Low-Temperature IR- and NMR-Studies of 3,3,6,6-Tetramethylcycloheptanone

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In an earlier publication the synthesis of 3,3,6,6-tetramethylcycloheptanone in nine steps from β,β-dimethylglutaric acid has been described.

As expected for a strained ring with an uneven number of carbon atoms the melting point for this compound was low, −7°C. The entropy and enthalpy of fusion were 11 cal/degree/mol and 3 kcal/mol, respectively. Calorimetric investigations of the melting process unveiled a transition

Fig. 1. Infrared spectra of 3,3,6,6-tetramethylcycloheptanone as a liquid (top) and as solid at −40° and −100°C.

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point at $-77^\circ$C, but only 3% of the total melting took place at the transition point.

The IR-spectra of the compound in the solid phase below the transition point, in the upper solid phase between $-77$ and $-7^\circ$C, and in the liquid at room temperature, are compared in Fig. 1. The changes in the absorptions are small from the lower to the upper solid phase, but in the liquid new bands appear, indicating a conformer mixture. The IR spectrum in carbon disulphide solution was the same as for the liquid.

Hendrickson’s calculations $^2$ show that the chair and the twist-chair forms of cycloheptane are favoured energetically over the boat and twist-boat forms, and Groth $^3$ has confirmed this in finding, by X-ray methods, the twist-chair conformation in the crystals of a gem-substituted cycloheptane, the dimeric cycloheptanone peroxide. Hydrogen site exchange may take place by pseudorotation over barriers calculated $^2$ to be only 1.5 kcal/mol.

As the gem-dimethyl groups might be expected to further hinder the pseudorotational interconversions, 3,3,6,6-tetramethylecycloheptanone was investigated by NMR at low temperatures.

The NMR-spectra of the compound, dissolved in carbon disulphide, down to $-115^\circ$C are shown in Fig. 2. At all high temperature there are three sharp signals for the three types of protons. By lowering the temperature, broadening starts at $-60^\circ$ in the signals of the $\gamma$-methylene protons, and they give a broad symmetrical absorption with at least eight peaks at $-115^\circ$. The coalescence temperature is ca. $-80$ to $-85^\circ$. The signal of the methyl protons splits into a doublet at $-100^\circ$. The line for the $\alpha$-protons remains sharp at $-115^\circ$, which was the lowest temperature reached with carbon disulphide as the solvent. In dichloromethane no splitting was obtained in the methyl protons at $-130^\circ$.

The energy barrier was estimated from the low-temperature spectra to be 8.5 kcal/mol.$^*$

As expected the two gem-dimethyl groups have raised the conformational barrier considerably. The lack of splitting in the alpha protons and the simplicity of the spectra as a whole makes it, however, difficult to believe that the observed low-temperature spectrum reflects the symmetry of one conformer.

First of all, the IR-spectrum suggests that the solution at room-temperature contains more than the crystal conformer. Even if such additional conformers become negligible at $-115^\circ$, the main species cannot possibly have a static conformation that gives rise to only two methyl lines and a single $\alpha$-CH$_3$-line. Thus, a methyl doublet would mean that in $C_4$ twist-chair or twist-boat forms the carbonyl and not

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$^*$ $G^\neq$ was calculated by J. Schaug using the method of Rogers and Woodbrey.$^4$

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*Fig. 2. Changes in NMR-spectra of 3,3,6,6-tetramethylecycloheptanone in carbon disulphide solution at low temperatures.*

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one gem-dimethyl group lies on the two-fold axis, and in \( C_3 \) chair and boat forms that the carbonyl group is in the symmetry plane, whereby methyl groups would interact syn-axially. Also a single \( \alpha \text{-CH}_3 \) line, instead of one or two quartets, is only expected for a planar molecule. It must therefore be concluded that partial pseudorotation is still fast at \(-115^\circ\), so that its averaging effect produces an apparent high symmetry.

A detailed analysis of the situation, to be published separately, shows that a low-barrier partial pseudo-rotation between two twist-chair forms will produce such averaging:

\[ \text{Scheme 1.} \]

It also shows that full exchange must occur by passage to the boat-family, partial pseudorotation, and passage back again to the chair family, a possibility first pointed out by Hendrickson.

The NMR spectra were recorded with a Varian HA 100 15 D instrument.


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The Conformation of 4,4,7,7-Tetramethylcyclononanone: Low-Temperature NMR-Spectroscopy in Conjunction with the Shift Reagent Eu(DPM)_3

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4,4,7,7-Tetramethylcyclononanone has earlier been shown to have a high barrier to inversion giving rise to an NMR coalescence temperature of \( 15 - 21^\circ\text{C}\). The conformation was found to have \( C_4 \) symmetry \((D_4\) symmetry for the carbon skeleton), with the gem-dimethyl and carbonyl groups in the three positions on the two-fold axes.

With the intention of improving the resolution, the high- and low-temperature NMR spectra of the same compound in the presence of a europium complex have now been investigated.

Fig. 1a shows the low-temperature spectrum without the shift reagent. Fig. 1b is the low-temperature spectrum with about 0.5 mol of tris(dipivalomethanato)europium per mol of tetramethylcyclononanone in carbon disulphide solution.

The increase in shift has resulted in a well-resolved spectrum indicating at least seven non-equivalent protons in the relative amounts \( 4 : 2 : 2 : 2 : 6 : 6 \), called A, B, C, D, E, F, and G.

By decoupling experiments the protons in the signals B and D were found to be coupled, as well as those in C and E. Irradiation at A also showed effect on B and D.

To further identify the different signals the amount of shift reagent has been varied while keeping the temperature constant at \( 5^\circ\), and, on the other hand, the temperature has been varied through the coalescence while keeping the amount of shift reagent constant.

From the spectra the conclusion can be drawn that the signals in the region A (Fig. 1b) belong to the \( \alpha \text{-CH}_3 \) protons, B and D are the \( \beta \text{-CH}_3 \) protons, C and E the \( 3 \text{-CH}_3 \) protons, F and G, which do not show any coupling, must belong to the protons in the gem-dimethyl groups.

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