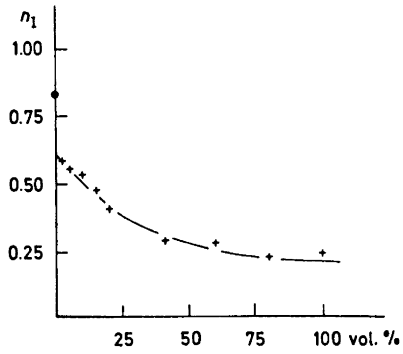

Fig. 3. The calculated molar fraction of isomer I as a function of the volumetric percentage of 2-furanaldehyde in tetrachloromethane. ● indicates the gas-phase value for n_I calculated from the microwave results.[1]

phase and gas-phase assessments of isomeric stability offer each other no contradiction.

Experimental. The spectra were recorded on a Varian HA 100 spectrometer at 31.4°C. The coupling constants were calculated using the Fortran IV program LAOCOON III. The necessary change in one coupling constant leading to a doubling of the rms error does not exceed 0.03 Hz.

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Received March 16, 1972.

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

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In an earlier publication[1] 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

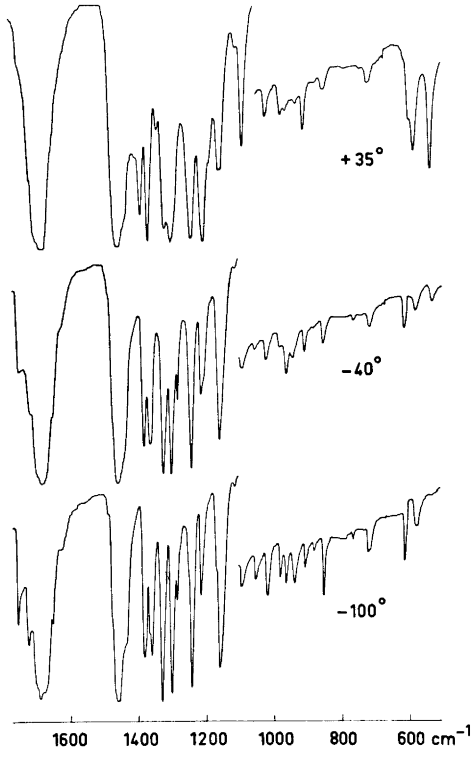


Fig. 1. Infrared spectra of 3,3,6,6-tetramethylcycloheptanone as a liquid (top) and as solid at −40 and −100°C.

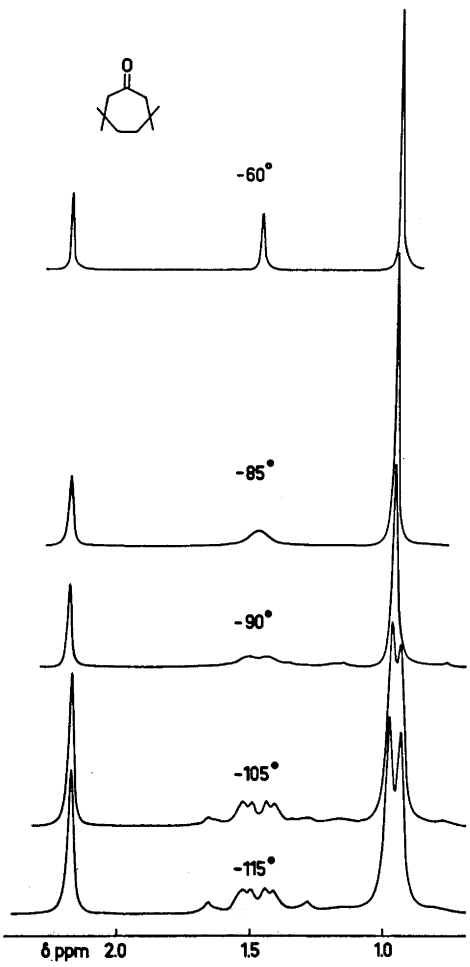


Fig. 2. Changes in NMR-spectra of 3,3,6,6-tetramethylcycloheptanone in carbondisulphide solution at low temperatures.

point at −77°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°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-tetramethylcycloheptanone was investigated by NMR at low temperatures.

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

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

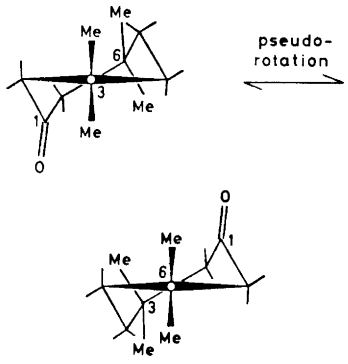
As expected the two *gem*-dimethyl groups have raised the conformational barrier considerably. The lack of splitting in the alpha protons and the simplicity of the spectra as a whole makes it, however, difficult to believe that the observed low-temperature spectrum reflects the symmetry of one conformer.

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°, the main species cannot possibly have a static conformation that gives rise to only two methyl lines and a single α-CH_2-line. Thus, a methyl doublet would mean that in C_2 twist-chair or twist-boat forms the carbonyl and not

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

one *gem*-dimethyl group lies on the twofold axis, and in C_s chair and boat forms that the carbonyl group is in the symmetry plane, whereby methyl groups would interact *syn*-axially. Also a single α-CH_2 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 $-115°$, so that its averaging effect produces an apparent high symmetry.

A detailed analysis of the situation, to be published separately,[5] shows that a low-barrier partial pseudo-rotation between two twist-chair forms will produce such averaging:



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.[6]

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

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Received April 17, 1972.

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 $15-21°C$.[1,2] The conformation was found to have C_2-symmetry (D_3-symmetry for the carbon skeleton), with the *gem*-dimethyl and carbonyl groups in the three positions on the twofold 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 : 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°, 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 α-CH_2 protons, B and D are the β-CH_2 protons, C and E the δ-CH_2 protons. F and G, which do not show any coupling, must belong to the protons in the *gem*-dimethyl groups.