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DETERMINATION OF THE MOST STABLE CONFORMERS OF BRANCHED ALKANES BY ^{13}C-NMR SPECTROSCOPY AT VERY LOW TEMPERATURES

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SUMMARY: ^{13}C-NMR measurements at 90,51 MHz at 85- 94 K lead to the conclusion, that for 2,3-dimethylbutane, 2,3-dimethylpentane as well as for meso- and DL- 3,4- dimethylhexane gauche is the minimum energy conformation

Conformational changes are influencing very sensitively the ^{13}C chemical shift [1-8]. Within the temperature range of fast conformational exchange populations of the conformers can be calculated from the chemical shifts as soon as the shifts of discrete conformations have been detected [9-11]. Knowledge of the temperature dependent populations gives the thermodynamic parameters of the conformers. For polymer molecules being of interest for us measurements in the range of slow exchange of segmental conformations are not to be performed however in solution because of their insolubility at lower temperatures. Magic angle technique may yield high resolution spectra even in solid polymers in the near future [12-13]. In order to clarify the correlation between chemical shift and conformation in polypropylenes we carried out measurements on relevant model-compounds. These compounds have been selected to fullfill the following conditions: 1. representation of defined segments in the polymer chain, 2. simple structure to enable interpretation of the spectra at low temperatures. Branched alkanes ideally satisfy these demands as models for polypropylenes [7,8,14]. Former measurements proofed, that these compounds show strong dependence of the chemical shift on conformational changes [8]. For the head-to head diads being present in atactic polypropylenes we chose 2,3-dimethylbutane, 2,3-dimethylpentane as well as the diastereomeric 3,4-dimethylhexanes as models. An alternative approach for conformational analysis from coupling constants was not applicable for the polypropylenes because of the

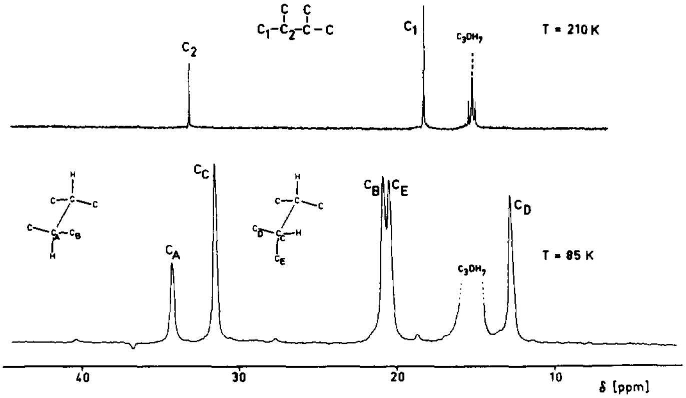
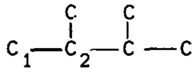


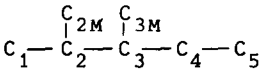
Fig. 1: ^{13}C- NMR spectra of 2,3- dimethylbutane in 1-monodeuteropropane at 210 and 85 K

insufficient resolution of their ^{1}H-NMR spectra.

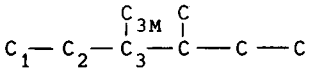
The three model substances were selected to clear up the influence of the chain length on the balance of the conformers in the diisopropyl unit. Therefore 2,3-dimethylpentane as well as meso- and DL-3,4-dimethylhexane were investigated besides 2,3-dimethylbutane. The 3,4-dimethylhexanes only are sufficient models for the diastereomeric forms of the head to head enchainments in polypropylenes [15]:



$$C_1-\overset{C}{\overset{|}{C_2}}-\overset{C}{\overset{|}{C}}-C$$



$$C_1-\overset{C_{2M}}{\overset{|}{C_2}}-\overset{C_{3M}}{\overset{|}{C_3}}-C_4-C_5$$



$$C_1-C_2-\overset{C_{3M}}{\overset{|}{C_3}}-\overset{C}{\overset{|}{C}}-C-C$$

meso
and
DL

Figure 1 presents ^{13}C-NMR spectra of 2,3-dimethylbutane measured in 1-monodeuteropropane at 210 and 85 K. Signals at 18.22 and 33.13 ppm from TMS in the 210 K spectrum are assigned to the carbon atoms C_1 and C_2. At 85 K five signals are detected. They belong to the carbons C_A and C_B of the anti- and to C_C, C_D and C_E of the gauche conformer, resp. Chemical shifts measured are noted in figure 2 at the corresponding carbons of the conformers 1 a (anti) and 1 b (gauche).

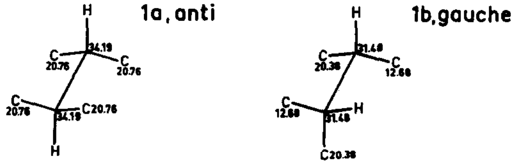


Fig. 2: Staggered anti (1a) and gauche (1b) conformations of 2,3-dimethylbutane

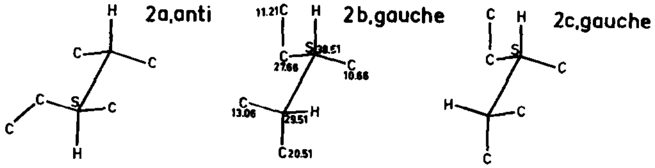


Fig. 3: Staggered anti (2a) and gauche (2b, 2c) conformations of S-2,3-dimethylpentane

These values are in good agreement with those derived and predicted by Lunazzi [16].

In a mixture of CHF_2Cl and CH_2FCl he could not separate the C_B from the C_E peak because of signal broadening. Especially for the analysis of longer alkanes a substantial improvement of the spectra is unavoidable however. Popula-

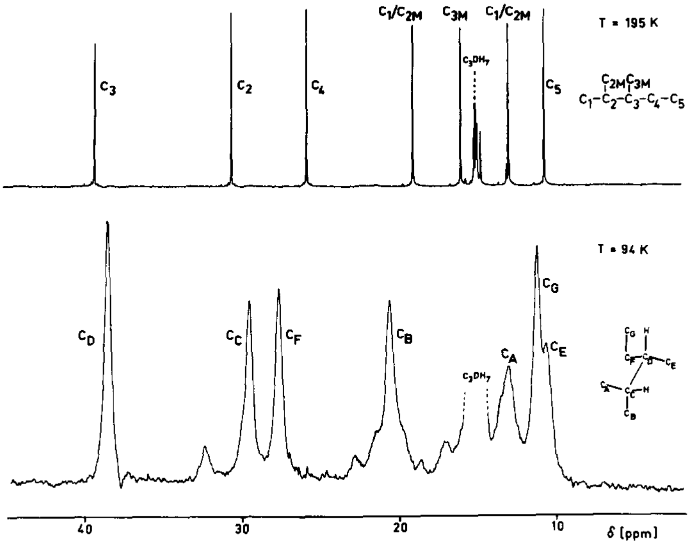


Fig. 4: ^{13}C-NMR spectra of 2,3-dimethylpentane in 1-monodeuteropropane at 195 and 94 K

tions of the conformers are not affected however by the change of the solvent.

For 2,3-dimethylpentane we have to discuss one anti (2a) and two gauche conformers (2b, 2c). Figure 3 represents the staggered conformations belonging to S-2,3-dimethylpentane. Figure 4 shows the ^{13}C-spectra at 195 and 94 K. C_1 and C_5 in the 195 K spectrum were assigned using empirical shift parameters of Lindemann and Adams [6] and with the aid of ^{1}H-coupling. By cooling the solution signals broaden strongly. At 94 K seven sharp signals occur, which could be assigned to the conformer 2b. Chemical shifts agree well with those of carbons - in identical conformational surrounding - in gauche 2,3-dimethylbutane. Conformers 2a and 2b are to be excluded, because e.g. 2a should show signals at about 20.8 ppm for C_1/C_{2M} and at about 18.3 ppm for C_{3M} . This shift value may be interpreted taking into account a shift effect of -2.5 ppm for an additional methyl group in γ-position to C_{3M}. Similar calculations predict chemical shifts of 12.7, 20.4 and about 19.9 ppm for C_1, C_{2M} and C_{3M} in the 2c gauche conformer. Analogous calculations may be carried out for all the other carbons. A detailed discussion will be presented elsewhere [17].

In addition we proofed that only the gauche conformers 3b and 4a in figures 5 and 6 exist for meso- and DL-dimethylhexane at 85 K in 1-monodeuteropropane. ^{13}C-NMR spectra of 1:1 mixtures of both diastereomeric forms at 143 and 85 K are given in figure 7 with the assignments.

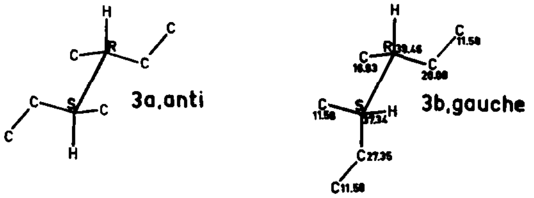


Fig. 5: Staggered anti (3a) and gauche (3b) conformations of meso-3,4-dimethylhexane

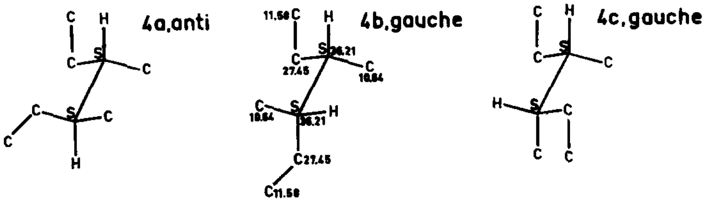


Fig. 6: Staggered anti (4a) and gauche (ab, 4c) conformations of DL-3,4-dimethylhexane

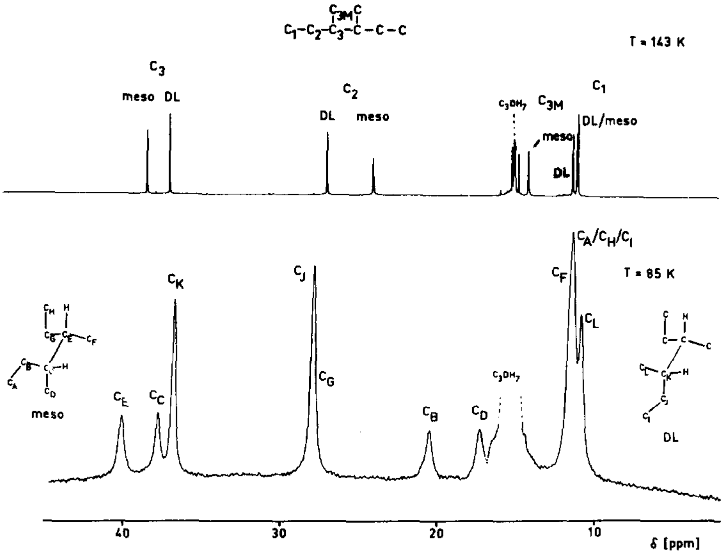


Fig. 7: ^{13}C-NMR spectra of meso- and DL-3,4-dimethylhexane in 1-monodeuteropropane at 143 and 85 K

The discussion of the chemical shift is correspondent like in the case of 2,3-dimethylpentane. E.g. conformational surroundings of carbons in the conformer 2b (2,3-dimethylpentane) and 4b (3,4-dimethalhexane) are almost identical. Chemical shifts measured for both molecules are in excellent agreement. The shift data can not be correlated to other conformations. No further resonance signals could be detected. Conformers which may be present additionally to those discussed consequently have populations below 10 %. According to the equation $\Delta G^o = RT \ln 10$ they are at least 1,6 KJ higher in free enthalpy. In consequence every molecule discussed here prefers the gauche conformation. Only the smallest one shows a little amount of the anti-conformation. ^{13}C-measurements on poly-(2,3-dimethyltetramethylene) as well as on models for head- to tail sequences in polyporpylenes are in progress. Spectra were run on a Bruker WH-360, which operates at 90.51 MHz for the ^{13}C-frequency. All spectra were taken with ^1H-broadband decoupling. 30 free induction decays consisting of 16 K data points were accumulated. Samples were prepared by solving 10 % by volume of 2,3-dimethylbutane, 2,3-dimethylpentane or 3,4-dimethylhexane in 1-monodeuteropropane. These solutions remained liquid within the temperature range from 200 to 85 K. Shifts given correspond to δ TMS = 0 ppm.

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