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# Tris(methyldiphenylsilylmethyl)amine

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**Abstract.** Tris(methyldiphenylsilylmethyl)amine, $C_{42}H_{45}NSi_3$, M.W. 648·09, rhombohedral, $R\bar{3}$, $a_{hex}=14{\cdot}942$ (10), $c_{hex}=29{\cdot}743$ (20) Å, $U=5750{\cdot}7$ Å$^3$, $d_m=1{\cdot}126$, $d_c=1{\cdot}123$ g cm$^{-3}$ for $Z=6$, $\mu$(Mo $K\alpha$)$=111$ m$^{-1}$. Monochromated data for 1079 planes were refined to a final $R$ of 0·065; the structure was solved by direct methods. The molecule possesses crystallographic symmetry 3 ($C_3$) and the geometry at the nitrogen atom is pyramidal with C–N–C$=111{\cdot}5$ (9)°; Si–C($sp^2$) is 1·875 and Si–C($sp^3$) is 1·873 Å.

**Introduction.** The transparent crystals show a variety of habits and the first one examined had the axes of a face-centred rhombohedral cell directed along its edges. The dimensions of this cell were measured from zero-layer precession photographs. Intensity measurements on a second crystal with $a_{hex}$ as the oscillation axis were made on a linear diffractometer (Mo $K\alpha$ radiation). Intensities with $I<2\sigma$ were rejected and the remaining 1079 independent planes with $\theta\leq 25°$ were used in the analysis. The structure was solved by direct methods with a program written by us for the Elliott 803B computer. The equivalent positions in the hexagonal cell have no translation vectors apart from those arising from lattice centring, so no negative signs could be found. Of the four unknown symbols used in the process two were indicated by the program to be strongly positive so these were accepted and the remaining two symbols were given a negative sign. The resulting $E$ map was easily interpreted to give the structure. Refinement was carried out by a block-diagonal ($3\times 6$ and $1\times 1$ or $6\times 6$) least-squares pro-

Table 1. *Final coordinates and standard deviations* (Å)

| | *x* | *y* | *z* |
|---|---|---|---|
| Si | 1·5885 (26) | 3·1746 (25) | 7·8003 (22) |
| C(1) | 1·2393 (88) | 1·5272 (85) | 6·6653 (71) |
| C(2) | 1·8035 (105) | 2·6365 (96) | 9·5360 (81) |
| C(3) | 3·4595 (92) | 4·8726 (87) | 7·2704 (77)) |
| C(4) | 4·8232 (99) | 4·7927 (110) | 7·3384 (101) |
| C(5) | 6·2513 (101) | 6·0535 (119) | 7·0338 (107) |
| C(6) | 6·3762 (117) | 7·4249 (113) | 6·6303 (112) |
| C(7) | 5·0540 (131) | 7·5200 (117) | 6·5483 (138) |
| C(8) | 3·6235 (110) | 6·2615 (103) | 6·8531 (112) |
| C(9) | 0·0010 (86) | 3·6628 (86) | 7·7264 (86) |
| C(10) | −0·5106 (106) | 3·8890 (106) | 6·4723 (101) |
| C(11) | −1·7109 (121) | 4·2292 (118) | 6·3965 (129) |
| C(12) | −2·3737 (121) | 4·3533 (116) | 7·5758 (115) |
| C(13) | −1·8952 (126) | 4·1396 (128) | 8·7941 (132) |
| C(14) | −0·7236 (111) | 3·8065 (112) | 8·8696 (105) |
| N | 0·0000 (–) | 0·0000 (–) | 7·1044 (101) |
| H(1*A*) | 2·22 (11) | 1·50 (11) | 6·73 (10) |
| H(1*B*) | 1·07 (11) | 1·63 (11) | 5·80 (10) |
| H(2*A*) | 2·20 (11) | 3·35 (11) | 10·08 (10) |
| H(2*B*) | 0·99 (12) | 1·72 (11) | 9·90 (10) |
| H(2*C*) | 2·60 (12) | 2·24 (11) | 9·62 (11) |
| H(4) | 4·69 (13) | 3·67 (13) | 7·60 (10) |
| H(5) | 7·24 (12) | 5·93 (13) | 6·90 (12) |
| H(6) | 7·26 (13) | 8·31 (13) | 6·48 (10) |
| H(7) | 5·00 (14) | 8·54 (14) | 6·33 (13) |
| H(8) | 2·86 (12) | 6·62 (12) | 7·01 (11) |
| H(10) | 0·01 (12) | 3·73 (13) | 5·60 (11) |
| H(11) | −2·18 (14) | 4·12 (13) | 5·50 (12) |
| H(12) | −3·29 (15) | 4·64 (16) | 7·60 (13) |
| H(13) | −2·37 (14) | 4·28 (15) | 9·53 (13) |
| H(14) | −0·36 (13) | 3·58 (13) | 9·59 (12) |

Table 2. *Final thermal parameters and standard deviations* (Å$^2$) *for the heavy atoms in the form* $exp\,[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2klb^*c^*U_{23}+2hla^*c^*U_{13})]$

All values have been multiplied by $10^4$. For nitrogen $U_{11}=U_{22}=2U_{12}$, $U_{23}=U_{13}=0$ by symmetry.

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $2U_{12}$ | $2U_{23}$ | $2U_{13}$ |
|---|---|---|---|---|---|---|
| Si | 471 (13) | 418 (12) | 517 (11) | 411 (21) | −66 (20) | −81 (20) |
| C(1) | 535 (49) | 451 (45) | 431 (41) | 580 (81) | −62 (69) | 131 (72) |
| C(2) | 710 (58) | 518 (52) | 545 (56) | 445 (94) | −5 (81) | −250 (90) |
| C(3) | 589 (52) | 405 (45) | 506 (47) | 358 (77) | −185 (71) | −146 (75) |
| C(4) | 475 (54) | 697 (63) | 868 (71) | 599 (101) | −158 (101) | −177 (94) |
| C(5) | 381 (53) | 900 (78) | 1003 (76) | 412 (106) | −291 (122) | −83 (101) |
| C(6) | 644 (65) | 571 (66) | 1189 (94) | 267 (105) | 197 (123) | 260 (120) |
| C(7) | 937 (76) | 608 (66) | 1371 (106) | 852 (122) | 365 (128) | 241 (142) |
| C(8) | 589 (60) | 465 (53) | 1085 (80) | 357 (95) | 294 (99) | 279 (108) |
| C(9) | 429 (44) | 419 (47) | 713 (55) | 538 (78) | −96 (77) | −91 (77) |
| C(10) | 610 (60) | 542 (55) | 911 (76) | 478 (97) | 145 (97) | −300 (100) |
| C(11) | 768 (72) | 618 (65) | 1363 (102) | 618 (116) | 218 (130) | −614 (138) |
| C(12) | 741 (73) | 587 (64) | 1804 (131) | 886 (121) | −130 (138) | 204 (146) |
| C(13) | 773 (74) | 862 (77) | 1461 (107) | 963 (127) | −367 (142) | 437 (143) |
| C(14) | 622 (62) | 785 (69) | 887 (69) | 745 (112) | −504 (110) | −41 (101) |
| N | 360 (36) | 360 (–) | 456 (59) | 360 (–) | 0 (–) | 0 (–) |

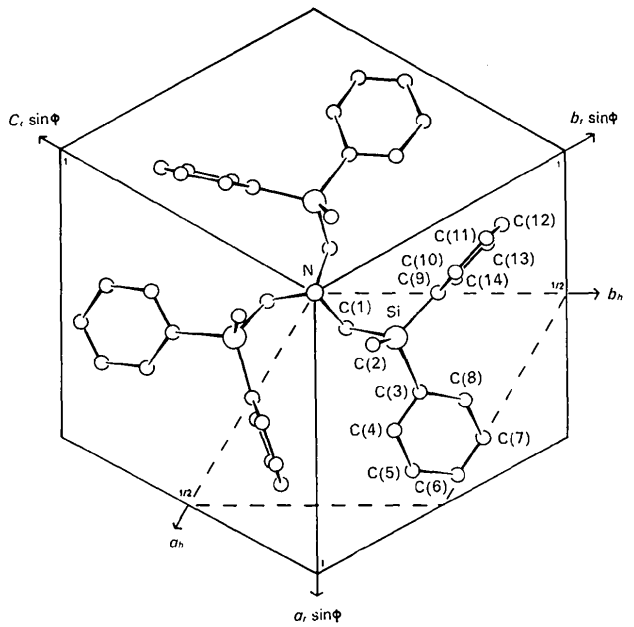


Fig. 1. The $N(CH_2SiPh_2Me)_3$ molecule projected down $c_{hex}$ and the labelling of the atoms. Hydrogen atoms have been omitted for clarity; $\cos\varphi = a_r(1+2\cos\alpha)/c_{hex}$.

Table 3. *Bond lengths* (Å) *and angles* (°) *with standard deviations*

| | | | |
|---|---|---|---|
| Si——C(1) | 1·884 (9) | Si——C(1)—N | 114·8 (5) |
| Si——C(2) | 1·861 (10) | Si——C(3)—C(4) | 119·6 (7) |
| Si——C(3) | 1·868 (9) | Si——C(3)—C(8) | 124·2 (7) |
| Si——C(9) | 1·881 (9) | Si——C(9)—C(10) | 119·7 (7) |
| C(1)—N | 1·473 (10) | Si——C(9)—C(14) | 123·0 (7) |
| C(3)—C(4) | 1·407 (13) | C(4)—C(3)—C(8) | 116·2 (9) |
| C(3)—C(8) | 1·382 (14) | C(3)—C(4)—C(5) | 121·7 (9) |
| C(4)—C(5) | 1·386 (15) | C(4)—C(5)—C(6) | 120·7 (10) |
| C(5)—C(6) | 1·374 (16) | C(5)—C(6)—C(7) | 118·4 (11) |
| C(6)—C(7) | 1·375 (17) | C(6)—C(7)—C(8) | 121·1 (11) |
| C(7)—C(8) | 1·386 (17) | C(7)—C(8)—C(3) | 121·9 (10) |
| C(9)—C(10) | 1·415 (13) | C(14)-C(9)—C(10) | 117·3 (9) |
| C(9)—C(14) | 1·402 (14) | C(9)—C(10)-C(11) | 120·5 (10) |
| C(10)-C(11) | 1·404 (16) | C(10)-C(11)-C(12) | 118·7 (11) |
| C(11)-C(12) | 1·388 (18) | C(11)-C(12)-C(13) | 121·6 (12) |
| C(12)-C(13) | 1·364 (18) | C(12)-C(13)-C(14) | 119·8 (12) |
| C(13)-C(14) | 1·366 (17) | C(13)-C(14)-C(9) | 122·1 (10) |
| C(1)—N-C(1′) | 111·5 (8) | C(2)—Si-C(3) | 108·6 (4) |
| C(1)—Si-C(2) | 107·9 (4) | C(3)—Si-C(9) | 110·2 (4) |
| C(1)—Si-C(3) | 106·7 (4) | C(2)—Si-C(9) | 110·3 (4) |
| C(1)—Si-C(9) | 113·1 (4) | | |

cess, first with isotropic and then with anisotropic temperature factors, and at a later stage hydrogen atoms were included with isotropic temperature factors 0·01 units of $U$ greater than the carbon atoms to which they were bonded. Further refinement of the coordinates converged with $R$ ($\sum|\Delta|/\sum|F_o|$) at 0·065. The quantity minimized was $R'$ ($=\sum w\Delta^2$) with $w^{-1}=(6{\cdot}55+|F_o|+0{\cdot}176|F_o|^2)/8$ if $|F_o|>6{\cdot}55$ or $w^{-1}=(6{\cdot}55/|F_o|)^2(6{\cdot}55+|F_o|+0{\cdot}176|F_o|^2)/8$ if $|F_o|\leq 6{\cdot}55$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962) and all calculations were carried out on an Elliott 803B computer with programs written in this laboratory (Daly, Stephens & Wheatley, 1964). The final parameters appear in Tables 1* and 2 and the bond lengths and angles involving the non-hydrogen atoms in Table 3.

**Discussion.** The compound shows abnormal hydrolytic properties (Fink, 1973) and it was suspected that there might be some unusual intramolecular interaction between silicon and nitrogen, or that the nitrogen valences might be planar as in $N(SiH_3)_3$ (Hedberg, 1955). In fact no unusual features were observed. The molecule has crystallographic symmetry 3 ($C_3$) and shows considerable departures from the higher symmetry $3m$ ($C_{3v}$) (see Fig. 1); models with $3m$ ($C_{3v}$) symmetry show unfavourable intramolecular contacts. The Si–C($sp^2$) average length of 1·875 Å is in good agreement with the value found in $Ph_4Si$ (Glidewell & Sheldrick, 1971; Párkányi & Sasvári, 1973). The average Si–C($sp^3$) length of 1·873 Å may be artificially low since no allowance has been made for the effect of thermal motion on the bond lengths, and the temperature factors of Si and C(2) show considerable differences. Very similar values for Si–C($sp^2$) and Si–C($sp^3$) lengths have been reported previously (Chioccola & Daly, 1963). The standard Si–C($sp^3$) length is 1·870 Å (Sutton, 1965). The average C–C length is 1·387 Å. The nitrogen atom adopts a pyramidal geometry with C–N–C = 111·4° and the bond angles at silicon show small distortions from the tetrahedral value. The ring angles at the carbon atoms bonded to silicon are both less than 120°; a similar distortion was observed in $Ph_4Si$ (Glidewell & Sheldrick, 1971).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30581 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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