear 1-alkenes were estimated by VFF calculations (the force field is described in Ref. 5(a), cross-terms were omitted), and the results are summarized in Table 3. For 1-butene the minimum energy conformation is as depicted in III. This is in agreement with earlier VFF calculations on this molecule⁵ and with results from several experimental methods like microwave,¹¹ vibrational spectroscopy¹² and ^1H n.m.r.,¹³ which all indicate a *syn* proton. Conformation V is considerably higher in energy than III and IV; the difference between the two latter conformations amounts to 0.96 kcal mol⁻¹ (see Table 3).



Therefore the differences brought about by changing the temperature of 1-butene will have to be correlated with a changing III \leftrightarrow IV equilibrium. In order to explain our experimental temperature-dependent chemical shifts we have to propose a steric interaction between C-2 and C-4 in III which causes shielding of both C-2 and C-4; the normal downfield shift on C-4 upon lowering the temperature is about 0.5 ppm, as in the alkanes. This may also explain the relatively small β effect of the C-4 methyl group on C-2: + 6.88 ppm (found by comparing shifts in propene and 1-butene). In normal alkanes the β effect is approximately + 9.8 ppm. Steric contributions to β effects in olefins were suggested earlier by Roberts *et al.*¹⁴ These authors also predicted a diminishing absolute value of the β effect on C-2 of an alkene upon multiple branching on C-3. This is indeed borne out by the ambient temperature chemical shifts of C-2 in such compounds. For example, the β effect on C-2 in 3-Me-1-butene is +5.45 ppm; in 3,3-diMe-1-butene, +3.33 ppm; in 3-Me-1-pentene, +5.57 ppm; in 3,3-diMe-1-pentene, +3.83 ppm (cf. chemical shifts in Table 1). Additional branching on C-4 seems to have only slight influence: the β effect of the 3-methyl group on C-2 in 3,4-diMe-1-pentene is +5.56 ppm, virtually identical to 3-Me-1-pentene.

TABLE 3. CONFORMATIONAL ENERGIES OF 1-BUTENE, 1-PENTENE AND 1-HEXENE IN kcal mol^{-1} AS CALCULATED USING THE LCFF3 FORCE FIELD (OMITTING CROSS-TERMS)

| Compound | Conformation | Energy |
|-----------|--------------|--------|
| 1-Butene | III | 1.489 |
| | IV | 2.453 |
| 1-Pentene | VI | 2.174 |
| | VII | 2.307 |
| | VIII | 2.613 |
| | IX | 3.318 |
| 1-Pentene | X | 3.944 |
| | VII | 3.944 |
| 1-Hexene | III | 2.975 |
| | IV | 3.200 |
| | XV | 4.094 |
| 1-Hexene | XVI | 3.126 |
| | XVII | 3.509 |
| | XVIII | 3.524 |
| 1-Hexene | XIX | 3.467 |
| | XX | 3.764 |
| | XXI | 5.577 |
| 1-Hexene | XXII | 4.127 |
| | XXIII | 4.568 |
| 1-Hexene | XXIV | 4.767 |
| | XXV | 5.216 |
| | XXVI | 6.268 |



For 1-pentene the VFF calculations indicate that upon cooling from $+20$ to -60 °C the major conformational change will be an increase of VI ($+5.0\%$) and a decrease of VIII (-3.1%). In VI, steric interaction between C-5 and C-1 is feasible, which will presumably lead to a downfield chemical shift on C-5.^{2,3,9} For C-1, C-2, C-3 and C-4 in 1-butene and 1-pentene very similar thermally induced shifts are observed—an upfield shift of C-2 and a downfield shift of C-4, which are significantly smaller than in the corresponding alkane fragment. This would indicate that in 1-pentene, as in 1-butene, the major contribution to the thermally induced shifts of C-1—C-4 is to be ascribed to a changing population of conformations with C-4 *syn* to the double bond. VFF calculations indicate a decrease of *c.* 2.7% for those conformations (IX and X) upon cooling from $+20$ to -60 °C. The comparable figure for 1-butene is *c.* 3.8% .

In 1-hexene the conformational equilibria as far as the C-1—C-5 fragment is concerned are very similar to those in 1-pentene. This is concluded from our VFF calculations. The experimental thermal shifts are also similar, except for C-3 which is in a relative 1,4 position with C-6. Our VFF calculations indicate that upon cooling conformations with C-3 and C-6 in a relative *anti*-position will increase by *c.* 5.4% . The corresponding γ effect of C-6 on C-3 in the ambient temperature spectrum of 1-hexene (by comparison with 1-pentene) amounts to -2.82 ppm.

Comparison of 1-alkenes with *n* carbon atoms in the main aliphatic chain with the appropriate model with one carbon atom less, yields results similar to those noticed already for the normal alkanes. In branched derivatives, extra effects may arise due to the larger number of possible 1,4 interactions.

In 3-Me-1-alkenes the α , β and γ effects in the saturated part of the molecules at ambient temperatures show a rather irregular pattern. Both the α and the β effect reach a minimum value in 3-Me-1-pentene. The β effect exerted on C-2 is always downfield but relatively small in magnitude,¹⁴ (*vide supra*).

The minimum value is reached in 3-Me-1-butene: $+5.45$ ppm. With longer chains the β effects increase gradually: $+5.57$ ppm in 3-Me-1-pentene and $+6.02$ ppm in 3-Me-1-hexene. The γ effects on C-1 show a trend in the same direction: smaller upfield shifts are associated with longer chains. These trends can be rationalized on the basis of increasing degrees of freedom with increasing chain length, and hence decreasing time-averaged steric interaction between the 3-methyl group and the C-1=C-2 fragment in longer chains.

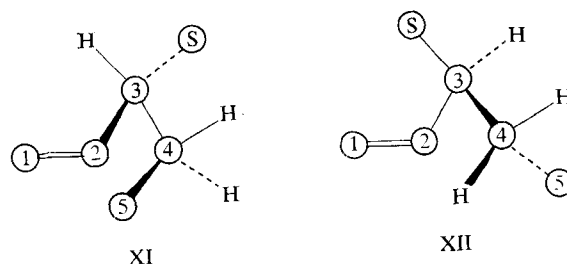
The thermally induced chemical shifts do not differ very much in 3-Me-1-butene and the 'parent' 1-butene

molecule. The slightly increased upfield shift on C-2 is attributable to increased steric interaction with the two (instead of one) β -methyl groups at lower temperatures. The most prominent feature of longer 3-Me-1-alkenes is the large downfield shift on C-1 (see Table 2). As yet, no VFF calculations have been applied to 3-alkyl-1-alkenes. It seems reasonable, however, to assume that in 3-Me-1-pentene the most favourable conformer will consist of VI with C-3—C-sub *anti* to C-4—C-5 (XI). This is also consistent with the relatively small downfield effect on C-4 (see Table 1).

The large downfield effect on C-1 upon cooling would imply a *negative* shielding induced by C-5 on C-1 in conformation XI. The relative positions of C-1 and C-5 in the present case are similar to those reported by Stothers *et al.*³ which result in negative sterically induced shifts, see also Ref. 9. The even larger downfield effect on C-1 in 3-Et-1-pentene is understandable in similar terms: the minimum energy conformation with an *anti-anti* conformation of the aliphatic part of the molecule will now have two δ -carbons interfering with C-1.

Another alternative structure of 3-Me-1-pentene with C-3—C-sub *anti* to C-4—C-5 has the substituent methyl group in a *syn* position with respect to the double bond (XII).

Methyl substitution at C-2 in 1-alkenes introduces rather constant α and β effects on the olefinic parts with the exception of C-2 in 2-Me-propene. This compound also possesses an unusually large downfield β effect on C-3. The γ effect is distinctly larger when C-4 is a methylene group.



Solely on the basis of the thermally induced chemical shifts in 2-Me-1-butene, especially on the methyl substituent, the minimum energy conformation presumably contains the two methyl groups in relative *anti* positions, i.e. C-4 approaches the *syn* position.¹⁵ This feature, which brings about a relatively large upfield shift on C-1 is apparently inherent in the presence of an ethyl substituent at C-2, as can be seen by comparison with the results for 2-Et-1-butene and 2-Et-1-pentene. A conformation of 2-Me-1-pentene, derived from conformation VIII of 1-pentene would have a sterically unfavourable *gauche* interaction between C-5 and the substituent, and therefore will presumably not contribute. Recent VFF calculations¹⁵ indicate that the CH_3 -*syn* H-*syn* energy difference in 1-butene is hardly influenced by the methyl substituent on C-2. At this time we are unable to account for the apparent discrepancy between the VFF calculations and the thermally induced shifts.

Rationalization of sterically-induced chemical shifts

There is a well-known relationship between overall atomic π -charges and ^{13}C n.m.r. chemical shifts for

sp_2 -hybridized carbon atoms: 160–180 ppm *per* electron.¹⁶ Recently, it was suggested that the charge-shift relationship for total charges on sp_3 -hybridized carbons would be of the order of 240 ppm *per* electron. These charge-shift relationships have been made in systems with relatively large charge separations like ions or fatty acids¹⁷ with the carbonyl group serving as an electric dipole inducing differential charges on nearby carbon atoms.

Fliszar *et al.*¹⁸ derived charge distributions in linear and branched alkanes from an inductive Taft-like equation. This method seems to give an acceptable theoretical background for the observed non-additivity of α - and β -substituent effects in alkanes with several geminal and/or vicinal side-chains. In the present case, however, shift differences induced by conformational changes within a given skeleton are discussed and the charge redistributions are very small. At this level, simple correlations of chemical shifts with charge densities are potentially dangerous because radial electron distributions are practically not considered.

In this study we combined VFF conformational energies with MINDO/2' calculations and charge-shift relationships in order to obtain calculated chemical shifts at different temperatures via changes in conformational equilibria. Results for 1-butene, 1-pentene and 1-hexene are presented in Table 4. Also included are results for 1-butene obtained using MINDO/2' optimized geometries. Comparison of the shifts calculated by the charge-shift model and experimentally observed thermal chemical shifts shows no correlation between the two sets; calculated shifts are too small by approximately an order of magnitude. Similar discrepancies were also observed for normal alkanes using the value of 700 cal mol⁻¹ as an average energy difference between *gauche* and *anti* 1,4 interactions. 'Rescaling' of our calculated charges as suggested by Fliszar would not remove the differences in order of magnitude between the two sets of results.

Overall atomic charges as calculated by semi-empirical MO calculations are obtained by integrating over the 2s- and 2p-orbitals of the carbon atom under considera-

TABLE 4. CALCULATED AND EXPERIMENTALLY OBSERVED ^{13}C n.m.r. CHEMICAL SHIFTS IN PPM UPON COOLING FROM +20 TO -60 °C FOR 1-BUTENE, 1-PENTENE AND 1-HEXENE^a

| | | C-1 | C-2 | C-3 |
|-----------|--------------------|-------|-------|-------|
| 1-Butene | calc. ^b | +0.02 | -0.02 | 0.03 |
| | calc. ^c | +0.04 | -0.03 | -0.02 |
| | obs. | +0.26 | -0.10 | +0.25 |
| 1-Pentene | calc. ^c | +0.01 | 0.00 | 0.00 |
| | obs. | +0.21 | -0.15 | +0.24 |
| 1-Hexene | calc. ^c | +0.01 | 0.00 | +0.03 |
| | obs. | +0.20 | -0.17 | +0.48 |
| | | C-4 | C-5 | C-6 |
| 1-Butene | calc. ^b | +0.06 | | |
| | calc. ^c | +0.04 | | |
| | obs. | +0.14 | | |
| 1-Pentene | calc. ^c | 0.00 | 0.00 | |
| | obs. | +0.03 | +0.32 | |
| 1-Hexene | calc. ^c | -0.03 | -0.03 | +0.06 |
| | obs. | +0.01 | +0.30 | +0.42 |

^a Positive values refer to downfield chemical shifts upon cooling.

^b Using MINDO/2' optimization of the molecular geometries and conformational energies as well as charge densities.

^c Combination of VFF conformational energies and MINDO/2' charge densities.

tion. However, ^{13}C n.m.r. chemical shifts also depend on other factors, such as radial charge distributions and bond orders via second and higher order effects in the paramagnetic shielding term. Recently, this was stated explicitly by Strong *et al.* in working out the Ramsey formula.²⁰ Application of the same procedure to larger molecules would be necessary to describe shielding effects more definitely. In an implicit way this problem was worked out by Woolfenden, Cheney and Grant for C—H bonds of CH_x groups in relative 1,4 positions.²¹ The interacting C—H bonds are polarized in such a way that the carbon atoms are shielded and the protons deshielded. This process involves small rehybridizations at the carbon and hydrogen atoms directly involved in the steric interaction. Later it was verified experimentally that the presence of polarizable C—H bonds is indeed crucial since quaternary α -carbons in (*Z*)- and (*E*)- di- and trisubstituted ethylenes do not show extra shielding in the (*Z*)-isomers.²² The results reported in this study as far as the direct shieldings on two carbons in a relative 1,4 position are concerned can be described in similar terms. Besides that, indirect shielding effects on the carbons in 2 and 3 positions also exist (*vide supra*). Finally, sizeable shieldings on C-2 and C-3 in conformation IX and on C-2 and C-4 in conformation VI need to be rationalized.

In 1970 Perlin and Koch²³ postulated a relationship between bond angles and chemical shifts stating that downfield chemical shifts would occur upon enlarging a C—C—C angle. On the other hand, Lippmaa *et al.*²⁴ suggested that steric interactions of the type discussed here do not influence ^{13}C n.m.r. chemical shifts to any measurable extent. Our own results, however, are fairly consistent, and suggest that an *upfield* chemical shift occurs for both C-2 and C-3 in conformation I while the appropriate bond angles are enlarged with respect to the corresponding *anti* conformation. The H—C—H bond angles will also change. Quite recently, it was stated that all carbon atoms involved in a γ -*gauche* interaction are shielded with respect to the same fragment lacking this interaction.²⁵ The detailed nature of the upfield shift on C-2 and C-3 in I, as well as the reason for the discrepancies between the various studies, remains veiled at this time.

In order to enable the assignment of some numerical results to the sterically-induced shifts in the several conformations of 1-alkenes the following approach was selected. In IV strong steric interaction between C-1 and C-4 will tend to enlarge the C-1, C-2, C-3 and C-2, C-3, C-4 bond angles. VFF calculations carried out in this and other studies indicate an angle deformation of *c.* 2.5–3.0° for C-1, C-2, C-3; this is also supported by MO optimization. It has been postulated²⁶ that for *small changes* in bond lengths and angles as a consequence of steric interactions in crowded ethylenes the resultant changes in spectral properties will be proportional to the magnitude of the deformation itself. Experimental verifications of this principle have been published for vibrational spectroscopy²⁶ and ^1H n.m.r.²⁷ The same procedure is now applied to ^{13}C n.m.r. chemical shifts. It should be emphasized that in using this simplification one probably combines a number of factors, which in fact need to be evaluated separately.

As a result of the angle enlargement of *c.* 2.8° of C-1, C-2, C-3 a rehybridization towards more *sp* character

will occur at C-2 and consequently also at C-1. The accompanying chemical shift will be upfield, the magnitude being approximately 2.3 ppm. This value is estimated by comparing the ^{13}C n.m.r. chemical shifts of 'genuine' sp_2 - and sp -hybridized carbon atoms like C-1, C-2 in 1-hexene versus the comparable atoms in 1-hexyne. Boltzmann averaging this effect by means of VFF conformational energies yields a downfield chemical shift of +0.14 ppm upon cooling from +20 to -60 °C. Additionally, the C-H bond polarization as postulated by Cheney and Grant²¹ will be active for C-1. In 1-butene this will yield an extra calculated downfield effect of +0.07 ppm. Thus, the estimated total downfield shift upon cooling amounts to +0.21 ppm, which compares reasonably well with the experimental value of +0.26 ppm.

As a consequence of C-1—C-4 interaction, C-4 will also shift upfield in III; the magnitude of this effect is comparable to that in alkanes. The observed downfield shift of C-4 in 1-butene upon cooling is, however, rather small. For C-2 even an upfield shift is consistently observed, in contradiction to the behaviour predicted by the rehybridization mechanism described above. In order to account for these discrepancies an upfield interaction between C-2 and C-4 must be assumed in conformation III. For C-2 this offsets the downfield shift with respect to conformation IV caused by the loss of sp -character on this atom. The experimental upfield shift of *c.* -0.10 ppm, after correction for the above mentioned downfield shift by $sp \rightarrow sp_2$ rehybridization, would lead to an estimated total upfield shift of about -4.6 ± 0.5 ppm for C-2 in IV. This is somewhat reminiscent of the upfield shift for C-2 and C-3 of norbornene caused by 7-*syn* substitution. This effect has been ascribed to steric interaction between the substituent and the C-2—C-3 π -cloud, i.e. the p_z -orbitals on C-2 and C-3. In the present case, the geometrical conditions and even the number of interconnecting bonds differ from the norbornene example.

Rehybridization as indicated above on C-1 and C-2 would have little direct influence on C-3. Carbons in an α -position to double bonds are too close to the zero shielding cone to experience any significant shielding difference with variations in diamagnetic anisotropy. On the other hand, this anisotropy would contribute only 5 ppm to the total observed shift difference between carbon atoms α to triple or double bonds of about 20 ppm. The remaining 15 ppm is presumably caused by differences in (substituent-) σ_d exerted by triple and double bonds on neighbouring carbon atoms. This will lead to a downfield shift upon cooling. Moreover, an effect similar to that in the normal alkanes on internal methylene groups will also be operative.

Since this publication was submitted, changes in ^{13}C n.m.r. chemical shifts of normal alkanes were also published by H. J. Schneider and W. Freitag, *J. Am. Chem. Soc.* **98**, 478 (1976). Their results, obtained in a different way, are generally in agreement with our experiments.

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