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2,8-Dibromo-5-ethyl-5,10-dihydro-10,10-dimethylphenazasiline

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Abstract. $C_{16}H_{17}Br_2NSi$, $M_r = 411{\cdot}22$; monoclinic; $P2_1/c$, $a = 9{\cdot}111\ (7)$, $b = 9{\cdot}451\ (12)$, $c = 19{\cdot}653\ (15)$ Å, $\beta = 99{\cdot}65\ (6)°$; $Z = 4$, $D_m = 1{\cdot}61\ (2)$, $D_c = 1{\cdot}64$ g cm^{-3}; $U = 1668{\cdot}3$ Å^3; μ(Mo $K\alpha$) = 52·2 cm^{-1}. The molecule adopts a folded conformation with a dihedral angle between benzo-group planes of 140·9°. The C–Si–C angle in the central ring is 98·7°; the mean C–Si bond length is 1·85 (2) Å. The sum of the angles about N is 358·2°.

Introduction. The title compound was prepared by the reaction of bis(2,4-dibromophenyl)ethylamine with *n*-butyllithium followed by ring closure with dichlorodimethylsilane. The product was purified and recrystallized from ethanol.† A crystal 0·25 × 0·22 × 0·22 mm was mounted on a Syntex $P2_1$ diffractometer and data were collected to $2\theta = 50°$ with Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å) radiation (graphite monochromator) and the θ–2θ scan technique at 2° min^{-1}. Backgrounds were measured at each end of the scan (2θ scan range: 2θMo $K\alpha_1 - 1{\cdot}0°$ to 2θMo $K\alpha_2 + 1{\cdot}0°$) for a total time equal to one-half the scan time. Systematic absences were $h0l$ l odd, $0k0$ k odd, uniquely determining the space group $P2_1/c$. Fifteen reflections with 2θ between 12 and 22° were centered with a programmed centering routine; cell parameters were obtained by least-squares refinement of these angles. During data collection the intensities of three standard reflections were measured every 97 reflections with no significant variation observed in intensity. The data were reduced to F_o^2 and $\sigma(F_o^2)$ by procedures similar to those described previously (Schmonsees, 1974). Standard deviations were assigned as follows: $\sigma(I) = [\sigma_{\rm counter}(I)^2 + (0{\cdot}03\ I)^2]^{1/2}$, where $\sigma_{\rm counter} = (I + K^2B)^{1/2}$, I = net intensity, B = total background count, and K = ratio of scan time to background time. No corrections for absorption were made. The 1328 data with $F_o^2 > 2\sigma(F_o^2)$ from 3228 data

Table 1. *Final positional* (×10^4) *and anisotropic thermal* (×10^4) *parameters with estimated standard deviations in parentheses*

Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	750 (15)	2579 (17)	680 (7)	79 (22)	142 (24)	18 (4)	−25 (21)	−3 (8)	11 (9)
C(2)	−633 (18)	2940 (16)	319 (7)	198 (31)	136 (29)	18 (4)	−37 (25)	22 (10)	−10 (9)
C(3)	−1506 (18)	4067 (20)	490 (7)	175 (32)	203 (33)	21 (5)	−63 (26)	−9 (10)	−15 (11)
C(4)	−892 (17)	4884 (15)	1073 (8)	151 (30)	123 (26)	40 (6)	19 (22)	22 (12)	−1 (11)
N(5)	1075 (13)	5398 (13)	2046 (6)	116 (22)	63 (20)	21 (4)	24 (16)	6 (8)	1 (7)
C(6)	1595 (15)	5224 (15)	3300 (7)	98 (26)	106 (25)	22 (5)	36 (19)	8 (9)	2 (9)
C(7)	2320 (18)	4609 (17)	3893 (7)	153 (31)	133 (29)	19 (5)	12 (24)	17 (10)	−1 (10)
C(8)	3313 (16)	3541 (15)	3867 (7)	105 (25)	81 (26)	21 (5)	38 (20)	1 (9)	17 (8)
C(9)	3637 (16)	3045 (16)	3241 (7)	129 (25)	96 (24)	19 (5)	−18 (19)	14 (9)	−5 (9)
Si(10)	3228 (4)	3144 (4)	1744 (2)	86 (6)	84 (6)	15 (1)	13 (5)	8 (2)	2 (2)
C(11)	1333 (15)	3424 (16)	1264 (6)	74 (22)	106 (25)	16 (4)	0 (20)	9 (8)	2 (8)
C(12)	518 (17)	4557 (17)	1460 (7)	76 (24)	104 (25)	17 (5)	3 (21)	−1 (9)	10 (9)
C(13)	1882 (15)	4755 (15)	2655 (7)	69 (22)	73 (22)	16 (4)	9 (19)	2 (8)	6 (8)
C(14)	2898 (14)	3683 (15)	2624 (6)	61 (22)	73 (21)	12 (4)	16 (17)	−6 (7)	4 (7)
C(15)	4553 (15)	4373 (16)	1429 (7)	74 (25)	163 (28)	21 (5)	−24 (20)	−5 (8)	−5 (9)
C(16)	3839 (17)	1294 (16)	1724 (7)	161 (31)	152 (28)	19 (5)	2 (23)	5 (9)	−3 (9)
C(17)	501 (16)	6858 (18)	2098 (7)	138 (29)	116 (26)	20 (5)	5 (24)	13 (9)	−2 (9)
C(18)	1725 (18)	7890 (17)	2350 (8)	216 (36)	104 (28)	32 (6)	−30 (24)	2 (11)	−11 (11)
Br(19)	−1463 (2)	1827 (2)	−474 (1)	190 (3)	211 (3)	17 (1)	−57 (3)	−2 (1)	−9 (1)
Br(20)	4285 (2)	2672 (2)	4696 (1)	202 (3)	234 (4)	17 (1)	44 (3)	2 (1)	13 (1)

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† Details of the synthetic procedures will be published at a later date.

scanned were used in the structure solution and refinement.

The structure was solved by an iterative application of the Σ_2 relationship (Long, 1965; Sayre, 1952) with 101 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 (0·996) gave the positions of the atoms for the major part of the structure; the additional atoms were located from a difference map. Least-squares refinement (Busing, Martin & Levy, 1962) of the nonhydrogen atoms with isotropic thermal parameters gave an $R_1 = \Sigma \| F_o| - |F_c\| / \Sigma |F_o| = 0{\cdot}159$. Refinement was continued with anisotropic thermal parameters for the non-hydrogen atoms; the H atoms were included in the calculations at ideal locations (Zalkin, 1974) with fixed H distances of 1·0 Å and isotropic thermal parameters 10% larger than the equivalent isotropic B's of the atoms to which they are bonded. The Br and Si scattering factors were corrected for anomalous dispersion. Tables 1 and 2 give final positional and thermal parameters wilth associated estimated standard deviations. Final discrepancy values were $R_1 = 0{\cdot}064$ and $R_2 = [\Sigma(w|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} = 0{\cdot}067$. The largest parameter shift in the final cycle of full-matrix refinement was less than 10% of its standard deviation; the error of fit was 2·31. Atomic scattering factors and real and imaginary anomalous dispersion corrections were

Table 2. *Final hydrogen-atom positional parameters* ($\times 10^3$) *and thermal parameters*

Isotropic thermal parameters have been assigned fixed values 10% greater than the equivalent B's of the atoms bonded to the H atoms.

	x	y	z	B (Å^2)
H(C1)	132	176	54	3·5
H(C3)	−251	428	22	5·2
H(C4)	−147	571	121	5·4
H(C6)	86	600	332	3·6
H(C7)	212	495	435	4·4
H(C9)	437	226	323	3·7
H'(C15)	425	537	150	3·8
H''(C15)	455	420	93	3·8
H'''(C15)	558	421	169	3·8
H'(C16)	383	100	123	4·7
H''(C16)	315	68	194	4·7
H'''(C16)	487	120	199	4·7
H'(C17)	−23	686	243	4·1
H''(C17)	−1	716	163	4·1
H'(C18)	245	790	202	5·4
H''(C18)	224	760	282	5·4
H'''(C18)	129	886	238	5·4

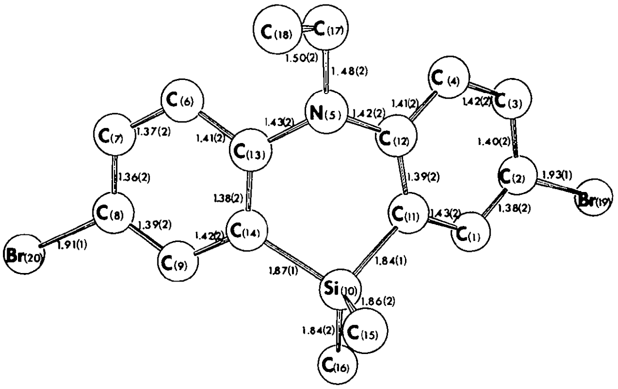

Fig. 1. Interatomic bond distances.

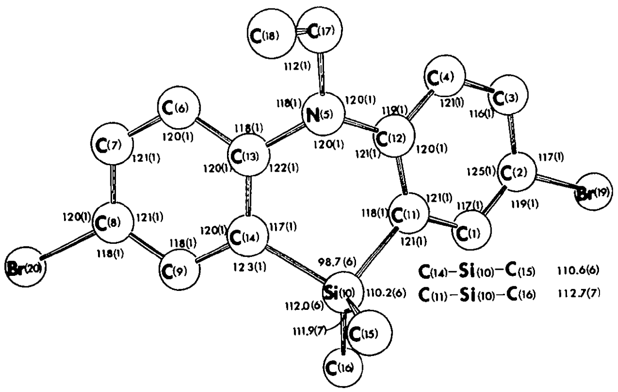

Fig. 2. Interatomic bond angles.

Table 3. *Least-squares planes and displacements* (Å) *of atoms from the planes*

Equations of planes: $AX + BY + CZ = D$, where X, Y, Z are orthogonal unit vectors defined by the equation $X = \mathbf{a}$, $Y = \mathbf{b}$, $Z = \mathbf{a} \times \mathbf{b}$. Atoms not included in the plane calculation are indicated by asterisks.

Plane	A	B	C	D
1	0·536	0·608	−0·586	0·960
2	−0·740	−0·671	−0·048	−3·894
3	0·694	0·648	−0·314	1·887

Benzo group planes				Plane of central ring benzo carbons	
(1)		(2)		(3)	
C(1)	0·00	N(5)*	0·06	N(5)*	0·38
C(2)	0·00	C(6)	0·00	Si(10)*	0·62
C(3)	0·00	C(7)	−0·01	C(11)	−0·01
C(4)	0·00	C(8)	0·00	C(12)	0·01
N(5)*	−0·02	C(9)	0·00	C(13)	−0·01
Si(10)*	0·14	Si(10)*	−0·01	C(14)	0·01
C(11)	0·00	C(11)*	1·02		
C(12)	0·00	C(12)*	0·88		
C(13)*	−0·79	C(13)	0·00		
C(14)*	−0·87	C(14)	0·00		
Br(19)*	0·00	Br(20)*	0·02		

Table 4. *Torsion angles* (°) *about the central ring*

Si(10)–C(14)	−34 (1)	N(5)–C(12)	−38 (2)
C(14)–C(13)	2 (2)	C(12)–C(11)	−5 (2)
C(13)–N(5)	40 (2)	C(11)–Si(10)	36 (1)

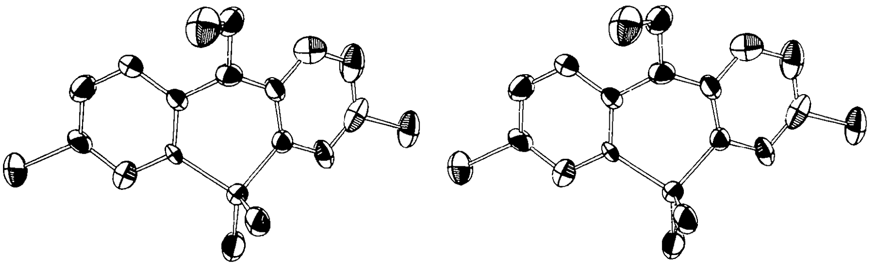

Fig. 3. A stereoscopic view of the molecule. The atoms are represented by 50% probability thermal ellipsoids.

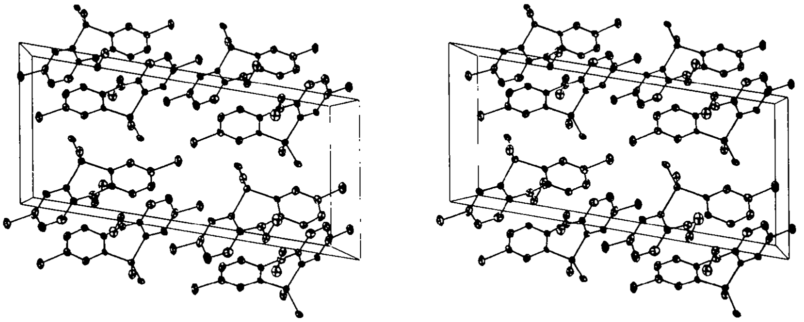

Fig. 4. A stereoscopic view of the unit-cell contents, excluding H atoms, viewed down **b**.

taken from *International Tables for X-ray Crystallography* (1974). The highest residual electron density in the final difference map was 0·60 e Å^{-3}.*

Discussion. 2,8-Dibromo-5-ethyl-5,10-dihydro-10,10-dimethylphenazasiline is one of a group of Si analogs of phenothiazine derivatives which are presently under investigation in an attempt to correlate the spatial characteristics of the tricyclic framework with heteroatom substitution in the central ring. The title compound adopts a folded conformation with the ethyl substituent extending toward the convex side of the tricyclic framework.

The molecule, excluding H atoms, is shown in Figs. 1 and 2 with the values of interatomic bond distances and angles included (Johnson, 1965; Busing, Martin & Levy, 1964). Least-squares planes are given in Table 3. Torsion angles about the central ring are presented in Table 4. A stereoscopic view of the nonhydrogen atoms in the asymmetric unit is shown in Fig. 3.

The conformation adopted by the title compound is similar to that of the reported *N*-alkyphenothiazines (Chu & van der Helm, 1974, 1975, 1976).† The deviation of the phenazasiline from the observed correlation of dihedral angle with the C—N—C bond angle in the central ring of the phenothiazines (Chu & van der Helm, 1975) can be explained in terms of the increased X—C bond length when X = Si.

The packing of the molecules of the title compound in the crystal is shown in the stereoscopic drawing, Fig. 4. There are no intermolecular contacts less than van der Waals distances. The closest intermolecular distance is 3·58 (2) Å between C(13) and C(17).

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* A list of structure factors has been deposited with the British Lending Division as Supplementary Publication No. SUP 32015 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† A table with comparison of structural features of these phenothiazines and the phenazasiline has been deposited with the structure factors. See previous footnote.

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Structural Studies of Highly Strained Hydrocarbons.
II. The *A—C′—C* Stereoisomer of Dodecahydrotriptycene

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Abstract. $C_{20}H_{26}$, triclinic, $P\bar{1}$, $Z = 2$, $a = 11{\cdot}101$ (3), $b = 10{\cdot}077$ (3), $c = 6{\cdot}696$ (2) Å, $\alpha = 86{\cdot}09$ (6), $\beta = 93{\cdot}81$ (6), $\gamma = 84{\cdot}96$ (6)° (from least-squares refinement of diffractometer data); $V = 742{\cdot}77$ Å^3, $D_x = 1{\cdot}19$, $D_m = 1{\cdot}17$ (3) g cm^{-3}. Crystals of quality suitable for X-ray analysis were obtained by slow evaporation from a benzene solution. The molecule contains two cyclohexane rings in the boat conformation *cis* bonded to a bicyclooctane cage.

Introduction. As part of a study of highly strained hydrocarbons, undertaken to determine their conformational properties in the solid state, we have studied the crystal structure of the title compound, which is a stable intermediate in the hydrogenation of triptycene. With the nomenclature of Brückner & Allegra (1976) this compound is the *A—C′—C* stereoisomer, where *A* refers to the presence of an aromatic ring and *C′* and *C* (in clockwise succession) refer to the arrangement of the cyclohexane rings along each of the bridges of the bicyclooctane moiety (Fig. 1). The prime indicates an anticlockwise orientation for one cyclohexane ring, as can be seen along the C_3 axis of the bicyclooctane cage.

The structure is also interesting with regard to the clarification of the nature of the intermediate steps in the hydrogenation reaction leading to a mixture of perhydrotriptycene isomers (Morandi, Mantica, Botta, Gramegna & Farina, 1973; Farina, Morandi, Mantica & Botta, 1976). Compared with other partially hydrogenated products (Farina *et al.*, 1976), this compound shows a remarkable resistance to complete hydrogenation.

The intensities of 2587 reflexions were collected up to $2\theta = 50°$ (graphite-monochromated Mo $K\alpha$ radiation) with a Philips automated four-circle diffractometer and the $\omega/2\theta$ scan technique (scan speed $0{\cdot}10°$ s^{-1}, scan range $1{\cdot}20°$). Two background counts (4 s each) for each reflexion were averaged. Three standard reflexions were measured every hour to check stability. No significant variations were observed. No absorption or extinction corrections were found necessary. 1915 reflexions with $I > 2{\cdot}5\sigma(I)$ were considered observed.

The structure was solved with *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974); all the C atoms were found on the *E* map and all the H atoms on a difference map. Block-diagonal refinement

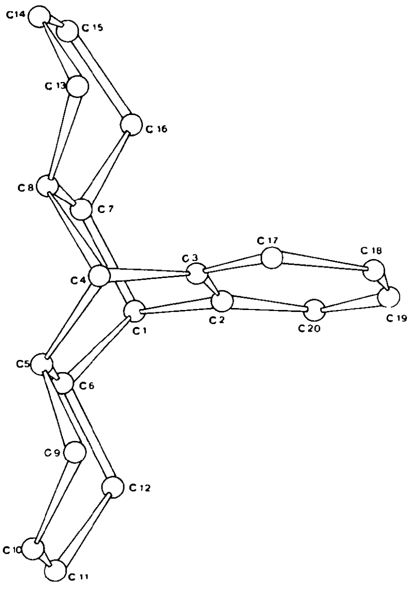

Fig. 1. A view of the molecule showing the numbering of the atoms.