Syntheses and Conformational Properties of *gem*-Dimethyl Substituted Cyclohexadecanes

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1,1-Dimethyl-, 1,1,9,9-tetramethyl- and 1,1,4,4-tetramethylcyclohexadecane have been prepared. The first two are shown by IR spectroscopy to have the same [4444] diamond lattice conformation in melt and solution as in the crystal. The latter is a conformer mixture in melt and solution.

Only one diamond-lattice-type conformation is possible for cyclohexadecane; it has a "square" projection and D_{2d} symmetry (Fig. 1), and has been designated [1] as [4444], each digit representing the number of CC-bonds in one "side". An infrared spectrum simple enough (few and well resolved sharp lines) to correspond to a single conformation of this high symmetry is, however, only observed [2,3] below a solid-solid transition point at −2 °C. In the expanded lattice of the higher solid phase, in the melt, and in solution, the infrared spectrum (Fig. 2) has a complexity (broad and new absorption regions) indicative of

a conformer mixture. Simple calculations show [1] that among other quadrangular conformations those of lowest enthalpy are, in increasing order, [3535], [3445], [3454], and [2545] (Fig. 1). The expected higher entropy of these non-diamond-lattice-type conformations may of course increase their importance at higher temperatures.
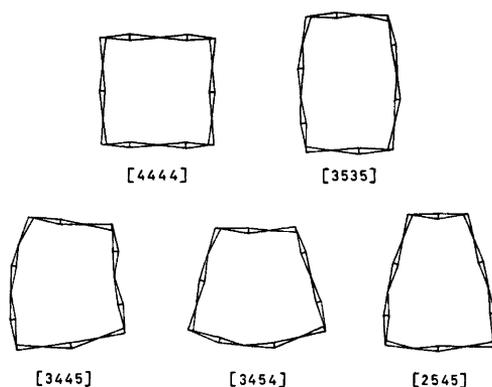
Geminal dimethyl substituents can be ac-

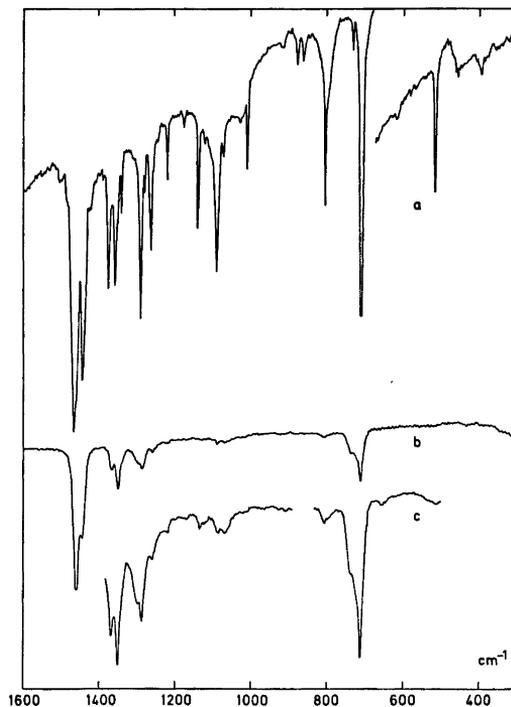*Fig. 1.* Conformations of lowest calculated energy for cyclohexadecane.[1]

Fig. 2. Infrared spectra of cyclohexadecane in the solid state at −80 °C (a), in the solid state at 40 °C (b), and in CS₂-solution (c).

Table 1. Melting points and first-order transitions for cyclohexadecanes.

	M.p. °C	Tr.p. °C	$\Delta H_m{}^a$	$\Delta H_{tr}{}^a$	$\Delta S_m{}^b$	$\Delta S_{tr}{}^b$	$\Delta S_{total}{}^b$
Cyclohexadecane	59	10	1.0	0.3	3.1	1.0	20.8
		− 2		4.5		16.7	
1,1-Dimethyl-cyclohexadecane	17	− 52	3.4	0.01	11.7	0.04	13.2
		− 57		0.3		1.5	
1,1,9,9-Tetramethyl cyclohexadecane	91		6.0		16.6		16.6
1,1,4,4-Tetramethyl-cyclohexadecane	30		6.0		19.8		19.8

a In kcal/mol. *b* In cal/mol deg.

commodated only in corner positions on any of these conformations.[4] Two, three or four such dimethyl groups in a given substitution pattern may therefore disfavour certain and favour other conformations. Thus, in 1,1,5,5,9,9,13,13-octamethylcyclohexadecane the substitution should fit all corner positions on the [4444] conformation and virtually exclude any other conformation. Although its attempted synthesis failed in the last step, the reduction of the intermediate 3,3,7,7,11,11,15,15-octamethylcyclohexadecane-1,9-dione, already the dione itself showed conformational homogeneity.[3,5] It is therefore extremely likely that this would be true also for the hydrocarbon.

We now present a study of three other cyclohexadecane derivatives, carrying one or two *gem*-dimethyl groups, obtained by full hydrogenation of acetylenic precursors reported earlier.[6,7] Since low-temperature NMR spectroscopy did not yield any information, the method used has been to compare IR spectra of solution, liquid and crystalline state in order to decide whether the solution and the liquid contains only the crystal conformer or a mixture of conformers. In addition, scanning calorimetry was used to check whether the whole melting process takes place at the melting point or is split into several steps, as for cyclohexadecane itself which has two solid-solid transition points (Table 1).

1,1-Dimethylcyclohexadecane. Substitution at a single corner is possible in one or more ways on any of the five conformations shown in Fig. 1, so that the conformational possibilities are even more numerous than for cyclohexadecane
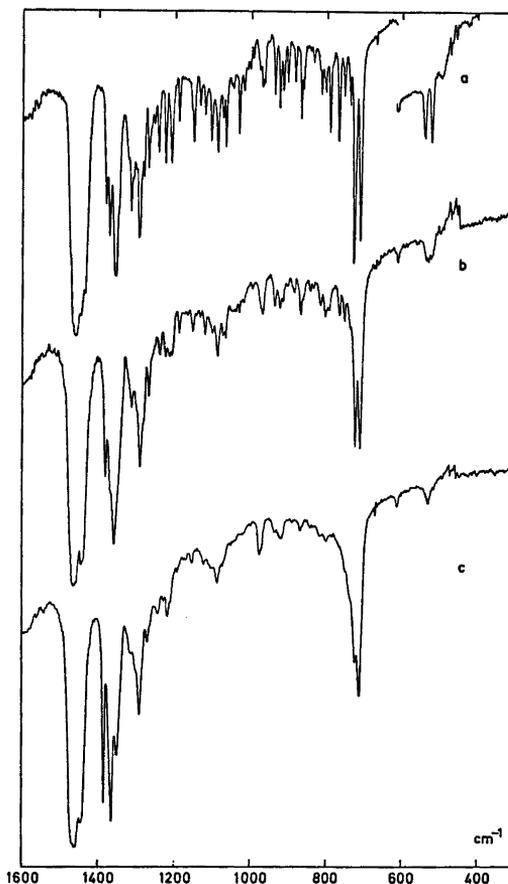
Fig. 3. Infrared spectra of 1,1-dimethylcyclohexadecane in the solid state at liquid N_2 temp. (a), in the solid state at − 20 °C (b), and in the melt at 40 °C (c).
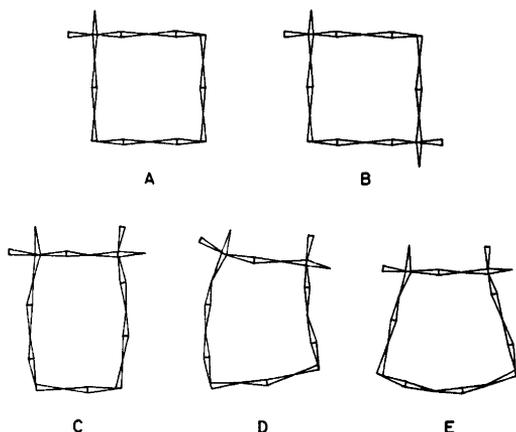
Fig. 4. Proposed conformations for 1,1-dimethyl-cyclohexadecane (A), for 1,1,9,9-tetramethyl-cyclohexadecane (B), and for 1,1,4,4-tetramethylcyclohexadecane (C, D, and E).

itself. Nevertheless, the infrared spectrum (Fig. 3) is similar in melt and solid, and the entropy of melting (Table 1) is too high to correspond to the melting of an expanded crystal lattice containing a mixture of conformers as in the case of cyclohexadecane. Transition points are in fact observed at − 52 and − 57 °C, but involve very small entropy changes, and the infrared spectrum of the low-temperature phase is different only in having sharper bands as generally expected for IR spectra of strongly cooled samples.
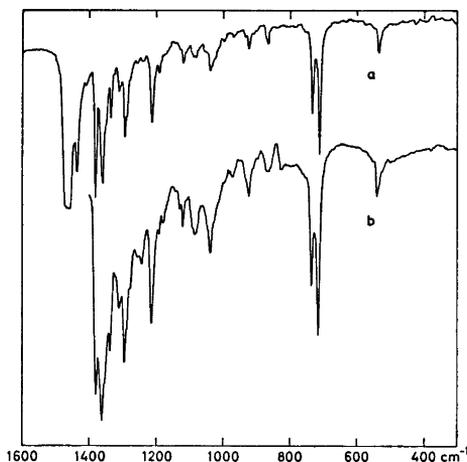

Fig. 5. Infrared spectra of 1,1,9,9-tetramethyl-cyclohexadecane in the solid state at 40 °C (a) and in CS_2-solution (b).

We conclude that the low-temperature crystal conformer is also present in the high-temperature solid and at least predominant in the liquid. It is extremely likely that it has the [4444] ring conformation (A, Fig. 4). There are two reasons why *gem*-dimethyl substitution at one corner should disfavour relatively the other ring conformations: Firstly, the ring valency angle at the substituted corner must be closer to the tetrahedral value of the diamond lattice, whereas at unbranched carbon atoms this angle is 112°. Secondly, the presence of the methyl substituents increases the torsional barriers in the adjoining CC bonds and fixes the torsional minimum at the diamond lattice dihedral angle of 60° instead of 65 − 70° without substitution.[1] Both changes must disturb the energy balance; the energy of that one conformation [4444] which is close to the diamond lattice is lowered, and the energy of all others are raised.

1,1,9,9-Tetramethylcyclohexadecane. This diametric substitution pattern fits only the [4444], the [3434] and the [3445] conformations. The sharpness of the IR-bands and identity of solid and liquid spectra (Fig. 5), the absence of a solid-solid transition point and a reasonable value of the entropy of melting (Table 1), suggest a single identical conformer in all phases. The spectral simplicity suggests a high symmetry, hence the [4444] ring conformation (B, Fig. 4) is again most likely.* The final identification has come from the crystal structure of the solid determined by Groth,[8] who finds in fact this conformation.

Thus, also for this molecule, the effect of *gem*-dimethyl substitution is to further favour that one of the three conformations which is of diamond-lattice type, and to disfavour the others, presumably to an even greater extent than in the 1,1-dimethyl derivative.

1,1,4,4-Tetramethylcyclohexadecane. This substitution does not fit the lowest-energy [4444]

* An observed broadening of the methyl line in the ^{1}H NMR spectrum in various solvent systems below − 60 °C might in itself have indicated a lower symmetry, but the broadening at the lowest attainable temperature (− 150 °C) was much too large to correspond to chemical shift differences, hence is ascribed to slow molecular tumbling of this large molecule as compared with the small spherical TMS molecule, for which a sharp line was still observed.
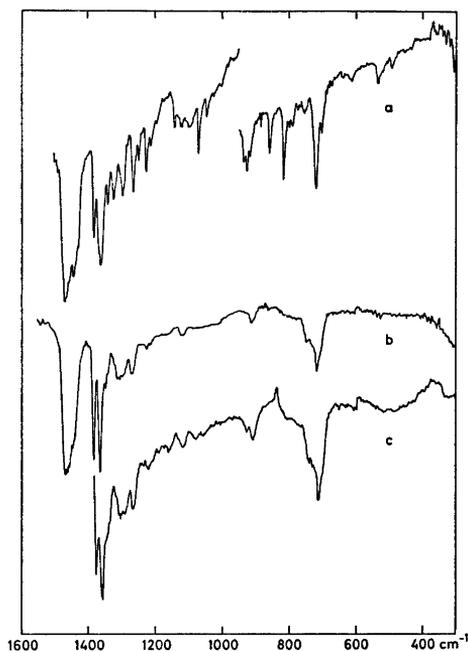
Fig. 6. Infrared spectra of 1,1,4,4-tetramethyl-cyclohexadecane in the solid state at − 80 °C (a), in the melt at 40 °C (b), and in CS$_2$-solution (c).

conformation, but only the [3535], the [3445] and the [3454] conformations, of which the first has the lowest energy. The infrared spectrum (Fig. 6) of the solid is now much simpler than that of the liquid, so that conformational selection by the crystal lattice is clearly indicated. This is also borne out by the relatively high entropy of melting (Table 1). We propose that the crystal conformer has the rectangular [3535] ring skeleton (C, Fig. 4) of lowest calculated energy.

The coexistence of other conformers in solution and liquid may either mean that the [3445] and [3454] conformations are not so much higher in energy as the calculations suggest,[1] or that the change of preferred valency angles and torsional angles at the substituted corners largely eliminate the energy differences. Thus, the [3535] conformation needs dihedral angles substantially larger than 60° at the *gauche*-bonds terminating the three-bond "sides",[1] and *gem*-dimethyl substitution at both ends will prevent these from opening up. The alternative

[3445] and [3454] conformations (D and E, Fig. 4) may be less affected by the substitution. We propose that these are the additional conformers in the liquid.

EXPERIMENTAL

1,1-Dimethylcyclohexadecane. To 13,13-dimethylcyclohexadeca-1,8-diyne [7] (0.2 g) dissolved in cyclohexane (50 ml) was added 5 % palladium on charcoal (0.1 g) and the solution hydrogenated at 3.5 atm. (40 h). The catalyst was filtered off, the solvent evaporated. Preparative gas chromatography, (column: 150 cm × 6 mm, 10 % OV 17 on chromosorb WAW DMCS,) gave *1,1-dimethylcyclohexadecane*, m.p. 17 °C. Mol.w. 252 (mass spectrometry). (Found: C 85.79; H 14.21. Calc. for C$_{18}$H$_{36}$: C 85.63; H 14.37).

1,1,9,9-Tetramethylcyclohexadecane. 5,5,13,13-Tetramethylcyclohexadeca-1,8-diyne [6] (0.23 g) was dissolved in cyclohexane (70 ml) and hydrogenated with palladium on charcoal (0.1 g) as described above. After evaporation of solvent recrystallization from ethanol gave *1,1,9,9-tetramethylcyclohexadecane*, m.p. 91 °C. Mol.w. 280 (mass spectrometry). (Found: C 85.46; H 14.54. Calc. for C$_{20}$H$_{40}$: C 85.63; H 14.37).

1,1,4,4-Tetramethylcyclohexadecane. 10,10,13,13-Tetramethylcyclohexadeca-1,5-diyne [6] (0.8 g) was dissolved in cyclohexane (150 ml) and hydrogenated with palladium on charcoal (0.35 g) at 4.2 atm. (20 h). Repeated hydrogenation with fresh catalyst was necessary. The catalyst was filtered off, the solvent evaporated, the residue dissolved in pentane and filtered through alumina. Recrystallization from ethanol gave *1,1,4,4-tetramethylcyclohexadecane*, m.p. 31 °C. Mol.w. 280 (mass spectrometry). (Found: C 85.56; H 14.48. Calc. for C$_{20}$H$_{40}$: C 85.63; H 14.37).

Calorimetric data. A Perkin-Elmer Differential Scanning Calorimeter 1 B was used down to a temperature of − 90 °C.

Infrared spectra. These were recorded with a Perkin-Elmer model 225 spectrometer. Solutions in CS$_2$ and CCl$_4$ were measured using 1 mm KBr cells. The low temperature spectra were obtained with a VLT-2 cell from RIIC, cooled with dry ice. The sample was contained between two pressed KBr or KJ discs.

NMR-spectroscopy. The NMR spectra were recorded with a Varian HA 100 15 D instrument. Solvent systems used for low-temperature studies were: CS$_2$, CHFCl$_2$, and a 2:1 mixture of CHFCl$_2$ and CF$_2$Cl$_2$.

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