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The Crystal and Molecular Structure of 6-(1,1-Dimethylethyl)-12,12-dimethyl-5,6-dihydro-7*H*,12*H*-dibenzo[*c*,*f*][1,5]silazocine

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The structure of the title compound [$C_{20}H_{27}NSi$, triclinic, space group $P\bar{1}$, $a = 9.936$ (2), $b = 11.588$ (3), $c = 8.654$ (3) Å, $\alpha = 101.03$ (2), $\beta = 111.05$ (2), $\gamma = 90.36$ (2)°, $Z = 2$] has been determined by iterative application of the Σ_2 relationship and refined by full-matrix least-squares techniques to a conventional R of 0·041 for 3850 counter reflections. The central ring adopts a distorted boat conformation with a dihedral angle between benzo group planes of 109·3°. The geometry about silicon is that of a distorted trigonal bipyramid, with the N atom of the central ring occupying an axial site; the Si···N transannular distance is 2·951 (2) Å.

Introduction

The crystal structures of three *N*-substituted dibenzazocines – the *N*-methyl derivative (Hardy & Ahmed, 1974*a*), the *N*-*tert*-butyl derivative (Hardy & Ahmed, 1974*b*) and the 3-bromo-*N*-methyl derivative (Ahmed, 1975) – have been determined by X-ray diffraction methods. In this report, the crystal structure of a dibenzosilazocine, the *N*-*tert*-butyl derivative, has been determined with the objective of determining the effect of replacement of CH_2 by $Si(CH_3)_2$ in the central eight-membered ring of these tricyclic systems. The NMR spectra of dibenzosilazocine derivatives exhibit sharp singlets for the methylene protons from room temperature to −60 °C which suggests the presence of the flexible twist-boat conformer in solution (in the absence of accidental isochrony) as reported in dibenzazocine systems (Fraser, Raza, Renaud & Layton, 1975). The presence of this conformer in the solid state was confirmed for 6-(1,1-dimethylethyl)-12,12-dimethyl-5,6-dihydro-7*H*,12*H*-dibenzo[*c*, *f*][1,5]silazocine (Paton, Paton, Corey & Corey, 1975).

Experimental

The title compound was prepared by the reaction of bis(*o*-bromomethylphenyl)dimethylsilane with 1,1-dimethylethylamine in CCl_4 and recrystallized from hexane (Paton, Paton, Corey & Corey, 1975). A crystal 0·61 × 0·53 × 0·49 mm was mounted on a Syntex $P2_1$ diffractometer. The space group was assigned on the basis of rotation and axial photographs and counter data. Fifteen reflections with 2θ greater than 18° were centered with a programmed centering routine; cell parameters (Table 1) were obtained by least-squares refinement of these angles. All reflections with $2\theta \leq 62°$ were measured with the θ–2θ scan technique and a variable scan rate from 2·0 to 10·0° min^{-1}. Backgrounds were measured at each end of the scan [2θ scan range: (2θ)Mo $K\alpha_1$ − 1·0° to (2θ)Mo $K\alpha_1$ + 1·0°] for a total time equal to the scan time. Intensity data were collected with Mo $K\alpha$ (graphite monochromator) radiation. During data collection, the intensities of three standard reflections were measured every 47 reflections with no significant variation in intensity observed. The data were reduced to F^2 and $\sigma(F^2)$ by procedures similar to those previously described (Schmonsees, 1974; Miyake, Togawa & Hosoya, 1964). Standard deviations were assigned as follows: $\sigma(I) = [\sigma_{\text{counter}}(I)^2 + (0.04 \times I)^2]^{1/2}$, where $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$, I = net intensity, B = total background count, and K = ratio of scan time to background time. No corrections were made for absorption, extinction or anomalous dispersion. The 3850 independent data with $F^2 > 3\sigma(F^2)$ from 6254 data scanned were used in the structure solution and refinement.

Table 1. *Crystal data*

$C_{20}H_{27}NSi$	$M_r = 309.53$
Triclinic	$D_c = 1.13$ g cm^{-3}
Space group $P\bar{1}$	$D_m = 1.11$ (2)
$a = 9.936$ (2) Å	$\alpha = 101.03$ (2)°
$b = 11.588$ (3)	$\beta = 111.05$ (2)
$c = 8.654$ (3)	$\gamma = 90.36$ (2)
$U = 909.7$ (4) Å^3	$Z = 2$
λ(Mo $K\alpha$) = 0·71069 Å	μ(Mo $K\alpha$) = 1·34 cm^{-1}

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Structure solution and refinement

The structure was solved by an iterative application of the Σ_2 relationship (Long, 1965; Sayre, 1952) using 244 normalized structure factors of magnitude 1·5 or greater. An E map based on the set of phases for the solution with the largest consistency index (0·97) yielded the positions of the 22 nonhydrogen atoms. Least-squares refinement (Busing, Martin & Levy, 1962) with isotropic thermal parameters gave a discrepancy value $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0{\cdot}115$. A difference Fourier map provided the positions of the H atoms near their ideal locations (Zalkin, 1974). The 27 H atoms were included in subsequent cycles of full-matrix least-squares refinement. Refinement, with anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for H atoms, converged with $R_1 = 0{\cdot}041$ and $R_2 = [\Sigma(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} = 0{\cdot}053$.* Tables 2 and 3 give positional and, for H, thermal parameters with estimated standard deviations. The largest nonhydrogen parameter shift in the final cycle of full-matrix refinement was less than 3% of its standard deviation; all H atom parameter shifts were less than 10% of the standard deviations. The error of fit was 1·80. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The highest residual electron density in the final difference map was 0·21 e Å^{3}.

Table 2. *Final positional parameters* ($\times 10^4$) *for the nonhydrogen atoms with estimated standard deviations in parentheses*

	x	y	z
C(1)	1282 (2)	1128 (1)	5017 (2)
C(2)	2015 (2)	216 (1)	4470 (2)
C(3)	3306 (2)	−44 (2)	5581 (2)
C(4)	3840 (2)	585 (2)	7228 (2)
C(5)	3828 (2)	2156 (2)	9613 (2)
N(6)	2788 (1)	2596 (1)	10390 (1)
C(7)	1761 (2)	1636 (1)	10284 (2)
C(8)	−689 (2)	1566 (1)	10484 (2)
C(9)	−2124 (2)	1817 (2)	10013 (2)
C(10)	−2681 (2)	2464 (2)	8788 (2)
C(11)	−1804 (2)	2846 (1)	8017 (2)
Si(12)	691·0 (5)	3032·2 (4)	7180·0 (5)
C(13)	1813 (2)	1806 (1)	6671 (2)
C(14)	3123 (2)	1507 (1)	7794 (2)
C(15)	211 (1)	1959 (1)	9738 (2)
C(16)	−345 (1)	2603 (1)	8458 (2)
C(17)	−744 (2)	3155 (2)	5101 (3)
C(18)	1718 (3)	4509 (2)	7993 (3)
C(19)	3501 (2)	3321 (1)	12149 (2)
C(20)	2324 (2)	3813 (2)	12777 (3)
C(21)	4456 (2)	2606 (2)	13393 (3)
C(22)	4448 (3)	4366 (2)	12143 (3)

Table 3. *Hydrogen-atom final position parameters* ($\times 10^3$) *and isotropic thermal parameters with estimated standard deviations in parentheses*

	x	y	z	B (Å^2)
H′(Cl)	34 (2)	127 (2)	422 (2)	2·1 (4)
H′(C2)	158 (2)	−25 (2)	335 (2)	2·8 (4)
H′(C3)	385 (2)	−70 (2)	527 (2)	3·2 (4)
H′(C4)	465 (2)	41 (2)	800 (3)	3·2 (4)
H′(C5)	454 (2)	163 (2)	1023 (2)	3·0 (4)
H″(C5)	444 (2)	283 (2)	963 (2)	3·3 (4)
H′(C7)	204 (2)	137 (1)	1134 (2)	1·6 (3)
H″(C7)	182 (2)	95 (1)	942 (2)	1·7 (3)
H′(C8)	−30 (2)	111 (2)	1135 (2)	1·7 (3)
H′(C9)	−268 (2)	156 (2)	1058 (2)	3·0 (4)
H′(C10)	−369 (2)	263 (2)	840 (2)	3·2 (4)
H′(C11)	−223 (2)	330 (2)	715 (2)	2·3 (4)
H′(C17)	−123 (3)	381 (2)	526 (3)	5·3 (6)
H″(C17)	−142 (3)	241 (2)	455 (3)	4·4 (6)
H‴(C17)	−35 (2)	328 (2)	429 (3)	4·8 (6)
H′(C18)	265 (3)	451 (2)	861 (3)	5·9 (7)
H″(C18)	124 (4)	497 (3)	856 (4)	8·7 (10)
H‴(C18)	164 (4)	474 (3)	708 (5)	8·8 (10)
H′(C20)	171 (3)	318 (2)	1296 (3)	4·3 (5)
H″(C20)	164 (3)	425 (2)	1193 (3)	4·4 (5)
H‴(C20)	273 (2)	440 (2)	1389 (3)	3·6 (5)
H′(C21)	526 (3)	237 (2)	1308 (3)	6·4 (7)
H″(C21)	394 (3)	182 (3)	1335 (3)	5·5 (6)
H‴(C21)	483 (3)	307 (2)	1441 (3)	4·8 (6)
H′(C22)	396 (3)	482 (2)	1131 (3)	4·3 (6)
H″(C22)	528 (3)	412 (2)	1194 (3)	3·6 (5)
H‴(C22)	479 (3)	486 (2)	1330 (3)	4·5 (5)

Discussion

A perspective view of the molecular structure showing the conformation and the numbering system is shown in Fig. 1 (Johnson, 1965). Table 4 gives the interatomic bond lengths and angles, excluding those that involve H atoms (Busing, Martin & Levy, 1964). The Si–C and C–C distances of the benzo groups are in agreement with values reported for related silicon heterocycles (Paton, Cody, Corey, Corey & Glick, 1976, and references therein); the C–N and C(benzo)–C(methylene) distances are similar to the values reported for dibenzazocines (Ahmed, 1975, and references therein). The mean values of the various bond types are: Si–C 1·881, N–C 1·480, C–C in benzo groups 1·392, C–C in the *tert*-butyl group 1·532, and C–H 0·96 Å (range: 0·86–1·03 Å). Intermolecular packing distances are normal; a stereoscopic drawing of the unit-cell contents and the molecular packing is given in Fig. 2.

The central ring in the title compound adopts a distorted boat conformation (Gellatly, Ollis & Sutherland, 1976) similar to that reported as twist-boat for the

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* Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms and least-squares planes of the benzo rings have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32704 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

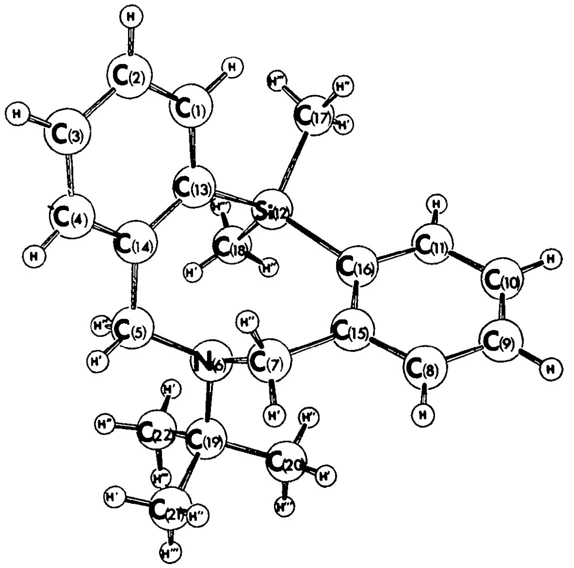

Fig. 1. Perspective view of the 6 (1,1-dimethylethyl)-12,12-dimethyl-5,6-dihydro-7*H*,12*H*-dibenzo[*c*,*f*][1,5]silazocine molecule.

Table 4. *Interatomic bond lengths* (Å) *and angles* (°)

C(1)–C(2)	1·391 (2)	C(9)–C(10)	1·371 (3)
C(1)–C(13)	1·403 (2)	C(10)–C(11)	1·388 (2)
C(2)–C(3)	1·375 (3)	C(11)–C(16)	1·406 (2)
C(3)–C(4)	1·378 (2)	Si(12)–C(13)	1·893 (2)
C(4)–C(14)	1·396 (2)	Si(12)–C(16)	1·885 (1)
C(5)–N(6)	1·468 (2)	Si(12)–C(17)	1·884 (2)
C(5)–C(14)	1·511 (2)	Si(12)–C(18)	1·862 (2)
N(6)–C(7)	1·472 (2)	C(13)–C(14)	1·409 (2)
N(6)–C(19)	1·501 (2)	C(15)–C(16)	1·404 (2)
C(7)–C(15)	1·512 (2)	C(19)–C(20)	1·528 (2)
C(8)–C(9)	1·384 (2)	C(19)–C(21)	1·537 (3)
C(8)–C(15)	1·395 (2)	C(19)–C(22)	1·530 (2)
C(2)–C(1)–C(13)	122·5 (2)	C(1)–C(13)–Si(12)	116·7 (1)
C(1)–C(2)–C(3)	119·5 (2)	C(1)–C(13)–C(14)	116·9 (1)
C(2)–C(3)–C(4)	119·5 (2)	Si(12)–C(13)–C(14)	126·3 (1)
C(3)–C(4)–C(14)	121·7 (2)	C(4)–C(14)–C(5)	117·1 (1)
N(6)–C(5)–C(14)	113·5 (1)	C(4)–C(14)–C(13)	119·8 (1)
C(5)–N(6)–C(7)	111·3 (1)	C(5)–C(14)–C(13)	123·0 (1)
C(5)–N(6)–C(19)	113·0 (1)	C(7)–C(15)–C(8)	118·9 (1)
C(7)–N(6)–C(19)	113·1 (1)	C(7)–C(15)–C(16)	121·3 (1)
N(6)–C(7)–C(15)	113·1 (1)	C(8)–C(15)–C(16)	119·8 (1)
C(9)–C(8)–C(15)	121·4 (2)	C(11)–C(16)–Si(12)	118·5 (1)
C(8)–C(9)–C(10)	119·7 (1)	C(11)–C(16)–C(15)	117·3 (1)
C(9)–C(10)–C(11)	119·6 (2)	Si(12)–C(16)–C(15)	123·9 (1)
C(10)–C(11)–C(16)	122·2 (2)	N(6)–C(19)–C(20)	108·5 (1)
C(13)–Si(12)–C(16)	111·0 (1)	N(6)–C(19)–C(21)	112·6 (1)
C(13)–Si(12)–C(17)	106·2 (1)	N(6)–C(19)–C(22)	110·4 (1)
C(13)–Si(12)–C(18)	113·2 (1)	C(20)–C(19)–C(21)	109·2 (2)
C(16)–Si(12)–C(17)	104·7 (1)	C(20)–C(19)–C(22)	107·9 (2)
C(16)–Si(12)–C(18)	116·2 (1)	C(21)–C(19)–C(22)	108·1 (2)
C(17)–Si(12)–C(18)	104·4 (1)		

N-tert-butyl derivative of dibenzazocine (Hardy & Ahmed, 1974*b*). The central-ring torsion angles (presented in Table 5) which involve C and N atoms are comparable to the corresponding angles in the dibenzazocine molecule. The dihedral angle of 108·1° between the benzo groups of the *N-tert*-butyl azocine [calculated from reported atomic coordinates (Hardy & Ahmed, 1974*b*)] differs little from the value of 109·3° between the least-squares planes of the benzo groups of the title compound.

A transannular interaction has been proposed to explain the distortion of geometry at the silicon from tetrahedral toward that of trigonal bipyramidal in a series of Si–N heterocycles containing eight-membered rings (Turley & Boer, 1968; Boer, Turley & Flynn, 1968; Turley & Boer, 1969; Boer & Turley, 1969; Daly & Sanz, 1974). In these silane derivatives, the Si–N transannular distances are from 2·34 to 2·12 Å; distances which may be assigned bond orders of 0·38 to 0·60 (Dräger, 1976). If either of the values 2·72 Å (Dräger, 1976) or 2·69 Å (Glidewell, 1975) is used to

Table 5. *Torsion angles* (°) *about the central ring*

C(5)–N(6)	56·0 (2)	C(16)–Si(12)	38·4 (1)
N(6)–C(7)	−135·2 (1)	Si(12)–C(13)	−76·0 (1)
C(7)–C(15)	40·8 (2)	C(13)–C(14)	−0·4 (2)
C(15)–C(16)	4·8 (2)	C(14)–C(5)	33·3 (2)

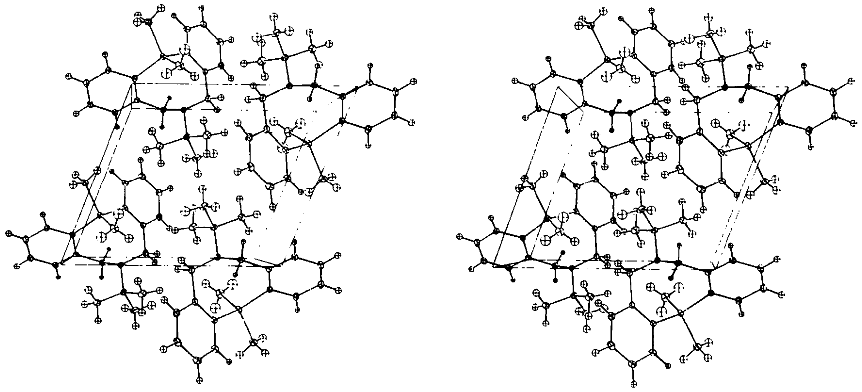

Fig. 2. A stereoscopic view of the unit-cell contents viewed down the *b* axis (the origin is at the upper left rear corner of the cell, the *a* axis is horizontal in the page, the *c* axis vertical in the page).

Table 6. *Interatomic angles* (°) *about silicon*

The idealized trigonal-bipyramidal angles are 180° for the first entry, 90° for entries 2 through 7 and 120° for the last three entries.

C(17)–Si(12)···N(6)	174·0 (1)
C(17)–Si(12)–C(13)	106·2 (1)
C(17)–Si(12)–C(16)	104·7 (1)
C(17)–Si(12)–C(18)	104·4 (1)
N(6)···Si(12)–C(13)	71·5 (1)
N(6)···Si(12)–C(16)	71·6 (1)
N(6)···Si(12)–C(18)	81·5 (1)
C(13)–Si(12)–C(16)	111·0 (1)
C(16)–Si(12)–C(18)	116·2 (1)
C(13)–Si(12)–C(18)	113·2 (1)

define the maximum distance that can be considered a bonding interaction between Si and N, the transannular distance of 2·951 (2) Å in the title compound implies only a weak interaction. The geometry about Si (Table 6) is distorted from that of a regular tetrahedron toward that of a trigonal bipyramid, as may be expected for such a weak interaction. In a recent study a N···C=O transannular distance of 2·76 Å was determined for 1-*p*-tolyl-1-azacyclooctan-5-one (Kaftory & Dunitz, 1975), and attributed to a weak donor–acceptor interaction such as may occur in a nucleophilic addition to a carbonyl group.

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