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APPLICATION OF LONG-RANGE SHIELDING IN ^{13}C NMR TO (Z)-(E) ASSIGNMENTS IN SUBSTITUTED ETHYLENES.

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Usually, it is found that ^{13}C NMR (CMR) chemical shifts of carbon atoms in spatially crowded alkyl groups are at higher fields than similar carbon atoms in systems without steric perturbation. Woolfenden and Grant$^{1)}$ first described these effects in the CMR spectra of several di- and polymethylbenzenes. Afterwards, Grant and Cheney offered an explanation assuming a mechanism of 1,4 non-bonded interactions between ortho methyl groups, giving rise to partial charge polarisation in the interacting carbon-hydrogen bonds$^{2)}$. Similar effects were also found in methylcyclohexanes$^{3)}$ and, more recently, for a series of substituted, strained, bicyclic systems by Lippmaa c.s.$^{4)}$ and by Roberts c.s.$^{5)}$.

The above phenomena can, of course, also be applied to the distinction of (Z) and (E) conformations as was shown by Lippmaa c.s. for a series of n-octenes$^{6a)}$, n-dodecenes$^{6b)}$ and some other derivatives$^{6c)}$. As expected, α-methylene and α-methyl carbon chemical shifts in (Z) conformers show a positive deviation from shifts calculated using the constitutive parameters of Savitsky c.s.$^{7)}$. On the other hand, the corresponding signals of (E) conformers show a small negative deviation$^{6a,b)}$. These differences have analytical significance and can be used along with the effects on olefinic carbon atoms, noted before$^{8)}$.

Up to now, only a few cases have been published were CMR was applied to (Z)-(E) isomerism in trisubstituted ethylenes$^{9)}$, none of these examples was concerned with hydrocarbons. Here, we present our results on a series of 13 (Z)-(E) isomeric hydrocarbons, including both branched disubstituted and trisubstituted ethylenes and also some conjugated di-olefins. Results will be interpreted in terms of conformational assignments.

Spectra were measured at 25.1 Mc/s on a Varian HA-100 spectrometer, using 8 mm spinning sample tubes. Enriched carbon disulfide in a 2 mm capillary served as an external standard.

The samples "cis" and "trans" 3-Me-2-hexene and "cis" and "trans" 3-Me-3-hexene were API standard samples$^{10)}$. All other samples were purchased from Chemical Samples Co. Neat compounds were measured with a few exceptions: "cis" and "trans" 3-Me-2-hexene were measured as 30% solutions in carbon tetrachloride and "cis" 3-Me-2-pentene was measured as a 50% solution in carbon disuldide.

Spectral assignments were made on the basis of signal multiplicities in off-resonance proton-decoupling experiments, of relative signal intensities and, in some cases, by means of comparisons between analogous skeletal parts of different compounds. For some of the trisubstituted ethylenes, CMR- and PMR-signals were correlated by means of selective decoupling experiments. Final assignments were then made by homonuclear, selective decoupling in PMR-spectra. More details will be given in a full paper. Resulting differential shieldings for α-carbons are given in the table.

It is seen that in (Z) conformers of disubstituted ethylenes, α-carbon signals are found invariably at higher fields than corresponding α-carbon signals in (E) conformers. This is consistent with the mechanism of carbon-hydrogen bond polarisation put forward by Grant c.s.$^{1,2)}$. In this view, of course, differential shieldings should be very different whenever one of the interacting carbon atoms does not carry hydrogen atoms, such as the quarternary carbon atom in tertiary butyl groups. This is indeed consistent with our results for 4,4-diMe-2-pentene and 2,2-diMe-3-hexene. For the quarternary carbon atoms, the differential shieldings are negative, the effects for C_1 in 4,4-diMe-2-pentene and for C_5 in 2,2-diMe-3-hexene are also unusually small.

Analogous differential shieldings as in disubstituted ethylenes, mutual diamagnetic shielding of cis alkyl groups might, a priori, also be expected for trisubstituted derivatives. Altogether, five parts of trisubstituted (Z)-(E) isomeric ethylenes have been measured in this work. Preliminary conformational assignments were made by comparing PMR spectra of our samples with published spectra of API$^{12)}$ or Sadtler$^{13)}$. We noticed, however, that in their latest catalog$^{11)}$, API reversed the labelling of the Standard Reference Materials nos 1032 and 1035 with respect to their 1967 catalog. Also, sample no 1074, up to 1967 labelled as "cis"-3-Me-2 hexene is now called "trans"-3-Me-2-hexene. The reverse happened with uncertified sample no 618. Thus, one is faced with a discrepancy between the assignments in the API catalog$^{11)}$ and in their PMR spectra$^{12)}$. Labelling according to the latest catalog$^{11)}$ brings complete consistency in our CMR results as can be seen in the table. The reversal with respect

Table. Differential shieldings[1] for α-carbon atoms in some (Z)-(E) isomeric di- and trisubstituted ethylenes.

Compound[2]	Type of α-carbon	$\Delta_{\text{exp.}}$[1]	$\Delta_{\text{theor.}}$[5]
4,4-diMe-2-pentene	${}^{13}CH_3-C=$	+3.77	+
	$-{}^{13}\underset{\mid}{\overset{\mid}{C}}-C=$	-0.35	
2,2-diMe-3-hexene	$-{}^{13}CH_2-C=$	+4.01	+
	$-{}^{13}\underset{\mid}{\overset{\mid}{C}}-C=$	-0.51	
4-Me-2-pentene	${}^{13}CH_3-C=$	+5.26	+
	$-{}^{13}\underset{\mid}{C}H\ -C=$	+5.14	+
4-Me-2-hexene	${}^{13}CH_3-C=$	+4.92	+
	$-{}^{13}\underset{\mid}{C}H\ -C=$	+5.48	+
2,5-diMe-3-hexene	$-{}^{13}\underset{\mid}{C}H\ -C=$	+4.45	+
1,3-pentadiene	${}^{13}CH_3-C=$	+4.69	+
	$H_2C={}^{13}CH\ -C=$	+5.25	+
2,4-hexadiene[3]	${}^{13}CH_3-C=$	+4.7	+
	$={}^{13}CH\ -C=$	+7.0	+
2,4-hexadiene[4]	${}^{13}CH_3-C=$	+5.0	+
	$={}^{13}CH\ -C=$	+2.8	+
3-Me-2-pentene	${}^{13}CH_3-\overset{\overset{C}{\mid}}{C}=$	-8.66	-
	$-{}^{13}CH_2-\overset{\overset{C}{\mid}}{C}=$	+7.13	+
3,4-diMe-2-pentene	${}^{13}CH_3-\overset{\overset{C}{\mid}}{C}=$	-4.70	-
	$-{}^{13}\underset{\mid}{C}H\ -\overset{\overset{C}{\mid}}{C}=$	+8.82	+
3-Me-2-hexene	${}^{13}CH_3-\overset{\overset{C}{\mid}}{C}=$	-7.80	-
	$-{}^{13}CH_2-\overset{\overset{C}{\mid}}{C}=$	+8.40	+
3-Me-3-hexene	${}^{13}CH_3-\overset{\overset{C}{\mid}}{C}=$	-7.30	-
	$-{}^{13}CH_2-\overset{\overset{C}{\mid}}{C}=$	+7.74	+
3-Me-1,3-pentadiene	${}^{13}CH_3-\overset{\overset{C}{\mid}}{C}=$	-5.98	-
	$={}^{13}CH\ -\overset{\overset{C}{\mid}}{C}=$	+8.10	+

1. Defined as $\delta_{\text{"cis"}} - \delta_{\text{"trans"}}$ (ppm), dependable to about ± 0.05 ppm.
2. API labelling according to 1969-1970 catalog.
3. "Cis"-"cis" versus "trans"-"trans" isomers.
4. "Cis"-"trans" isomer.
5. Sign of Δ, assuming that "cis" alkyl groups shield each other diamagnetically.

to former API labellings therefore seems justified.

In a forthcoming full paper, we hope to present more evidence in favor of the (Z)-(E) assignments as proposed here. Also, we hope to interpret some of the results in terms of preferred rotational orientations of the α-substituents.

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