gem-Dimethyl Substituted Cyclo-octadecanes; Conformational Homogeneity of the 1,1,4,4,10,10,13,13-Octamethyl Derivative

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FOR the cyclo-octadecane molecule[1] three conformations are possible with only staggered bonds (corresponding to cyclic paths on the diamond lattice) if the closest admitted nonbonded H–H distances correspond to *gauche*-butane interactions (Figure 1 *a*, *b*, and *c*). Of these conformations, *a* has the advantage of being most compact, and would be the one adopted by the crystal lattice below the transition point.[2]

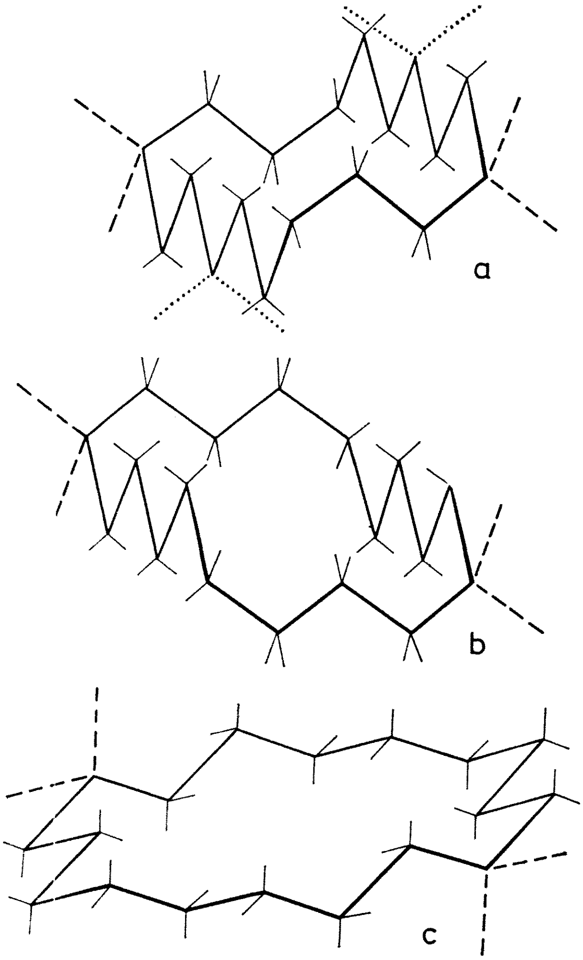


FIGURE 1

The entroduction of *gem*-dimethyl substituents may be expected[1,3] to have the following effects:

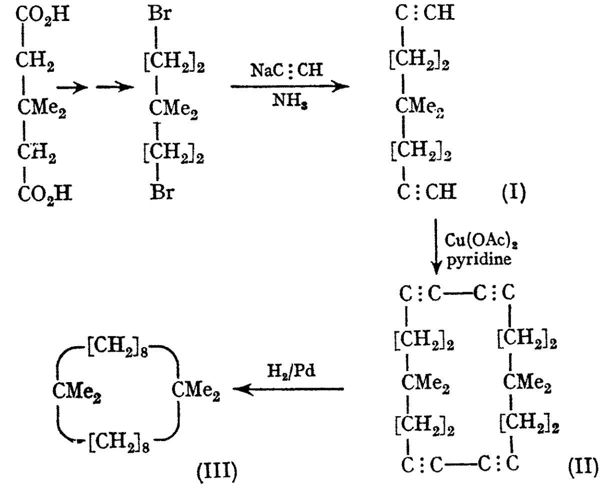
(i) Conformations *a*, *b*, and *c* would depart sufficiently from the gross shape of round or rectangular discs[1] so as to prevent "rotation" of these molecules about an axis perpendicular to the molecular "plane."

(ii) The substituents would favour the rectangular conformations *a* and *b*, since with *gem*-dimethyl groups at corner positions the chain bend created with the two $-CH_2-CMe_2$-*gauche* bonds does not represent extra energy as compared with *anti*-bonds.[1]

(iii) The *gem*-dimethyl groups would have to avoid most positions other than corner positions, also for simple steric reasons. When judiciously placed at relative positions corresponding to all four corners of conformations *a* (or *b*), they could make this conformation the only one possible,

(iv) Because of the increasing conformational homogeneity, the entropy of fusion should decrease,[1] and the melting point should increase.

1,1,10,10-Tetramethylcyclo-octadecane (III) was synthesized by the following route:



It melted at 86° with a heat of fusion corresponding to a "normal" melting point (see Table), and no solid–solid transition† could be observed by differential calorimetry. As the entropy of fusion is not very much smaller than the total entropies of transition and fusion for cyclo-octadecane (see Table), it may be concluded that other conformers than the crystal conformer are also present in the liquid phase of the tetramethyl derivative. As indicated in Figure 1, diagonal positions on all three conformations can accommodate the four methyl groups. This was confirmed by i.r. spectral differences between the solid and solution in CS_2.

In addition to the "dimer" (II) the oxidative coupling of the diyne (I) gave also cyclic "trimer" and "tetramer". The hydrogenated "trimer", 1,1,10,10,19,19-hexamethylcycloheptacosane, was a liquid, as to be expected[1] for an odd-membered cycloalkane, while the hydrogenated "tetramer," 1,1,10,10,19,19,28,28-octamethylcyclohexatriacontane, having again an even-membered ring, melted at 78°.

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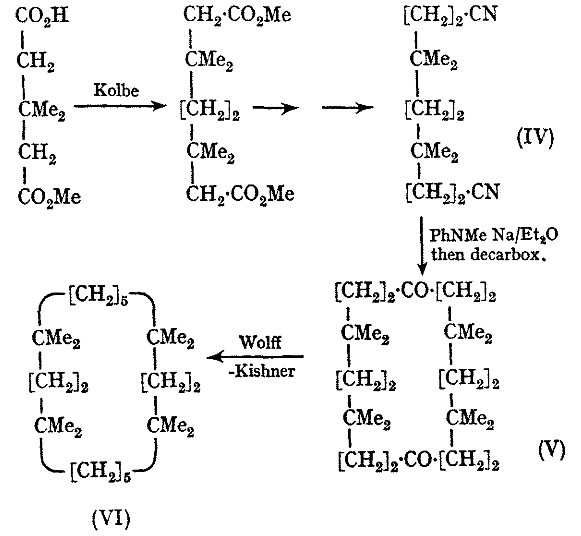
† *cf.* Cyclo-octadecane, which undergoes such a transition at 25°; the heat of transition accounts for most of the heat of the "melting" process.

First-order transitions for cyclo-octadecanes[a]

	M.p.	Tr.p.	ΔH_m[b]	ΔH_{tr}[b]	ΔS_m[c]	ΔS_{tr}[c]
Cyclo-octadecane	73°	25°	2·36	7·00	6·8	23·3
Tetramethylcyclo-octadecane (III)	86°		9·46		26·3	
Octamethylcyclo-octadecane (VI)	165°	154°	4·82	1·61	11·1	3·8

[a] Determined on Dr. J. Oth's calorimeter, ERA, Brussels, and on a Perkin–Elmer Differential Scanning Calorimeter.
[b] In kcal./mole.
[c] In cal./mole deg.

1,1,4,4,10,10,13,13-Octamethylcyclo-octadecane (VI) was synthesized as follows:



The Ziegler cyclization[4] of the dinitrile (IV) at high dilution gave as a by-product a cyclic monomer, 4,4,7,7-tetramethylcyclononanone, m.p. 44°. The desired dimer 4,4,7,7,13,13,16,16-octamethylcyclo-octadecane-1,10-dione (V), was the main cyclic compound. It melts substantially higher (220°) than cyclo-octadecane-1,10-dione itself[5] (96°), and we take this as indicative of a higher conformational homogeneity. Since the relative orientation of the ketone dipoles in the most likely conformation must be anti-parallel (Figure 2), it may be taken as supporting evidence that the observed dipole moment in benzene was only 1·7 D, far lower than the value of 3·8 D calculated[6] for free relative orientation of the dipoles. The corresponding hydrocarbon (VI) melted at 165° with a strikingly small entropy of fusion. A transition point did show up at 154°, but can have nothing to do with a conformational change, since the entropy involved is very small, and since the i.r. spectra in the solid and in CS_2 solution were identical. There can be little doubt that the molecule has one exclusive conformation, the compact rectangular one of Figure 1*a*, and that all eight methyl groups are confined to corner positions as shown for the diketone in Figure 2.

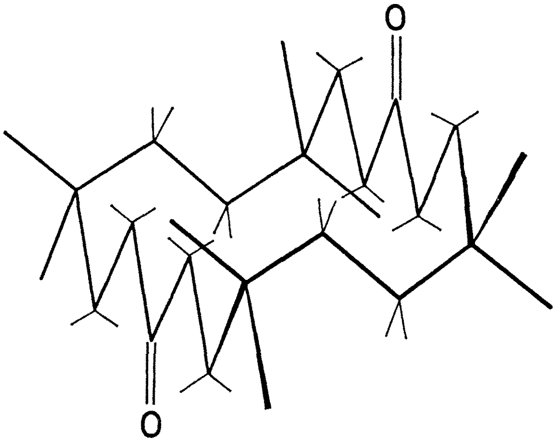


FIGURE 2

All the 18-membered rings described possessed temperature-invariable n.m.r. spectra down to −60°. A single methyl resonance was always observed. Ring inversion is therefore not hindered, but gives an identical conformation.

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[1] J. Dale, *J. Chem. Soc.*, 1963, 93.
[2] *cf.* Cyclotetratriacontane; H. F. Kay and B. A. Newman, *Acta Cryst.*, 1968, **24**, *B*, 615.
[3] J. Dale, *Angew. Chem.*, 1966, **78**, 1070.
[4] K. Ziegler, in Houben-Weyl, "Methoden der organischen Chemie," G. Thieme, Stuttgart, 1955, Band IV, Teil 2, p. 758.
[5] L. Ruzicka, M. Stoll, H. W. Huyser, and H. A. Boekenoogen, *Helv. Chim. Acta*, 1930, **13**, 1152.
[6] C. P. Smyth, "Dielectric Behaviour and Structure," McGraw-Hill, New York, 1955, p. 371.