IR-Spectroscopic Investigations of Cycloalkanes*

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Summary

A homologous series of cycloalkanes from $(CH_2)_{14}$ up to
$(CH_2)_{96}$ as model systems for tight folding in CH_2-chain
molecules was investigated by infrared spectroscopy. In
comparison with the corresponding spectra of the n-
alkanes we found two additional new absorption bands at
700 cm^{-1} and 1442 cm^{-1} which can be assigned to a
characteristic fold vibration. The already known fold
band in the wagging region at about 1344 cm^{-1} could
also be found in all cycloalkane spectra. A numerical
decomposition of the bands enables the calibration of
the fold concentration. The Davydov splitting of the
(CH_2)-rocking and (CH_2)-bending vibration in the melt
crystallized form of the molecules $(CH_2)_{72}$ and $(CH_2)_{96}$
show the occurence of a orthorhombic subcell of the
larger rings whereas the smaller rings and the larger
ones in the solution crystallized form only crystallize
in a monoclinic form.

Introduction

In order to investigate the influence of tight chain
folding in polymethylene chains on the spectroscopic
behaviour it is useful to have an appropriate model
system. Cycloalkanes represent such a system because
this molecules crystallize as double stems linked by
two folds (NEWMAN and KAY, 1976; TRZEBIATOWSKI and
STROBL, 1980). From semiempirical atomistic calcula-
tions with a proved potential set one finds three
different fold conformations for PE with rather low
defect energies (fig.1). Because of the low energy and
the good packing of the b-axis fold (fig.1a) it is a
reasonable assumption that this type of conformation
(··ttggtggtt··) will also form the folds in crystals

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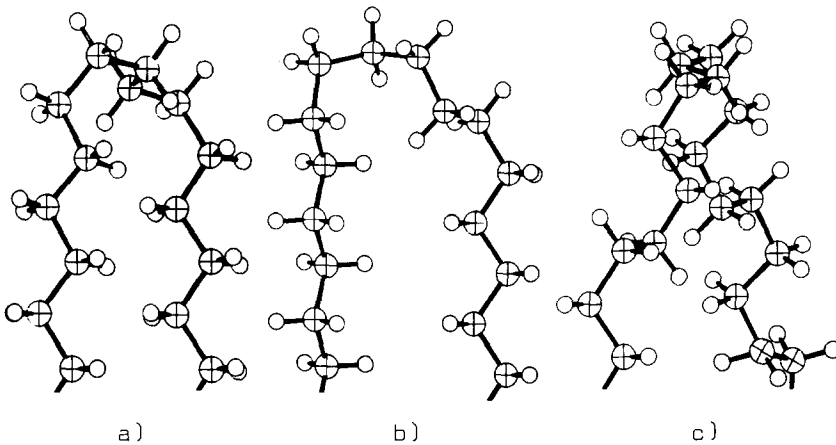 march 24, 1980 in Leoben, Österreich

Fig. 1 a,b,c: Possible fold conformations in PE
a) b-axis fold, defect energy 16.3 kJ/mole,
b) diagonal fold, defect energy 20.4 kJ/mole,
c) fold in a CH_2-chain molecule existing as $4 \times 1/1$
   helix, defect energy 13.4 kJ/mole. (GROSSMANN, 1977)

which are grown from solution. In the melt crystallized
material of the larger ring molecules the diagonal fold
(fig.1b) may be favoured because of the orthorhombic
position of the straight chain sequences between the
folds. Fig.2 shows a model of the $(CH_2)_{30}$-molecule
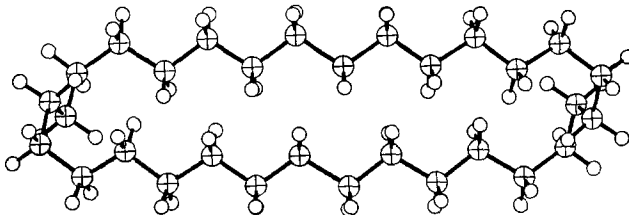formed by parallel trans segments linked by two tight
folds.

Fig. 2: Possible conformation for a $(CH_2)_{30}$-molecule
in the solid state.

Experimental

The IR-spectra were measured with a grating spectro-
meter model 283 from Perkin Elmer. Because of the
limited quantity of specimen material some of the
experiments were done with KBr moulding technique. For
most of the quantitative analysis of the absorption
bands we used cells with KBr windows. The temperature
dependent measurements were done with a self-made cell
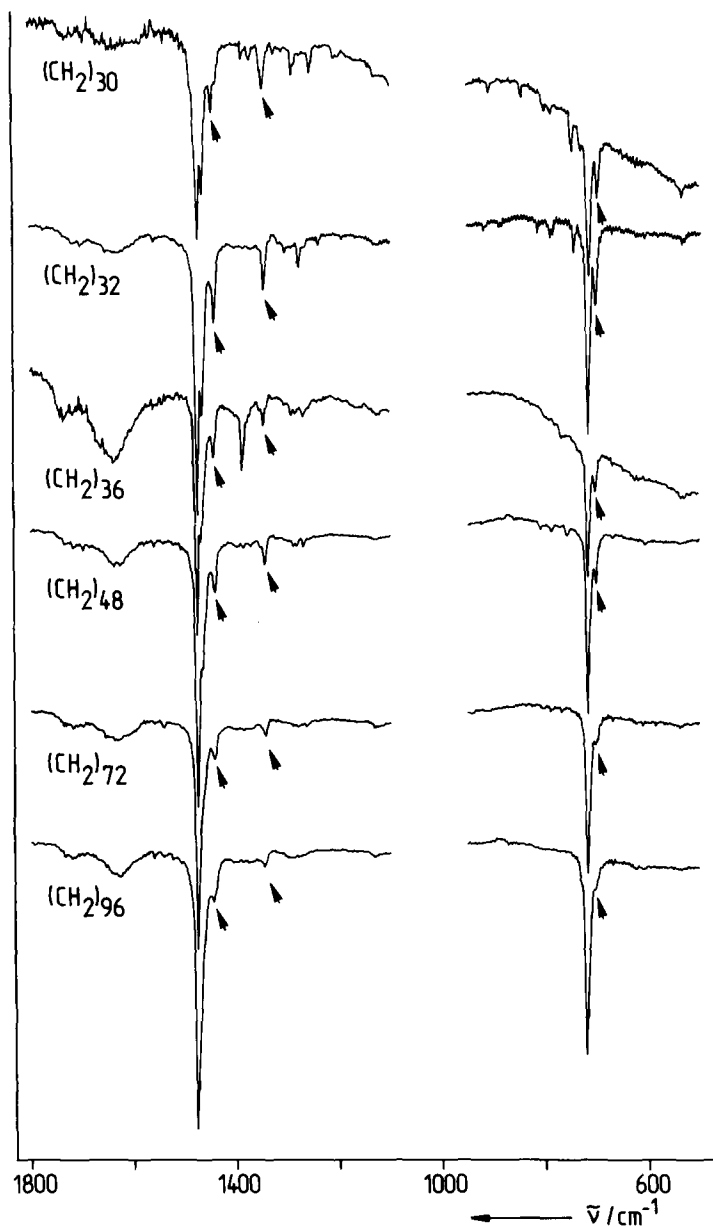for liquids which is temperature controlled by an

Fig. 3: Spectra of the rocking, wagging and bending vibrations for some cycloalkanes. $((CH_2)_{72}$ and $(CH_2)_{96}$ monoclinic modification) (ARNOLD, 1979; see also TRZEBIATOWSKI et al., 1980).

extern liquid thermostat. The cycloalkanes were
synthesized by SCHILL and coworkers with a special
method reported some years ago (SCHILL et al., 1976).

Results and discussion

IR-spectra: Fig. 3 shows the IR-spectra of the cyclo-
alkanes in the region of the rocking vibrations and the
spectra in the wagging and bending region. A comparison
of the band positions with the vibrational analysis by
KRIMM et al. (KRIMM and JAKES, 1971) for $(CH_2)_{34}$
support the assignment 1368 cm^{-1} (gtg),   1352 cm^{-1} (gg
and contributions of other g-conformations), 1344 cm^{-1}
(ggtgg). These bands could be found in all cycloalkanes
investigated. The intensity of the 1344 band with
respect to the rocking mode decreases with increasing
molecular weight. If we compare the IR-spectra of the
n-alkanes with those of the ring molecules (fig.3, fig.
4) we can establish that there appear two additional
bands. One of them is proposed to be a rocking CH_2-mode,
located at 700 cm^{-1} exactly. The other one, located at
1442 cm^{-1}, is assumed to be a CH_2-bending vibration.
The position of these two additional bands is unaltered
for all cycloalkanes investigated whereas the intensi-
ties of the bands decrease with increasing number of
CH_2-groups per molecule. This is why in the spectra of
the larger molecules the bands are no longer peaks but
are reduced to shoulders of the rocking and the bending
vibration, respectively.

If we look at the spectra of the $(CH_2)_{72}$ and $(CH_2)_{96}$ we
find differences between the melt crystallized (fig.4)
and the solution grown form. In the melt crystallized
material the spectra of these molecules show the
characteristic Davydov-splitting of the rocking and
bending vibration. This indicates a orthorhombic
crystalline subcell. The asymmetry of the band split-
ting - more pronounced for $(CH_2)_{72}$ than in the $(CH_2)_{96}$
spectrum - shows that the melt crystallized material
contains already monoclinic or triclinic parts besides
the orthorhombic crystallites. The existence of the
orthorhombic components can be also seen in the corres-
ponding raman-spectra of $(CH_2)_{72}$ and $(CH_2)_{96}$ as the
occurence of the characteristic band at 1418 cm^{-1}
(GROSSMANN and BÖLSTLER, 1980; BÖLSTLER, 1978).

Band-analysis: In order to obtain a quantitative result
the intensities and the integral intensities of the
bands (as compared with reference bands at 715 cm^{-1}
(rocking CH_2) and 1472 cm^{-1} (bending CH_2)) were calcu-
lated from the measured spectra. In some cases,
especially for the band complex in the wagging region
we had to decomposite the single bands numerically. For
this purpose we used a computer method (PITHA and JONES,
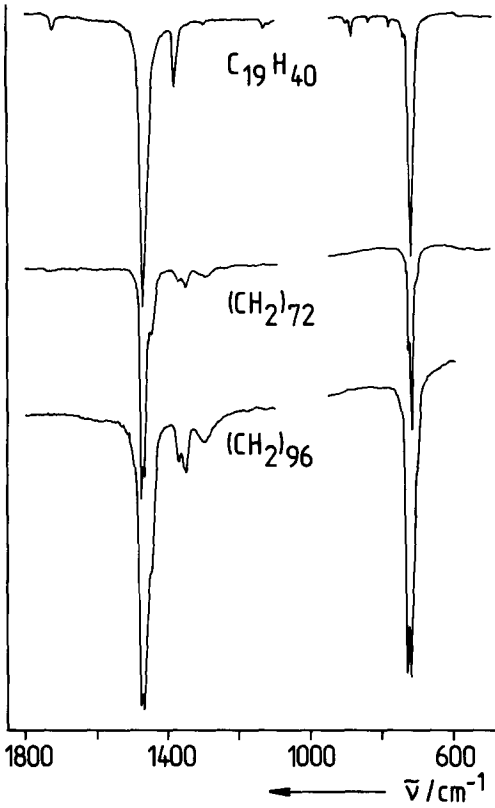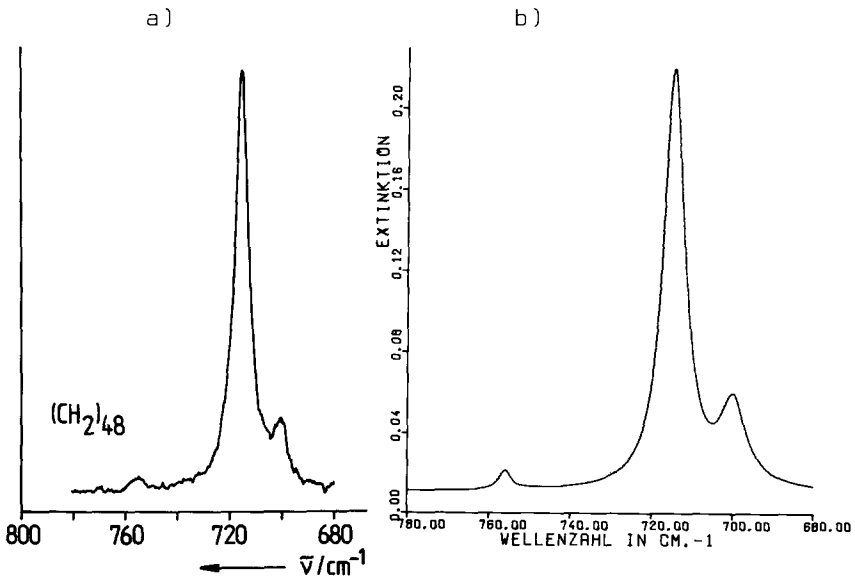1968) which gives the possibility to fit each band to

Fig. 4: Spectra of the rocking, wagging and bending vibrations for $C_{19}H_{40}$, $(CH_2)_{72}$ and $(CH_2)_{96}$. $(CH_2)_{72}$ and $(CH_2)_{96}$ orthorhombic modification.

Fig. 5 a,b: Numeric decomposition of the rocking bands for $(CH_2)_{48}$;
a) experimental spectrum
b) fitted spectrum, consisting of three curves of Lorentzian type and a constant baseline.

a)

b)

a Gaussian or a Lorentzian or a mixed shape. Fig.5
gives an example for this method.

Band-intensities: Fig.6 shows the relative absorbance
of the bands at 700 cm^{-1} , 1442 cm^{-1} and 1344 cm^{-1} of
the cycloalkanes at room temperature. The nearly linear
dependence on the reciprocal molecular weight as well
as the fixed position of these bands for all ring mole-
cules show that these bands must be caused from the
tight fold conformation in the molecules. The strong
deviation from the linear dependence (fig.6) for the
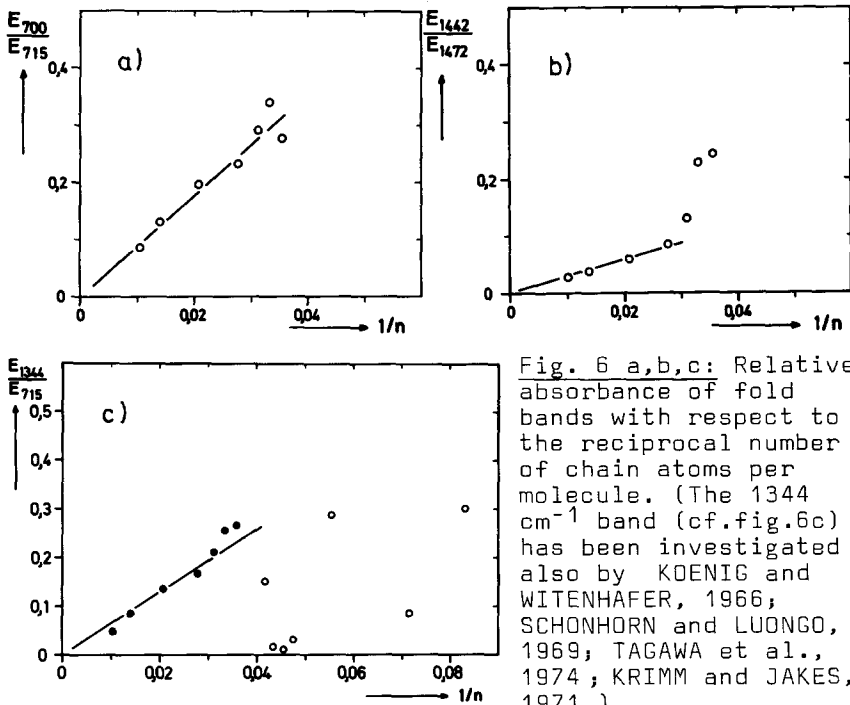molecules with about n < 28 is certainly caused by per-

Fig. 6 a,b,c: Relative
absorbance of fold
bands with respect to
the reciprocal number
of chain atoms per
molecule. (The 1344
cm^{-1} band (cf.fig.6c)
has been investigated
also by KOENIG and
WITENHAFER, 1966;
SCHONHORN and LUONGO,
1969; TAGAWA et al.,
1974 ; KRIMM and JAKES,
1971).

turbation of the fold structure because of the inner
stress of the smaller molecules. The relative integral
intensity of the various fold bands shows the same de-
pendence on the molecular weight as the relative absor-
bance shown in fig.6. The comparison of the IR-spectra
in the monoclinic phase with those of the orthorhombic
phase (fig.3,4) in $(CH_2)_{72}$ and $(CH_2)_{96}$ shows that the
integral intensity of the 1368 cm^{-1} band is greater in
the orthorhombic modification. This increase of gtg
sequences can be understood with a increasing number of
diagonal folds (fig.1b) each containing a gtg sequence.
A detailed consideration of the variation of the defect
intensities with temperature will be given elsewhere.

For a rough classification one can establish that the
melt transition of the ring molecules (n > 30) causes a
strong increase of the 1368 cm^{-1} and 1352 cm^{-1} band
intensities and a decrease of the intensity at 1344 cm^{-1}.
The same rule shall apply for the smaller rings (n < 30)
with the restriction that these molecules have a rela-
tively strong absorption at 1368 cm^{-1} already at room
temperature (fig.7). Common to all melt spectra is the
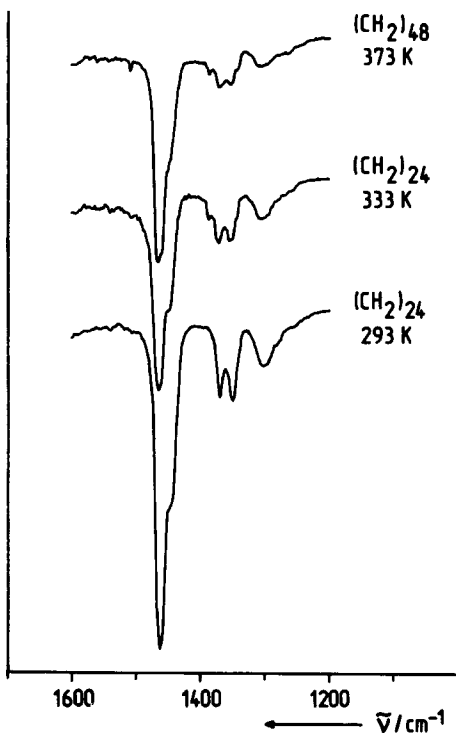appearence of a small band at 1385 cm^{-1} which we are
not able to assign.

Fig. 7: Spectrum in the
wagging region for molten
$(CH_2)_{48}$ and $(CH_2)_{24}$ in
the molten and the solid
state.

Nevertheless we think we have described all effects of
tight chain folding on the IR-spectra of CH_2-chain
molecules. Whether they can be found also in the spec-
trum of polyethylene has to be investigated in further
experiments.

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