Syntheses and Conformations of *gem*-Dimethyl Substituted Cyclo-octadecanes. The 1,1-Dimethyl and the 1,1,4,4-Tetramethyl Derivatives

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Two *gem*-dimethyl substituted cyclo-octadecanes have earlier been synthesized; a tetramethyl derivative diametrically substituted in positions 1 and 10 and an octamethyl derivative symmetrically substituted in the four positions 1, 4, 10, and 13.¹⁻³ Increased substitution in cyclo-octadecane was shown to raise the melting point, to lower the melting entropy and to increase the conformational stability. The octa-methyl substituted derivative was found to be conformationally homogeneous and to take the same compact conformation in solution as in the crystal.

We have now extended this investigation to cyclo-octadecanes substituted with *gem*-dimethyl groups in only one position and in positions 1 and 4, giving molecules with lower constitutional symmetry than those studied earlier.

Fig. 1. Possible diamond-lattice conformations of cyclo-octadecane. g = gauche bonds. * = allowed positions for *gem*-dimethyl groups.

1,1-Dimethylcyclo-octadecane and 1,1,4,4-tetramethylcyclo-octadecane were synthesized by hydrogenation of the corresponding cyclic diynes.^{4,5} In Table 1 are shown the melting points and the enthalpies and entropies of

melting of these compounds together with the results of those earlier determined.

The infrared spectra were taken of the compounds as crystals in potassium bromide and dissolved in carbon disulphide. The spectra of the two phases were not identical.

In Fig. 1 are shown⁶ the four possible diamond lattice conformations of cyclo-octadecane and the "allowed" positions for the space-demanding *gem*-dimethyl group. Conformations of lowest energy will, however, be obtained when those of the allowed ring positions which are situated between two *gauche* bonds carry the *gem*-dimethyl groups because thereby a minimum of new *gauche*-butane interactions are introduced. Dimethyl substitution in the relative positions 1, 4, 10, and 13 between two *gauche* bonds is only possible in conformation A and this is in accordance with the observation that 1,1,4,4,10,10,13,13-octamethylcyclo-octadecane is conformationally homogeneous. A similar rectangular 3-bond bridge conformation as Fig. 1A is also found by X-ray analyses in an unsubstituted cyclic hydrocarbon, cyclotetradecacontane.⁷

For dimethyl substitution in the relative positions 1 and 10 low-energy and, at the same time, sterically allowed positions exist both in conformation A and C, also in accordance with the observation that more conformers than the crystal conformer exist in solution.

Fig. 2. Infrared spectra of 1,1,4,4-tetramethylcyclo-octadecane as KBr-disc at -50°C . (upper curve) and in CS_2 -solution (lower curve).

Conformational inhomogeneity in 1,1-dimethylcyclo-octadecane is as expected. For the 1,1,4,4-tetramethylcyclo-octadecane the above reasoning should lead to conformational homogeneity. The IR-spectrum in Fig. 2 shows, however, that although the crystal conforma-

Table 1. Melting points, enthalpies, and entropies of melting and conformational homogeneity of cyclo-octadecanes.

	M.p. °C	ΔH kcal/mol	ΔS e.u.	Conformational homogeneity in solution
Cyclo-octadecane	73	9.4 ^a	30.1 ^a	Inhomogeneous
1,1-Dimethylcyclo-octadecane	10	5.7	20.1	»
1,1,4,4-Tetramethylcyclo-octadecane	37	7.8	25.1	»
1,1,10,10-Tetramethylcyclo-octadecane	86	9.5	26.1	»
1,1,4,4,10,10,13,13-Octamethyl- cyclo-octadecane	165	6.4 ^a	14.9 ^a	Homogeneous

^a The compounds have transition points¹ and the values represent the total of transition and melting.

tion is obviously present in solution, the broadening of the bands seems too pronounced to be due to vibrational scattering and could be caused by the existence of other conformers in solution.

In our earlier investigation of *gem*-dimethyl substituted cyclo-octadecanes a raise in melting point and a drop in melting entropy was found with increased degree of substitution.¹ The two new *gem*-dimethyl substituted derivatives of cyclo-octadecane did not follow this regularity. Although the changes in entropies when going from the crystal to the melt are of the expected magnitude, the melting points and melting enthalpies for both compounds are surprisingly much lower than for cyclo-octadecane itself. We think that this is explained by the fact that the first two *gem*-dimethyl substituted cyclo-octadecanes investigated both had a centre of symmetry while the two new compounds, 1,1-dimethyl- and 1,1,4,4-tetramethylcyclo-octadecane both lack this high degree of symmetry. As the crystal packing of the molecules may not be so tight in unsymmetrical molecules as in symmetrical and the melting enthalpy thereby lowered⁸ the result is a low melting point in unsymmetrical molecules that is not necessarily due to lower conformational stability.

Experimental. *1,1-Dimethylcyclo-octadecane.* To 5,5-dimethylcyclo-octadeca-1,8-diyne⁴ (0.2 g) dissolved in cyclohexane (50 ml) was added palladium on charcoal (0.1 g) and the solution fully hydrogenated at 344 kPa (40 h). The catalyst was filtered off, the solvent evaporated, the residue dissolved in pentane and filtered through alumina. Evaporation of pentane gave: *1,1-dimethylcyclo-octadecane*. M.p. 10 °C. Mol.w. 280. (Mass spectrometry). (Found: C 85.72; H 14.35. Calc. for C₂₀H₄₀: C 85.63; H 14.37).

1,1,4,4-Tetramethylcyclo-octadecane. 12,12,15-15-Tetramethylcyclo-octadeca-1,7-diyne⁵ (0.47 g) was hydrogenated as described above. Recrystallization from ethanol gave: *1,1,4,4-tetramethylcyclo-octadecane*. Mol.w. 308 (Mass

spectrometry). (Found: C 85.69; H 14.39. Calc. for C₂₂H₄₄: C 85.63; H 14.37).

The infrared spectra were recorded in a Perkin-Elmer Grating Infrared Spectrophotometer 457. For the calorimetric measurements a Perkin-Elmer Differential Scanning Calorimeter IB was used.

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