Occlusion of Solvent Molecules by 20-Membered Rings

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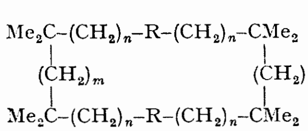
Summary 1,1,5,5,11,11,15,15-Octamethylcycloeicosane and its derivatives crystallize with, and retain, solvent molecules; no occlusion occurs with cycloeicosane itself and the analogous derivatives.

A SERIES of macrocyclic 14-, 16-, 18-, 20-, 22-, and 24-membered-ring diketones and hydrocarbons (I), which all contain four *gem*-dimethyl groups in such relative positions as to fit the corners of "rectangular" diamond-lattice conformations, have been synthesized by methods similar to the one already outlined[1] for one of these, the 18-membered ring, and to be published in detail elsewhere.



$$\begin{array}{ccc} Me_2C & -(CH_2)_n-R-(CH_2)_n- & CMe_2 \\ | & & | \\ (CH_2)_m & & (CH_2)_m \\ | & & | \\ Me_2C & -(CH_2)_n-R-(CH_2)_n- & CMe_2 \end{array}$$

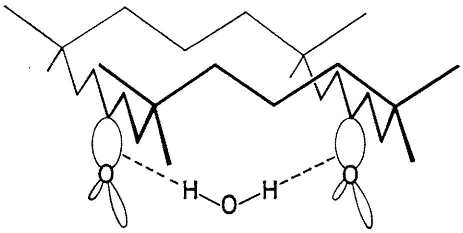
(I)

	(I)	
$R =$	$C{=}O$	CH_2
$m =$	2 or 3	2 or 3
$n =$	1, 2, or 3	2 or 3

Of these, the 20-membered rings, (I; $m = 3$, $n = 2$), but none of the others, showed a strong tendency to co-crystallize with solvent molecules. Thus, 4,4,8,8,14,14,18,18-octamethylcycloeicosane-1,11-dione (m.p. 145°), crystallized from methanol, retained about 0·6 mole of methanol even after drying at 25° and 6 mm Hg, while cycloeicosane-1,11-dione itself trapped no methanol under the same conditions. Similarly, 1,1,5,5,11,11,15,15-octamethylcycloeicosane (m.p. 166°) retained about 0·05 mole of CCl_4 even after drying in high vacuum at 70° (2·7% Cl by elemental analysis), while cycloeicosane itself presented no problem in this respect. The sublimed solvent-free octamethyl-substituted rings also rapidly picked up humidity. In the case of the diketone, the i.r. spectrum in KBr did not show the usual broad water absorption at 3400 cm^{-1}, but two sharper bands at higher frequency (3530 and 3610 cm^{-1}) indicative of a weakly hydrogen-bonded water molecule.[2] To prove that the two bands represented the symmetric and asymmetric O–H stretching[2] of one type of water molecule in symmetrical surroundings rather than unsymmetrically bound water or water molecules in two different functions, the water was partly replaced by deuterium oxide. There appeared indeed in the centre (at 3570 cm^{-1}) a third OH-stretching band representing HDO molecules as well as three OD-stretching bands at 2580 and 2680 cm^{-1} for D_2O and at 2630 cm^{-1} for HDO. We therefore suggest that the water molecule is bridging the two carbonyl groups situated opposite each other (Figure). As the geometry cannot then be correct for strong coplanar hydrogen bonds to the lone pairs on carbonyl oxygen, we further suggest that both OH groups form perpendicular hydrogen bonds to the C=O double bond electrons, and that this explains their weakness.

The corresponding bis-methylene compound (R = >C=CH$_2$, m.p. 119°) was subsequently synthesized in a Wittig reaction, but although this substance also retained CCl$_4$ and was hygroscopic, the water present gave rise only to an unresolved absorption in the region 3400—3600 cm^{-1}. Apparently, the C=C double bond is not a sufficiently good hydrogen acceptor to compete with other water molecules.

No solvent occlusion was of course expected for the octamethyl-substituted 14-, 18-, and 22-membered rings ($m = 2$) since the relative position of the *gem*-dimethyl groups imposes compact, two-carbon-bridged ring conformations.[3] The octamethyl-substituted 16-, 20-, and 24-membered rings ($m = 3$) fit the more open three-carbon-bridged ring conformations of the type shown in the Figure. We have just given evidence[4] to show that the 16-membered rings crystallize in such a diamond-lattice conformation even when no *gem*-dimethyl groups are present and without the need of using solvent molecules. The size of the hole is much larger in the 20-membered rings, but the corner positions have to be defined by *gem*-dimethyl groups in order to stabilize the open conformation and induce occlusion of solvent. The 24-membered ring seemingly gives up this completely even when *gem*-dimethyl groups are present.



FIGURE

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[1] G. Borgen and J. Dale, *Chem. Comm.*, 1969, 447.

[2] E. Greinacher, W. Lüttke, and R. Mecke, *Z. Elektrochem.*, **1955**, **59**, **23**.

[3] J. Dale, *Angew. Chem.*, 1966, **78**, 1070.

[4] G. Borgen and J. Dale, preceding communication.