

Pulsed ^1H Nuclear Magnetic Resonance Studies of Molecular Motion and Plastic Crystallinity in Dodecamethylcyclohexasilane

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Summary Dodecamethylcyclohexasilane exhibits plastic crystalline behaviour from 77 to 253 °C, with molecular rotation taking place both in the crystalline (<77 °C) and plastic crystalline (>77 °C) phases; activation energies for various molecular motions are reported.

DODECAMETHYLCYCLOHEXASILANE (Me_2Si)₆ is important as a model compound and precursor to a variety of linear and cyclic polysilicon compounds.^{1,2} The properties of (Me_2Si)₆ and other permethylcyclopolysilanes show evidence for extensive electron delocalization, resembling that in aromatic substances.¹ We now find that (Me_2Si)₆ also shows unusual motional behaviour in the solid state.

Using the methods described in earlier papers^{3,4} we have measured ^1H n.m.r. relaxation times T_1 (spin lattice), $T_{1\rho}$ (rotating frame spin lattice), T_{1D} (dipolar), and second moments (M_2) for (Me_2Si)₆; the relaxation data are presented in the Figure. A transition^{5,6} from the crystalline 'brittle' phase to an orientationally disordered 'plastic crystal'^{7,8} phase can clearly be seen at $10^3/T$ ca. 3 (ca. 75 °C) from the large discontinuous change in $T_{1\rho}$ of greater than three orders of magnitude. Differential thermal analysis shows an endotherm corresponding to this transition at 77 ± 1 °C, 176 °C below the normal m.p. of (Me_2Si)₆.

In the crystalline phase, at the lowest temperatures ($10^3/T > 5$), T_1 , $T_{1\rho}$, and T_{1D} increase with increasing temperature. These are portions of high temperature arms of relaxation minima, which we attribute to random reorientation of methyl groups about their C_3 axes. From the gradients of the linear portions below $10^3/T$ ca. 5, we estimate an activation barrier of 5 kJ mol⁻¹ for methyl reorientation. Between $10^3/T$ ca. 5 and the phase transition, contributions to all three relaxation times from a second motional process can be seen. These are portions of low temperature arms of relaxation minima. This second process is characterized by an activation barrier of 45 kJ mol⁻¹, and the motion results in a reduction of the

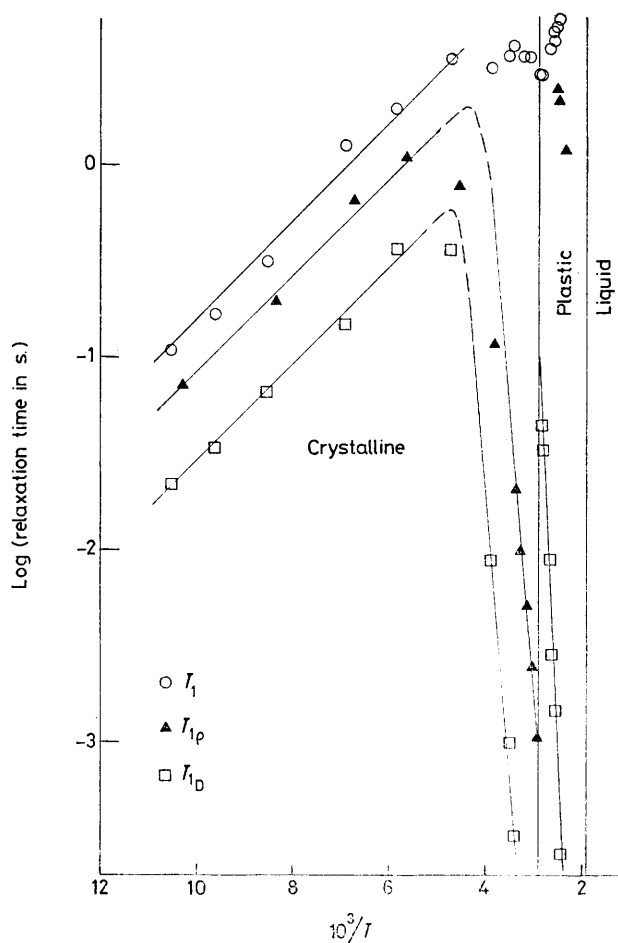


FIGURE. Log n.m.r. relaxation times vs. reciprocal temperature for solid dodecamethylcyclohexasilane.

second moment to *ca.* 1 G^2 just below the phase transition. Since it is known that $(\text{Me}_2\text{Si})_6$ exists in a chair conformation,⁹ the second motion most likely involves reorientation about the three-fold molecular axis or reorientation about a six-fold molecular axis with participation from ring inversion.

In the plastic phase, T_1 appears to be controlled by molecular reorientation, and T_1 by two processes, molecular reorientation and self-diffusion. T_{1D} shows linear behaviour, decreasing with increasing temperature, and the n.m.r. line is observed to narrow further above *ca.* 130°C . The T_{1D} behaviour in the plastic phase corresponds^{5,6} to the low temperature arm of the translational

diffusion minimum. From the gradient, we estimate an activation barrier of 100 kJ mol^{-1} for the self-diffusion process.

Preliminary examination indicates that $(\text{Me}_2\text{Si})_5$ also shows orientational disorder, undergoing transition to a plastic-crystalline phase at -39°C , about 220°C below its m.p. The temperature ranges over which plastic crystalline phases are stable for this compound and $(\text{Me}_2\text{Si})_6$ are unusually large; among monocyclic compounds these appear to be the longest plastic crystalline ranges known.†

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† Even longer plastic crystalline ranges have, however, been observed for polycyclic compounds, for example adamantane (247°C) (H. A. Resing, *Mol. Cryst. Liq. Cryst.*, 1969, **9**, 101) and norbornane (230°C), (R. Folland, R. L. Jackson, J. H. Strange, and A. V. Chadwick, *J. Phys. Chem. Solids*, 1973, **34**, 1713).

¹ R. West and E. Carberry, *Science*, 1975, **189**, 179.

² S. Yajima, M. Omori, J. Hayashi, K. Okamura, T. Matsuzawa, and C. Liaw, *Chem. Letters*, 1976, 551.

³ D. W. Larsen and J. Y. Corey, *J. Amer. Chem. Soc.*, 1977, **99**, 1740.

⁴ D. W. Larsen and T. A. Smentkowski, *J. Magnetic Resonance*, 1977, **28**, 171.

⁵ J. M. Chezeau, J. Dufourcq, and J. H. Strange, *Mol. Phys.*, 1971, **20**, 305.

⁶ A. V. Chadwick, J. M. Chezeau, R. Folland, J. W. Forrest, and J. H. Strange, *J.C.S. Faraday I*, 1975, **71**, 1610.

⁷ J. Timmermans, *J. Chim. phys.*, 1938, **35**, 331; *J. Phys. Chem. Solids*, 1961, **18**, 1.

⁸ J. G. Aston, 'Physics and Chemistry of the Organic Solid State,' eds. D. Fox, M. Lages, and A. Weissberger, Vol. 1, Interscience, New York, 1963, p. 543.

⁹ H. L. Carrell and J. Donahue, *Acta. Cryst.*, 1972, **B28**, 1566.