

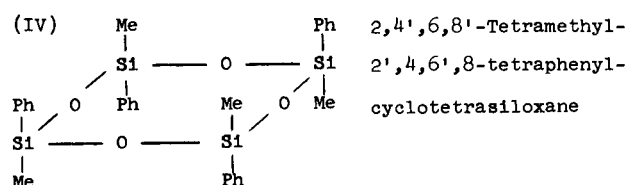
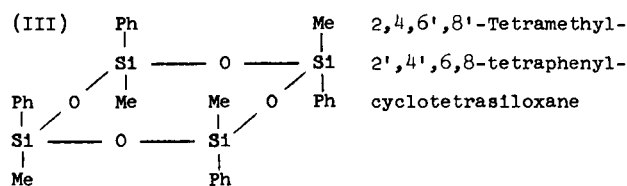
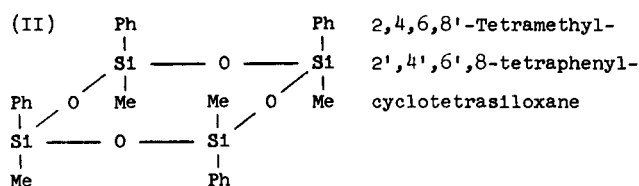
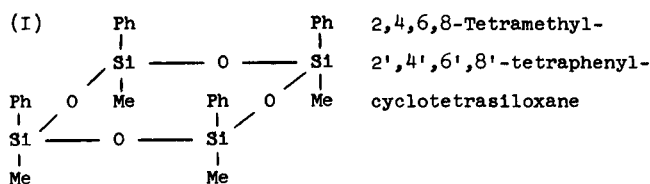
Central Research Department, Monsanto Company

Structure of 2,4,6',8'-Tetramethyl-2',4',6,8-tetraphenylcyclotetrasiloxane

Emile D. Pierron, Charles F. Hobbs, Donald L. Parker and Donald J. Bauer

The separation and characterization of the stereoisomeric 2,4,6-trimethyl-2,4,6-triphenylcyclotrisiloxanes and 2,4,6,8-tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxanes have recently been reported (1).

Similar studies in our laboratories have confirmed the conclusions of Hickton, *et al.* (1). The four isomeric tetramers identified were:



Structural assignments have been based, as shown in Table I, solely on methyl-proton shifts and in accordance with the discussion presented by Hickton, *et al.* (1). Although all of the individual isomers were not separated, an assignment of peaks at δ -0.43, -0.42 and -0.20 could be made independently

and unambiguously to isomer II since the relative ratio of these peaks to each other remained constant at 1:2:1, respectively, as the isomer ratios varied between distillation fractions. Further justification of such assignment is the presence of a methyl group at relatively high field (-0.20 ppm). This could be explained only by a high shielding effect of the phenyl groups. Considering the four isomers, the three *cis*-phenyl groups of structure II should cause the highest chemical shift thus confirming our assignment.

Upon standing, the liquid mixture of isomeric tetramers deposited a crystalline isomer, m. p. 99° (1,2). This isomer exhibited one methyl singlet at δ -0.31, which was shifted to -0.32 in the tetramer mixture. Structure III was assigned to this isomer.

We wish to report additional confirmation of the 2,4,6',8'-tetramethyl-2',4',6,8-tetraphenylcyclotetrasiloxane structure establish from crystallographic data as shown in Table II.

The crystals of isomer III precipitated from a methanol solution are monoclinic, space group $P2_1/a$ with two molecules per unit cell. The presence of only two molecules in this space group demands that the molecule is centrosymmetric and confirms therefore the structure of isomer III.

TABLE I

Methyl-proton Shifts in 2,4,6,8-Tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxanes

| Isomer | Methyl Position | Shift (δ) (a) |
|--------|-----------------|------------------------|
| (I) | 2,4,6,8 | -0.51 |
| (II) | 4 | -0.43 |
| | 2,6 | -0.42 |
| | 8' | -0.20 |
| (III) | 2,4,6',8' | -0.32 |
| (IV) | 2,4',6,8' | -0.30 |

(a) Shifts reported are 0.03 to 0.05 ppm downfield from those determined by Hickton, *et al.* (1). This is probably due to dilution effects.

TABLE II

Crystal Data of 2,4,6',8'-Tetramethyl-2',4',6,8-tetraphenylcyclotetrasiloxane

| | |
|--------------------------|--|
| Monoclinic, space group: | $P2_1/a$ |
| Unit cell dimensions: | $a_0 = 11.927 \pm 0.008 \text{ \AA}$ $b_0 = 13.740 \pm 0.010 \text{ \AA}$ $c_0 = 9.760 \pm 0.008 \text{ \AA}$ $\beta = 106^\circ 30' \pm 10'$ |
| Molecules per unit cell: | 2 |
| Density: | |
| determined | $1.180 \pm 0.01 \text{ g. cm}^{-3}$ |
| calculated | $1.177 \pm 0.01 \text{ g. cm}^{-3}$ |

EXPERIMENTAL

Melting points are corrected. They were determined on a Reichert hot-stage melting point apparatus. N.M.R. spectra were recorded at 60 Mc by means of the Varian A-60 spectrometer, all signals being recorded in p.p.m. (δ) downfield from tetramethylsilane as the internal standard. The methyl proton shifts were determined using 33% (v/v for liquids and wt/v for the solid) solutions in carbon tetrachloride.

Hydrolysis of phenyldichloromethylsilane according to the method of Lewis (3), followed by distillation yielded 2,4,6-trimethyl-2,4,6-triphenylcyclotrisiloxane, b.p. 144-142° (0.07-0.06 mm), three fractions of 2,4,6,8-tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxane, b.p. 184-187° (0.06-0.07 mm), n_D^{25} 1.5480-1.5460, and 2,4,6,8,10-pentamethyl-2,4,6,8,10-pentaphenylcyclopentasiloxane, b.p. 219-224° (0.07-0.08 mm), n_D^{25} 1.5495.

Approximately 50 mg. of the precipitate deposited from the liquid mixture of isomeric tetramers was dissolved in 5 ml. of methanol and allowed to recrystallize very slowly (8 days) at room temperature. Clear transparent crystals were obtained.

The unit cell dimensions were determined from rotation and Weissenberg photographs using copper $K\alpha$ radiation. There were no general absences among the (hkl) reflections. The special absences (OKO) for k odd and (hol) for h odd fixed the space group as $P2_1/a$. Flotation of the crystals in a mixture of chlorobenzene and bromobenzene yielded a measured density of $1.180 \pm 0.01 \text{ g. cm}^{-3}$ in good agreement with the value of $1.177 \pm 0.01 \text{ g. cm}^{-3}$ computed from the unit cell parameters and the assumption of two formula weights in the unit cell.

REFERENCES

- (1) H. J. Hickton, A. Holt, J. Homer, and A. W. Jarwie, *J. Chem. Soc. (C)*, 149 (1966).
- (2) C. W. Young, P. C. Servais, C. C. Currie, and H. J. Hunter, *J. Am. Chem. Soc.*, 70, 3758 (1948).
- (3) R. N. Lewis, *ibid.*, 70, 1115 (1948).

Received September 12, 1966

St. Louis, Missouri 63166