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1,10-Bis(trimethylsilyl)phenothiazine

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Abstract. $C_{18}H_{25}NSSi_2$, $M_r = 343\cdot6$, monoclinic, Cc, $a = 13\cdot674\ (6)$, $b = 13\cdot983\ (5)$, $c = 10\cdot186\ (3)$ Å, $\beta = 93\cdot8\ (3)^\circ$, $V = 1943\ (1)$ Å^3, $Z = 4$, $D_x = 1\cdot17$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0\cdot71073$ Å, $\mu = 2\cdot8$ cm^{-1}, $F(000) = 1472$, $T = 296$ K, $R = 0\cdot039$ for 1555 observed reflections. The easy preparation and observed geometry of the title compound show that the phenothiazine ring system with the N atom substitutent in the synclinal (quasi-axial or *extra*) conformation (presumed necessary for antidepressant activity) can accommodate very bulky substituents in the 1- and 10-positions simultaneously; steric repulsion is relieved by bending of the bulky groups away from one another.

Introduction. Until very recently, all of the many X-ray studies on phenothiazine derivatives related to the antipsychotic promazine showed the N(10) substituent to be in flattened synperiplanar [quasi-equatorial or *intra* (Malreau & Pullman, 1964)] positions (Bell, Blount, Briscoe & Freeman, 1968; Marsau & Cam, 1973; Marsau & Busetta, 1973; Malmstrom & Cordes, 1973; Chu & van der Helm, 1974, 1975, 1976; Phelps & Cordes, 1976; Chu & Yang, 1977; Chu, Napoleone, Ternay & Chang, 1982*a*,*b*), as depicted in Fig. 1 for 10-methylphenothiazine (1) (Chu & van der Helm, 1974). Even with a 1-isopropyl substituent, the N(10) proton was found in this conformation (Chu, Napoleone, Ternay & Chang, 1982*a*). Recently, however, two derivatives bearing both N(10) and C(1)

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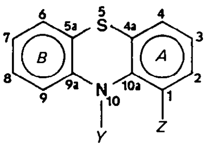
substituents, *i.e.* 1-isopropyl-10-methylphenothiazine (3) (Chu, Narayana & Rosenstein, 1984) and 1-chloro-10-[3-(dimethylamino)propyl]phenothiazine (2) (Martin, Hallberg, Kramer, Svensson, Bates & Ortega, 1984), have been found to have somewhat flattened synclinal [quasi-axial or *extra* (Malreau & Pullman, 1964)] conformations due to steric interactions between the 1- and 10-substituents. The change in activity from neuroleptic for promazine (synperiplanar 10-substituent) to antidepressant for (2) (synclinal 10-substituent) was attributed to the conformational difference in the 10-substituent. We recently found a dimetalation route to 1,10-disubstituted phenothiazines (Svensson & Martin, 1985) and now report the preparation by this route of 1,10-bis(trimethylsilyl)-phenothiazine (4), which has much bulkier 1- and 10-substituents than those of (2) and (3), and a comparison of its geometry, obtained *via* an X-ray study, with that of (2) and (3).



	Y	Z
(1)	Me	H
(2)	$(CH_2)_3NHMe_2^+\ Br^-$	Cl
(3)	Me	*i*-Pr
(4)	$Me_3\overset{1}{S}i$	$Me_3\overset{2}{S}i$

Experimental. (4) was prepared by the dropwise addition of 14·5 ml (23·2 mmol) of 1·65 *N* *n*-butyllithium in hexane to a stirred solution of 2·3 g (7·75 mmol) of 1-bromophenothiazine and 2·9 ml (23 mmol) of trimethylsilyl chloride in anhydrous ether at 195 K. After 4 h, water was added and the organic phase was separated, extracted, dried (anhydrous magnesium sulfate) and evaporated and the residue chromatographed (silica, 95:5 hexanes/ethyl acetate) to give 0·4 g (15%) of pale-yellow prisms from hexane, m.p. 378–380 K, NMR ($CDCl_3$): δ 7·5–7·0 (*m*, 7H, arom.), 0·39 [*s*, 9H, $NSi(CH_3)_3$], 0·09 [*s*, 9H, $CSi(CH_3)_3$]. M_r calc. for $C_{18}H_{25}NSSi_2$: 343·1246. Found (high-resolution MS): 343·1245.

Pale-yellow prism, 0·4 × 0·4 × 0·5 mm. Four-circle Syntex $P2_1$ diffractometer. Cell constants from 25 reflections with $15 < 2\theta < 25°$. Graphite-monochromated Mo $K\alpha$ radiation, θ–2θ scan technique, $0 < 2\theta < 50°$. Range of *hkl*: 0–16, 0–16, −12–12. Two check reflections collected every 98 data points showed negligible crystal decay. 1555 of 1735 reflections with $I > 3\sigma(I)$. Lp but no absorption or extinction correction. $R_{\rm int} = 0·021$. Direct methods (*MULTAN*80, Main *et al.*, 1980). Positional and anisotropic thermal parameters for all non-H atoms refined (on F^2) by full-matrix least squares. Most H atoms found on difference maps, rest put in calculated positions with $B = 5·0$ Å^2. $R = 0·039$, $wR = 0·050$, $S = 2·3$. Weighting scheme of Corfield, Doedens & Ibers (1967) with $p = 0·03$. $(\Delta/\sigma)_{\rm max} = 0·01$. $\Delta\rho = -0·3$–$0·3$ e Å^{-3}. Atomic scattering factors from Cromer & Waber (1974). Programs *SDP* (Frenz, 1978), including plotter program *ORTEP* (Johnson, 1976), run on PDP 11/34.

Table 1. *Positional and equivalent isotropic thermal parameters and their e.s.d.'s*

	x	*y*	*z*	$B_{\rm eq}$*(Å^2)
S(5)	0·500	0·7785 (1)	0·500	4·79 (3)
Si(1)	0·6254 (1)	0·65932 (9)	0·2025 (1)	3·98 (2)
Si(2)	0·7574 (1)	0·91557 (9)	0·1306 (1)	3·60 (2)
N(10)	0·6564 (3)	0·7543 (3)	0·3128 (3)	3·21 (7)
C(10a)	0·6082 (3)	0·8452 (3)	0·3036 (4)	2·93 (7)
C(1)	0·6395 (3)	0·9174 (3)	0·2176 (4)	3·41 (8)
C(2)	0·5823 (3)	1·0008 (3)	0·2073 (4)	3·88 (9)
C(3)	0·5033 (4)	1·0157 (3)	0·2827 (5)	4·3 (1)
C(4)	0·4793 (3)	0·9518 (4)	0·3725 (5)	4·3 (1)
C(4a)	0·5308 (3)	0·8629 (3)	0·3834 (4)	3·60 (9)
C(5a)	0·6196 (4)	0·7337 (3)	0·5430 (5)	4·2 (1)
C(6)	0·6464 (5)	0·7050 (4)	0·6714 (5)	5·4 (1)
C(7)	0·7369 (5)	0·6657 (4)	0·7002 (5)	5·9 (1)
C(8)	0·8021 (4)	0·6551 (4)	0·6029 (6)	5·6 (1)
C(9a)	0·6852 (3)	0·7247 (3)	0·4456 (4)	3·43 (8)
C(9)	0·7757 (4)	0·6853 (3)	0·4767 (5)	4·3 (1)
C(10)	0·7373 (5)	0·6106 (4)	0·1352 (7)	6·8 (1)
C(11)	0·5683 (5)	0·5594 (4)	0·2935 (7)	6·6 (1)
C(12)	0·5373 (4)	0·7033 (4)	0·0727 (6)	5·7 (1)
C(13)	0·7909 (5)	1·0400 (4)	0·0962 (6)	6·2 (1)
C(14)	0·7447 (4)	0·8530 (5)	−0·0322 (5)	5·7 (1)
C(15)	0·8587 (3)	0·8601 (4)	0·2376 (5)	4·4 (1)

* $8\pi^2(U_{11} + U_{22} + U_{33})/3$.

Table 2. *Bond distances* (Å) *and bond angles* (°)

Numbers in parentheses are e.s.d.'s in the least-significant digits.

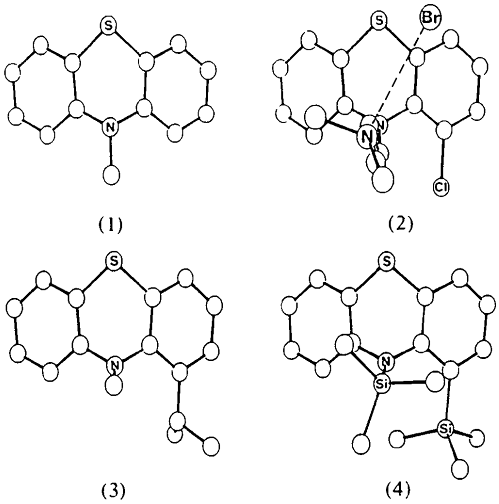
S(5)–C(4a)	1·746 (3)	C(10a)–C(1)	1·421 (4)
S(5)–C(5a)	1·779 (3)	C(10a)–C(4a)	1·398 (4)
Si(1)–N(10)	1·772 (2)	C(1)–C(2)	1·404 (5)
Si(1)–C(10)	1·848 (4)	C(2)–C(3)	1·382 (5)
Si(1)–C(11)	1·875 (5)	C(3)–C(4)	1·335 (5)
Si(1)–C(12)	1·835 (4)	C(4)–C(4a)	1·430 (4)
Si(2)–C(1)	1·891 (3)	C(5a)–C(6)	1·393 (4)
Si(2)–C(13)	1·839 (4)	C(5a)–C(9a)	1·387 (6)
Si(2)–C(14)	1·872 (4)	C(6)–C(7)	1·368 (6)
Si(2)–C(15)	1·873 (3)	C(7)–C(8)	1·385 (6)
N(10)–C(10a)	1·432 (4)	C(8)–C(9)	1·378 (5)
N(10)–C(9a)	1·443 (4)	C(9a)–C(9)	1·373 (5)
C(4a)–S(5)–C(5a)	98·4 (1)	Si(2)–C(1)–C(10a)	125·4 (2)
N(10)–Si(1)–C(10)	110·1 (2)	Si(2)–C(1)–C(2)	117·7 (2)
N(10)–Si(1)–C(11)	109·5 (2)	C(10a)–C(1)–C(2)	116·6 (3)
N(10)–Si(1)–C(12)	108·9 (2)	C(1)–C(2)–C(3)	122·4 (3)
C(10)–Si(1)–C(11)	106·9 (2)	C(2)–C(3)–C(4)	121·1 (3)
C(10)–Si(1)–C(12)	112·1 (2)	C(3)–C(4)–C(4a)	119·5 (3)
C(11)–Si(1)–C(12)	109·3 (2)	S(5)–C(4a)–C(10a)	120·1 (2)
C(1)–Si(2)–C(13)	107·9 (2)	S(5)–C(4a)–C(4)	120·0 (3)
C(1)–Si(2)–C(14)	113·0 (2)	C(10a)–C(4a)–C(4)	119·8 (3)
C(1)–Si(2)–C(15)	110·7 (1)	S(5)–C(5a)–C(6)	120·9 (3)
C(13)–Si(2)–C(14)	106·5 (2)	S(5)–C(5a)–C(9a)	118·9 (2)
C(13)–Si(2)–C(15)	108·6 (2)	C(6)–C(5a)–C(9a)	120·2 (3)
C(14)–Si(2)–C(15)	110·1 (2)	C(5a)–C(6)–C(7)	119·7 (3)
Si(1)–N(10)–C(10a)	122·3 (2)	C(6)–C(7)–C(8)	120·3 (3)
Si(1)–N(10)–C(9a)	114·7 (2)	C(7)–C(8)–C(9)	119·6 (4)
C(10a)–N(10)–C(9a)	114·3 (3)	N(10)–C(9a)–C(5a)	119·7 (3)
N(10)–C(10a)–C(1)	121·1 (3)	N(10)–C(9a)–C(9)	121·2 (4)
N(10)–C(10a)–C(4a)	118·8 (3)	C(5a)–C(9a)–C(9)	119·1 (3)
C(1)–C(10a)–C(4a)	120·1 (3)	C(8)–C(9)–C(9a)	121·0 (4)

Table 3. *Conformational parameters for* (1)–(4)

		(1)	(2)	(3)	(4)
Angle of *Y*–N to C(9a)–N–C(10a) plane (°)		23·9	−24·9	−33·8	−28·3 (3)
Sum of angles around N (°)		354·2	353·7	348·3	351·3 (2)
Distance of *Z* from *A*-ring plane (Å)		—	0·141	0·104	0·360 (4)
Torsion angles (°)					
	Z–C(1)–C(10a)–N	—	1·4	2·9	11·8 (4)
	Y–N–C(9a)–C(9)	−12·5	−62·7	−75·0	−75·3 (4)
	Y–N–C(10a)–C(1)	12·5	68·2	78·3	84·9 (3)
A ring	C(1)–C(2)–C(3)–C(4)	0·3	−2·8	−0·4	−2·0 (5)
	C(2)–C(3)–C(4)–C(4a)	2·5	5·0	1·6	5·4 (5)
	C(3)–C(4)–C(4a)–C(10a)	−3·0	−1·2	−1·0	−2·5 (5)
	C(4)–C(4a)–C(10a)–C(1)	0·7	−4·6	−0·8	−3·8 (5)
	C(4a)–C(10a)–C(1)–C(2)	2·1	6·9	2·0	7·0 (5)
	C(10a)–C(1)–C(2)–C(3)	−2·6	−3·3	−1·4	−4·3 (6)
Central ring	C(10a)–C(4a)–S–C(5a)	−36·2	−31·5	−31·9	−33·8 (3)
	C(4a)–S–C(5a)–C(9a)	36·2	33·5	33·1	36·8 (4)
	S–C(5a)–C(9a)–N	−3·5	−6·2	−2·7	−1·7 (7)
	C(5a)–C(9a)–N–C(10a)	−40·2	−32·4	−37·3	−45·7 (4)
	C(9a)–N–C(10a)–C(4a)	40·2	35·2	38·3	49·2 (4)
	N–C(10a)–C(4a)–S	3·5	1·7	0·6	−4·5 (5)
Twist |av. of C(5a)–C(9a)–C(10a)–C(4a) and C(9a)–C(5a)–C(4a)–C(10a)| (°)		0	2·4	1·2	3·0 (4)
Skew |C(5a)–C(4a) − C(9a)–C(10a)| (°)		0·26	0·26	0·25	0·25 (1)
Angle between aromatic rings (°)		143·7	145·6	143·1	136·7 (4)

Discussion. Atomic parameters for (4) are given in Table 1, bond parameters in Table 2, and Table 3 and Fig. 1 compare conformational parameters of 1,10-disubstituted phenothiazines (2)–(4) and 10-methylphenothiazine (1).* In the molecules in Fig. 1, the horizontal axis is defined by C(8) and C(2), and the vertical axis by N(10) and S; arbitrary spheres of identical size are used for all atoms. In Table 3, *Y* refers to the first atom in the N(10) side chain and *Z* to the first atom in the C(1) side chain.

As expected, the 10-trimethylsilyl substituent in (4) is found in the synclinal position. The much bulkier substituents in (4) as compared to the next most crowded substance (3) are accommodated not by further puckering of the N substituents toward an sp^3 configuration (see Fig. 1 and Table 3, first two entries), but by bending of the trimethylsilyl groups away from one another [*Y*–N–C(10a) is 122·3 (2)° in (4) *vs* 116·5 (2)° in (3); *Z*–C(1)–C(10a) is 125·4 (2)° in (4) *vs* 121·9 (2)° in (3); also Table 3, distance of *Z* from *A*-ring plane and first three torsion angles]. Ring *A* in (2) and (4) is much less planar than in the other compounds [*A*-ring torsion angles in Table 3; distances from the *A*-ring plane in (4) are −0·038, 0·007, 0·029, −0·031, −0·002, and 0·035 Å for C(1), C(2), C(3), C(4), C(4a), and C(1a), respectively, and about the same in (2), compared to <0·011 Å for (3)]. The central-ring torsion angles and twist and skew (Table 3) in (4) are not unusual. The angle between the aromatic rings in (4) is smaller than in (1)–(3) but very similar to that found in several simple 10-alkylphenothiazines (Chu & van der Helm, 1975, 1976; Chu, Napoleone, Ternay & Chang, 1982*a*).



(1) (2)

(3) (4)

Fig. 1. *ORTEP* drawings of (1)–(4). The dashed line indicates a hydrogen bond.

The easy preparation of (4) and its observed geometry show that the phenothiazine ring system in the synclinal conformation [present in the antidepressant (2)] will readily accommodate much bulkier 1- and 10-substituents simultaneously than had been previously placed on it.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates and a packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42316 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Polymorphs of 4,5-Dichloro-6(1*H*)-pyridazinone

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Abstract. $C_4H_2Cl_2N_2O$, $M_r = 164{\cdot}99$; form (I): monoclinic, $P2_1/c$, $a = 5{\cdot}1967\ (12)$, $b = 9{\cdot}046\ (2)$, $c = 12{\cdot}901\ (3)$ Å, $\beta = 100{\cdot}090\ (15)°$, $V = 597{\cdot}1\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}84$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 9{\cdot}93$ cm^{-1}, $F(000) = 328$, $T = 163$ K, $R = 0{\cdot}028$ for 1552 reflections; form (II): monoclinic, $P2_1/c$, $a = 5{\cdot}3384\ (7)$, $b = 13{\cdot}827\ (2)$, $c = 7{\cdot}9107\ (12)$ Å, $\beta = 94{\cdot}397\ (14)°$, $V = 582{\cdot}20\ (14)$ Å^3, $Z = 4$, $D_x = 1{\cdot}88$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 10{\cdot}18$ cm^{-1}, $F(000) = 328$, $T = 163$ K, $R = 0{\cdot}025$ for 1597 reflections. The compound, in each form, exists in the oxo form and crystallizes as hydrogen-bonded dimers. Infinite layers of dimers result from C—H···O- and C—H···Cl-type H bonds for forms (I) and (II), respectively [H···O 2·25 (2), C···O 3·076 (2); H···Cl 2·74 (2), C···Cl 3·534 (1) Å]. There are only minor differences in the bond distances and angles of the two forms.

Introduction. Syntheses of many heterocyclic systems containing a pyridazine ring rely on the pivotal and highly versatile starting material 4,5-dichloro-6(1*H*)-pyridazinone. For example, syntheses of 2,3-diazaphenothiazines (Yoneda, Ohtaka & Nitta, 1965, 1966; Scapini, Duro & Pappalardo, 1968; Maki, Suzuki, Toyota & Takaya, 1973) and the isosterically related phenoxathiins (Womack, Martin, Martin & Smith, 1982; Musmar, Martin, Lynch & Simonsen, 1985) have been based on this precursor. Electronically, the 4-halo substituent is the most readily displaced, and the molecule behaves like a *β*-halovinyl ketone (Benson & Pohland, 1964). Interestingly, when 4,5-dichloro-6(1*H*)-pyridazinone was reacted with the disodium salt of 2-mercaptophenol (Womack *et al.*, 1982) both of the possible phenoxathiins, 1-oxo-1,2-dihydro- and 4-oxo-3,4-dihydro-2,3-diazaphenoxathiin, were formed. The pathway for the reaction was hypothesized to be *via* a Smiles rearrangement (Truce, Kreider & Brand, 1970) which would require the pyridazinone to be in the oxo form throughout the reaction rather than in its hydroxy tautomeric form. In an effort to support partially the proposed reaction pathway, we report the crystal

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