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Proton Magnetic Resonance Study of Solid Hexamethylethane

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The molecular motion of solid hexamethylethane was studied by the proton magnetic resonance method from the liquid nitrogen temperature to 20°C. In the temperature range between about −160°C and −120°C, the methyl group rotates about its own axis, and also the molecule rotates about the molecular axis as a whole. Above −120°C, the molecule rotates almost freely. On the other hand, the molecular motion of hexamethyldisilane in the high-temperature phase has been explained in terms of the facts that the molecule rotates freely and also has a degree of translational freedom. The difference in the molecular motion between hexamethylethane and hexamethyldisilane is caused mainly by the difference in the molecular interaction.

The compounds which are composed of molecules more or less globular in shape have small entropies of fusion and exhibit plasticity below their melting points. Their crystals below the melting point were named "plastic crystals" by Timmermans.[1] In these plastic crystals, the molecules are capable of rotational motion, if they are not completely free; this has been revealed by studies of the X-ray diffraction, the nuclear magnetic resonance, the dielectric absorption, *etc.*

The molecule of hexasubstituted-ethane derivatives of the formula $X_n(CH_3)_{3-n}C-C(CH_3)_{3-m}Y_m$, where X and Y denote methyl group or halogen atoms and $n, m=0, 1, 2$ or 3, may be regarded as having an octahedron form with large spheres at the corners, as in Fig. 1. Therefore, the hexasubstituted-ethane-derivative molecules may resemble the globular molecule.

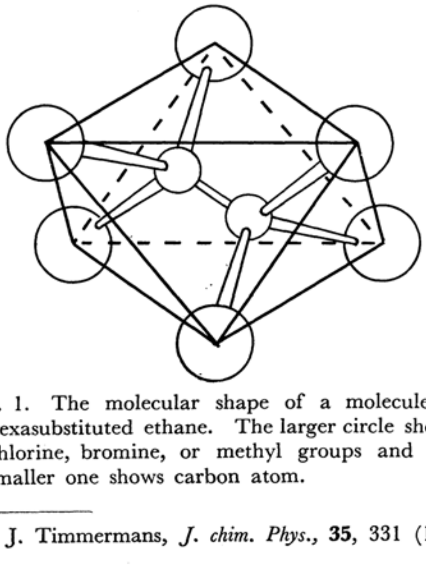

Fig. 1. The molecular shape of a molecule of hexasubstituted ethane. The larger circle shows chlorine, bromine, or methyl groups and the smaller one shows carbon atom.

The molecule of hexamethylethane, $(CH_3)_3C-C(CH_3)_3$, is a typical octahedral molecule. It has a phase transition at 152.5°K[2] accompanying by entropy change of 3.13 e. u., which is comparable with 4.82 e. u., the melting entropy change at 373.8°K. The crystal structure was studied by West,[3] who reported that the high-temperature crystal structure is a body-centered cubic lattice and that the molecule orients in a random manner with a vigorous thermal molecular motion. These facts indicate that hexamethylethane belongs to the category of plastic crystals.

Hexamethyldisilane and 1, 1, 1, 2-tetrachloro-2-methylpropane are also octahedral-type molecules. They have a phase transition,[4,5] above which these crystals are a body-centered cubic lattice.[6,7] Seki *et al.* investigated the molecular motion in the crystal lattice of hexamethyldisilane, $(CH_3)_3Si-Si(CH_3)_3$, by proton magnetic resonance absorption[8] and reported that the molecule rotates completely freely, accompanied by self-diffusion in the cubic lattice. On the other hand, in the high-temperature phase of 1, 1, 1, 2-tetrachloro-2-methylpropane, $Cl_3C-C(CH_3)_2Cl$, the molecule rotates nearly freely and does not show any self-diffusion.[5]

The difference in the molecular motion between hexamethyldisilane and 1, 1, 1, 2-tetrachloro-2-methylpropane arouses one's interest in investigating how the molecular motion is in the solid state

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[1] J. Timmermans, *J. chim. Phys.*, **35**, 331 (1938).

[2] D. W. Scott, D. R. Douslin, M. E. Gross, G. D. Oliver and H. M. Huffman, *J. Am. Chem. Soc.*, **74**, 883 (1952).

[3] C. D. West, *Z. Krist.*, **88**, 195 (1934).

[4] H. Suga and S. Seki, This Bulletin, **32**, 1088 (1959).

[5] T. Koide and T. Oda, *ibid.*, **40**, 764 (1967).

[6] H. Suga, S. Seki, Y. Chatani and I. Taguchi, *Ann. Report Inst. Fiber Res. (Osaka Univ.)*, **8**, 51 (1954).

[7] T. Koide, T. Oda and I. Nitta, This Bulletin, **29**, 738 (1956).

[8] T. Yukitoshi, H. Suga, S. Seki and J. Itoh, *J. Phys. Soc. Japan*, **12**, 506 (1957).

of hexamethylethane. Form this point of view, this paper will report on a proton magnetic resonance study of solid hexamethylethane and will discuss molecular motion in the crystalline lattice.

Experimental

First-grade hexamethylethane (Tokyo Kasei Co.) was recrystallized from ether and sublimed under a high-vacuum of about 10^{-5} mmHg. The melting point was found to be 100.5°C. A broad line spectrometer (JNM-W30 type of the Japan Electron Optics Laboratory Co.) operating at 30 Mc/sec was used for the proton magnetic resonance measurements. The temperature range observed was from the liquid nitrogen temperature to room temperature. The temperature of the specimen was observed by a copper-constantan thermo-couple with a potentiometer. The temperature of the sample was maintained ± 1°C.

Results and Discussion

The line widths (peak to peak) are shown in Fig. 2 as a function of the temperature. Below -180°C the line width shows a constant value, 9.5 gauss. The absorption line width decreases with the increases in the temperature from -180°C to -160°C, from which up to -125°C the line shape has a constant line width of 4.0 gauss. The line shape above the transition temperature (-121°C) is a sharp one, with the line width of about 3.2 gauss, and stays the same up to room temperature.

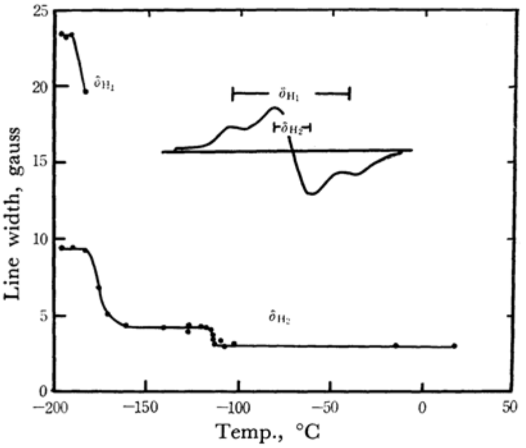

Fig. 2. The line widths of $(CH_3)_3C$–$C(CH_3)_3$.

The experimental second moments are shown in the last column of Table 1 and in Fig. 3 as a function of the temperature. The modulation broadening for the second moments was corrected by the method of Perman and Bloom.⁹⁾ Below -190°C, the second moment has a constant value of 45.0 gauss^2. It changes abruptly to the value of 3.5 gauss^2 in the temperature range from -180°C to -160°C. At about -122°C, it drops sharply to 2.2 gauss^2, and this value is maintained up to room temperature. The abrupt reductions of the second moment and the line width are to be associated with the onset of the molecular reorientation at the corresponding temperatures.

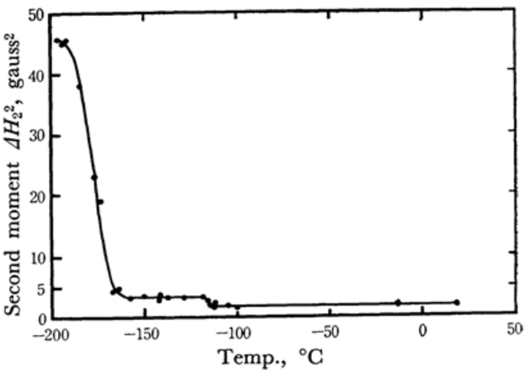

Fig. 3. The second moments of $(CH_3)_3C$–$C(CH_3)_3$.

The theoretical second moments were calculated by the formulae given Gutowsky and Pake,¹⁰⁾ assuming the molecular motion and the crystal structure to be as follows. According to the results of X-ray studies of the high-temperature phase, two molecules are placed at the lattice points 0, 0, 0 and 1/2, 1/2, 1/2 of a body-centered cubic lattice of $a=7.69$ Å, orienting the molecular axis statistically parallel to four body-diagonal directions of the unit cell with equal probabilities. Since no crystal data have been given for the low-temperature phase, the author assumed tentatively that the molecular volume and the packing of the molecules in the crystal lattice are not much changed by the phase transition; the unit cell length and the molecular orientation are taken as the same as in the high-temperature phase.

For the molecular motion, five models are taken into account. In the first one, all of the thermal mitions in the crystal are frozen (abbreviated as Fix.); in the second one, all the methyl groups of the molecule rotate around their own C_3-axes (C_3-Rot.). In the third one, the molecules rotate axially as a whole around the molecular axis, the central C–C bond axis (C_3'-Rot.) in the fourth, the over-all rotational motion of the molecule is about the axis perpendicular to the central C–C axis (C_2-Rot.). The last model is the free spherical rotation of the molecule as a whole around its center of gravity. The parameters employed in the calculation assumed the bond length of C–C to be 1.54 Å, C–H to be 1.1 Å, and all the bond angles of the carbon atom to be tetrahedral angles.

The values of calculated second moments are shown in eighth column of Table 1. By comparing the observed second moments with the calculated

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9) M. M. Perlman and M. Bloom, *Phys. Rev.*, **88**, 1290 (1952).

10) J. W. Powles and H. S. Gutowsky, *J. Chem. Phys.*, **21**, 1695, 1704 (1953).

Table 1. The theoretical and exprimental second moments of solid hexamethylethane, in gauss^2

State of molecular motion	Interaction temperature range	Between three protons in a methyl group	of inter-methyl groups	of inter-molecules	Total	Experimental second moment
Fix.	Below $-190°C$	21.8	6.4	2.4	30.6	45.0
C_3-Rot.	$-160°C$—$-122°C$	5.4	3.8	1.2	10.4	
C_3+C_3'-Rot.		0.6	1.4	0.8	2.8	3.5
$C_3+C_3'+C_2$-Rot.	$-120°C$— Room temp.	0.4	0.8	0.7	1.9	2.2
Free Rot.		0	0	0.7	0.7	

Table 2. Molecular size and entropy changes of transition, fusion, and heat of sublimation

	R_0, Å	R, Å	$\eta=\frac{R-R_0}{R}$	ΔS_t, e. u.	ΔS_f, e. u.	ΔH_s kcal/mol
$(CH_3)_3Si\text{-}Si(CH_3)_3$	7.34	8.50	0.136	10.5	2.51	9.64
$(CH_3)_3C\text{-}C(CH_3)_3$	6.66	7.71	0.136	3.13	4.82	10.36
$Cl_3C\text{-}C(CH_3)_2Cl$	6.46	7.80	0.172	6.54	4.93	—

ones of Table 1, the molecular motion at each temperature range may be presumed. Below $-190°C$, all of the motions will be frozen. The discrepancy between the observed value, 45.0 gauss^2, and the theroetical one, 30.6 gauss^2, may be caused mainly by using the high-temperature crystal structure parameters in the calculation. The abrupt drop of the second moments between $-180°C$ and $-160°C$ is caused by the onset of the C_3+C_3'-Rot. of the molecule, that is, the methyl groups of the molecule rotating around their own C_3-axes (C_3-Rot.) and also about the molecular axis (C_3'-Rot.). Above the transition temperature, $-121°C$, the observed value of the second moment lies between the calculated values of 2.2 gauss^2 of the $C_3+C_3'+C_2$-Rot. model and 0.7 gauss^2 of the free rotational model. Therefore, it may be concluded that the molecule rotates nearly freely at the lattice point in the high-temperature phase. The molecular motion of hexamethylethane in the high-temperature phase resembles that of the case of $Cl_3C\text{-}C(CH_3)_2Cl$ discussed in Ref. 5. Although $(CH_3)_3Si\text{-}Si(CH_3)_3$ has the same number of methyl groups in a molecule as $(CH_3)_3C\text{-}C(CH_3)_3$, the molecular motion in the high-temperature phase is different. In the $(CH_3)_3Si\text{-}Si(CH_3)_3$ case, the observed second moments are smaller than the values calculated by the free rotation model.(8) Skei *et al.* have presumed that the self-diffusion of the molecule as a whole occurred in the plastic phase.

Here, this difference in molecular motion between the two cases will be discussed from the standpoint of molecular packing. The crystals of $(CH_3)_3Si\text{-}Si(CH_3)_3$(6) and $Cl_3C\text{-}C(CH_3)_2Cl$(7) are isostructural with that of $(CH_3)_3C\text{-}C(CH_3)_3$.(3) The unit cell length of $(CH_3)_3Si\text{-}Si(CH_3)_3$ is 8.47 Å,(6) that of $(CH_3)_3C\text{-}C(CH_3)_3$ is 7.69 Å,(3) and that of $Cl_3C\text{-}C(CH_3)_2Cl$ is 7.46 Å.(7) From these data, the shortest intermolecular distances, R_0, in the high-temperature phase are calculated. The required diameter for the free rotation of a molecule, R, is calculated with the bond distances of Si-Si, 2.34 Å;(11) Si-C, 1.88 Å;(11) C-C, 1.54 Å;(12) and C-Cl, 1.76 Å(12), and the van der Waals radii(12) are 2.0 Å for the methyl group and 1.8 Å for chlorine. The obtained values of R_0 and R are shown in Table 2. The difference between R and R_0 of 1.05 Å for $(CH_3)_3C\text{-}C(CH_3)_3$ is smaller than that of 1.16 Å for $(CH_3)_3Si\text{-}Si(CH_3)_3$ or 1.32 Å for $Cl_3C\text{-}C(CH_3)_2Cl$, suggesting that the most favorable molecule to rotate in the crystal lattice is $(CH_3)_3C\text{-}C(CH_3)_3$. This conclusion does not, however, accord with the results of the nuclear magnetic resonance study.

Now, defining η as $(R-R_0)/R$, which will give a criterion of the facility of molecular motion in the solid state, one obtains almost similar values of η for $(CH_3)_3C\text{-}C(CH_3)_3$ and $(CH_3)_3Si\text{-}Si(CH_3)_3$ (see Table 2). This fact indicates the same order of facility of molecular rotation in both crystals. Discussions based on the molecular dimensions and the molecular packing are unsuccessful in interpreting the problem of which molecules favor rotation. These discrepancies arose from assuming that the molecule is fixed at the lattice point, while in the actual state the molecule fluctuates at the lattice point because of the thermal motion. This fluctuation of the molecule is more or less related to the intermolecular interaction.

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11) M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953).

12) L. Pauling, "The Nature of Chemical Bond," 3rd Ed., Cornell Univ. Press, Ithaca, New York (1960), p. 90 for electro-negativity, p. 246 for covalent radii and p. 260 for van der Waals radii.

The intermolecular interaction is given by the heat of sublimation. In Table 2, the heat of sublimation (ΔH_s) of the high-temperature phase, the entropy of transition (ΔS_t), and the entropy of fusion (ΔS_f) are shown. The value of ΔH_s 10.4 kcal/mol for $(CH_3)_3C\text{-}C(CH_3)_3$, larger than the 9.6 kcal/mol for $(CH_3)_3Si\text{-}Si(CH_3)_3$, indicates that the intermolecular interaction of $(CH_3)_3C\text{-}C(CH_3)_3$ is greater than that of $(CH_3)_3Si\text{-}Si(CH_3)_3$. The smaller molecular interaction of the latter suggests that this molecule is more likely to fluctuate. The entropy changes of transition and of fusion support this suggestion. The ΔS_t value for $(CH_3)_3Si\text{-}Si(CH_3)_3$ is greater than that of $(CH_3)_3C\text{-}C(CH_3)_3$, while the ΔS_f of the former is smaller than that of the latter. The ΔS_f value, 2.51 e. u., of $(CH_3)_3Si\text{-}Si(CH_3)_3$[4)] is very close to the value, 2.0 e. u., calculated theoretically for a common entropy of fusion,[13)] whereas the 4.82 e. u. value of $(CH_3)_3C\text{-}C(CH_3)_3$[2)] is greater than 2.0 e. u. The entropy changes of transition and melting show that the rotational motion of the $(CH_3)_3Si\text{-}Si(CH_3)_3$ molecule is excited almost to free rotation at the transition point; then, on melting, the molecule will obtain only the freedom of the translational motion, while in $(CH_3)_3C\text{-}C(CH_3)_3$ the molecular motion is not very much excited in the high-temperature phase.

The considerations from the intermolecular interaction and from the entropy change suggest that the smaller interaction between the molecules of $(CH_3)_3Si\text{-}Si(CH_3)_3$ makes it easy for the molecule to fluctuate at the lattice point, and also gives a chance to produce the free volume, passing through which a molecule transfers from one lattice point to the next.

Therefore, it may be concluded that the difference in the molecular motion between both crystals is mainly caused by the difference in the intermolecular interaction of these crystals.

Some considerations must be added here about the intermolecular interaction. Pitzer[14)] has suggested that bonds between first- and second-row elements should be shorter than the sum of the appropriate covalent radii because of difference in "inner shell" repulsions for the two rows. Actually, the bond distance of C-Si, 1.88 Å, obtained by Huggins[11)] from his electron diffraction measurements is shorter than the sum of the covalent radii[12)] of C and Si, 1.94 Å.[*1] This suggests there may be some differences in bond nature between C-C and Si-Si bonds. Concerning this, the proton magnetic resonance spectra of the tetramethyl derivatives of the group IVb elements have been studied by Alltred and Rochow.[15)] They concluded that the relative electro-negativities are C > Pb > Ge > Sn > Si, contrary to the usually accepted values. The effect of C-C and C-Si bonds on the methyl group was studied by Brown and Webster[16)] by observing the chemical shifts of $(CH_3)_4M$, $(CH_3)_3M\text{-}M(CH_3)_3$, and $(CH_3)_6M_2$ (M=C, Si, Ge or Sn). They showed that the proton magnetic resonance shielding value for $(CH_3)_3Si\text{-}Si(CH_3)_3$, 9.963 ± 0.002, is greater than that for $(CH_3)_3C\text{-}C(CH_3)_3$, 9.130 ± 0.007. The diversities of the bond properties of C-C, C-Si, and Si-Si mentioned above may be connected in some way with the difference in the intermolecular interaction between $(CH_3)_3C\text{-}C(CH_3)_3$ and $(CH_3)_3Si\text{-}Si(CH_3)_3$.

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13) H. Eyring and J. Hirschfelder, *J. Phys. Chem.*, **41**, 249 (1937).

14) K. S. Pitzer, *J. Am. Chem. Soc.*, **70**, 2140 (1948).

[*1] The depatures from additivity of the bond distance have been interpreted by Pauling[12)] as resulting from differences in the "degree of double-bond character." On the other hand, Schomaker and Stevenson (*J. Am. Chem. Soc.*, **63**, 37 (1941)) attributed these depatures to varying "degree of bond polarity."

15) A. L. Alltred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 269 (1958).

16) M. P. Brown and D. E. Webster, *J. Am. Chem. Soc.*, **64**, 698 (1960).