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UNUSUAL CONFORMATIONS OF ISOELECTRONIC $(SiO)_4$, $(SiOSiN)_2$ AND $(SiN)_4$ RINGS

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Summary

The crystal structures of three compounds containing eight-membered $Si_4(N,O)_4$ rings have been determined: $[t\text{-}Bu_2SiOSiMe_2O]_2$ (I), $[t\text{-}Bu_2SiOSiMe_2NH]_2$ (II) and $[i\text{-}Pr_2SiNH]_4$ (III). I forms monoclinic crystals, space group $C2/c$, with a 14.124(4), b 13.191(4), c 16.156(6) Å, β 108.09(2)°, $Z = 4$. II also crystallizes in $C2/c$, with a 14.234(5), b 13.372(6), c 16.142(8) Å, β 108.87(3)°, $Z = 4$. The structure determinations show that I and II are essentially isostructural, with effectively planar eight-membered rings lying on crystallographic inversion centres. However the Si–O–Si angle in II is almost linear (178.0(1)°) and the Si–N–Si angle is 145.2(2)°, whereas intermediate values are observed for the Si–O–Si angles in I (156.0(1), 164.2(1)°). III is tetragonal, space group $I\bar{4}$, with a, b 13.722(1), c 8.911(2) Å, $Z = 2$. The ring adopts a tub conformation with Si–N–Si 139.1(2)°, and the molecule possesses crystallographic $S_4(\bar{4})$ symmetry. The structures were refined to $R = 0.039$, 0.053, and 0.040 for 2285, 2081, and 696 unique observed reflections, respectively.

Introduction

Silanols are direct precursors of cyclosiloxanes [1]. Starting from an aminosilanol we were able to isolate the eight-membered ring II, which is isoelectronic with the cyclotetrasiloxane I [2]. Elimination of LiF from lithiated fluorodiisopropylsilylamine gave the eight-membered cyclotetrasilazane III [3]. In order to compare the geometries of these isoelectronic ring systems, we have determined the crystal structures of I–III.

Experimental

Crystal data

I: $C_{20}H_{48}O_4Si_4$, $M = 464.9$, monoclinic, space group $C2/c$, a 14.124(4), b 13.191(4), c 16.156(6) Å, β 108.09(2)°, U 2861.2 Å^3, $Z = 4$, D_c 1.079 g cm^{-3},

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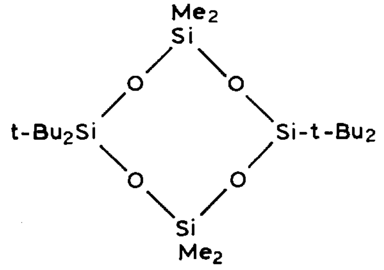
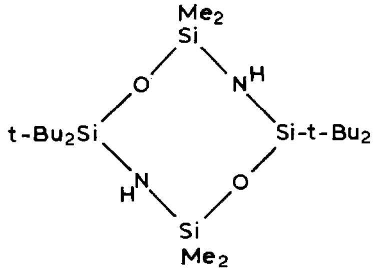
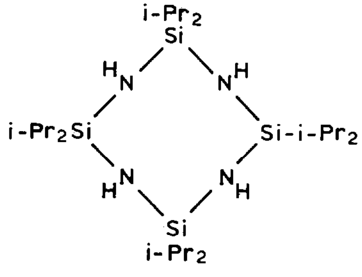


(I)



(II)



(III)

$F(000) = 1024$, λ(Mo-K_α) 0.71069 Å, μ 2.21 cm^{-1}, crystal size $0.4 \times 0.4 \times 0.5$ mm^3, sealed in capillary; Stoe–Siemens AED diffractometer, unit cell parameters from 2θ values of 40 reflections centred at $\pm\omega$ ($20 < 2\theta < 25°$), 3714 reflections with $2\theta < 50°$ measured by profile analysis [4], 2285 unique data with $F > 3\sigma(F)$ used for structure determination; no absorption corrections.

II: $C_{20}H_{50}N_2O_2Si_4$, $M = 463.0$, monoclinic, space group $C2/c$, a 14.234(5), b 13.372(6), c 16.142(8) Å, β 108.87(3)°, U 2907.3 Å^3, $Z = 4$, D_c 1.058 g cm^{-3}, $F(000) = 1024$, μ 2.15 cm^{-1}, crystal size $0.7 \times 0.7 \times 0.8$ mm^3, 4402 reflections with $2\theta < 50°$, 2081 unique data with $F > 3\sigma(F)$, other details as I.

III: $C_{24}H_{60}N_4Si_4$, $M = 517.1$, tetragonal, space group $I\bar{4}$, a, b 13.722(1), c 8.911(2) Å, $U = 1677.9$ Å^3, $Z = 2$, D_c 1.023 g cm^{-3}, $F(000) = 576$, μ 1.89 cm^{-1}, crystal size $0.3 \times 0.3 \times 0.6$ mm^3, 1655 reflections with $2\theta < 50°$, 696 unique data with $F > 4\sigma(F)$, other details as I.

Structure determination

The structures were determined by multisolution direct methods and refined with anisotropic non-H atoms to a minimum of $\Sigma w\Delta^2$ ($\Delta = |F_o| - |F_c|$; $w^{-1} = \sigma^2(F) + gF^2$ with $g = 0.0003$, 0.0004 and 0.0001, respectively). A riding model was employed for the hydrogens with C–H 0.96 Å and $U(\mathrm{H}) = 1.2\ U_{eq}$, where U_{eq} is the equivalent isotropic thermal displacement parameter for the C or N atom to which the H was attached. Complex scattering factors were employed [5]. For the non-centrosymmetric structure III, the absolute assignment of the axes was confirmed by a Rogers η refinement [6], though the result was not significant (η refined from -1 to 0.8(8)).

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($Å^2 \times 10^3$) FOR I (Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor)

	x	y	z	U_{eq}
Si(1)	3193(1)	951(1)	5385(1)	38(1)
Si(2)	3160(1)	2582(1)	3906(1)	37(1)
O(1)	3267(1)	1661(1)	4594(1)	48(1)
O(2)	2516(1)	1513(1)	5893(1)	48(1)
C(11)	2613(2)	−267(2)	4934(2)	63(1)
C(12)	4452(2)	735(2)	6148(1)	64(1)
C(2)	2469(2)	2059(2)	2796(1)	52(1)
C(21)	1443(2)	1699(2)	2818(2)	76(1)
C(22)	2304(2)	2864(2)	2081(1)	98(1)
C(23)	3010(2)	1148(2)	2564(2)	93(1)
C(3)	4446(1)	3117(1)	4096(1)	48(1)
C(31)	4823(2)	3478(2)	5051(1)	69(1)
C(32)	4440(2)	4039(2)	3520(2)	84(1)
C(33)	5173(2)	2325(2)	3967(2)	94(1)

TABLE 2

ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($Å^2 \times 10^3$) FOR II

	x	y	z	U_{eq}
Si(1)	1778(1)	4034(1)	4618(1)	45(1)
Si(2)	3139(1)	2608(1)	3891(1)	44(1)
N	2431(2)	3568(2)	4014(2)	72(1)
O	3186(1)	1776(1)	4624(1)	64(1)
C(11)	480(2)	4254(3)	3916(2)	85(2)
C(12)	2298(3)	5235(2)	5126(3)	86(2)
C(21)	2498(2)	2031(3)	2778(2)	64(1)
C(22)	2364(3)	2774(3)	2029(2)	112(2)
C(23)	3047(3)	1111(3)	2616(3)	110(2)
C(24)	1455(2)	1697(3)	2756(3)	100(2)
C(25)	4445(2)	3097(2)	4105(2)	58(1)
C(26)	5126(2)	2291(3)	4012(3)	110(2)
C(27)	4816(3)	3478(3)	5051(2)	92(2)
C(28)	4475(3)	3979(3)	3511(3)	98(2)

TABLE 3

ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($Å^2 \times 10^3$) FOR III

	x	y	z	U_{eq}
Si	1522(1)	383(1)	5574(1)	54(1)
N	796(2)	1124(2)	4491(4)	60(1)
C(1)	1480(4)	763(3)	7593(5)	80(2)
C(11)	1784(6)	−9(4)	8727(6)	136(3)
C(12)	2052(4)	1715(4)	7859(7)	115(3)
C(2)	2805(3)	522(3)	4801(6)	80(2)
C(21)	2885(4)	464(4)	3120(6)	112(3)
C(22)	3508(3)	−206(5)	5522(10)	141(3)

TABLE 4

BOND LENGTHS (Å) AND ANGLES (°) FOR I

Si(1)-O(1)	1.614(2)	Si(1)-O(2)	1.620(2)
Si(1)-C(11)	1.848(3)	Si(1)-C(12)	1.845(3)
Si(2)-O(1)	1.621(2)	Si(2)-C(2)	1.886(3)
Si(2)-C(3)	1.883(3)	Si(2)-O(2′)	1.623(2)
C(2)-C(22)	1.533(4)	C(2)-C(21)	1.536(4)
C(3)-C(31)	1.542(3)	C(2)-C(23)	1.531(4)
C(3)-C(33)	1.525(4)	C(3)-C(32)	1.530(4)
O(1)-Si(1)-O(2)	109.3(1)	O(1)-Si(1)-C(11)	108.8(1)
O(2)-Si(1)-C(11)	109.8(1)	O(1)-Si(1)-C(12)	109.5(1)
O(2)-Si(1)-C(12)	109.3(1)	O(1)-Si(2)-C(2)	106.7(1)
O(1)-Si(2)-C(3)	106.8(1)	C(2)-Si(2)-C(3)	118.7(1)
O(1)-Si(2)-O(2′)	110.5(1)	C(2)-Si(2)-O(2′)	107.3(1)
C(3)-Si(2)-O(2′)	106.8(1)	Si(1)-O(1)-Si(2)	164.2(1)
Si(1)-O(2)-Si(2′)	156.0(1)	Si(2)-C(2)-C(21)	107.7(2)
Si(2)-C(2)-C(22)	112.1(2)	Si(2)-C(2)-C(23)	111.7(2)
Si(2)-C(3)-C(31)	107.2(2)	Si(2)-C(3)-C(32)	112.1(2)
Si(2)-C(3)-C(33)	112.2(2)	C(31)-C(3)-C(32)	107.4(2)
C(21)-C(2)-C(22)	107.9(2)	C(31)-C(3)-C(33)	108.1(2)
C(21)-C(2)-C(23)	108.0(2)	C(32)-C(3)-C(33)	109.7(2)
C(22)-C(2)-C(23)	109.3(2)	C(11)-Si(1)-C(12)	110.2(1)

Final difference syntheses showed no significant features. I: 151 parameters, $R = 0.039$, $R_w (= (\Sigma w\Delta^2/\Sigma wF_0^2)^{1/2}) = 0.050$; II: 127 parameters, $R = 0.053$, $R_w = 0.057$; III: 85 parameters, $R = 0.040$, $R_w = 0.039$. The slope of the normal probability plot [7] was 1.56, 1.34 and 1.54, respectively.

TABLE 5

BOND LENGTHS (Å) AND ANGLES (°) FOR II

Si(1)-N	1.670(3)	Si(1)-C(11)	1.852(3)
Si(1)-C(12)	1.846(3)	Si(1)-O′	1.622(2)
Si(2)-N	1.682(3)	Si(2)-O	1.609(2)
Si(2)-C(21)	1.897(3)	Si(2)-C(25)	1.895(3)
C(21)-C(23)	1.525(5)	C(21)-C(22)	1.528(5)
C(25)-C(26)	1.524(5)	C(21)-C(24)	1.539(5)
C(25)-C(28)	1.529(5)	C(25)-C(27)	1.533(4)
N-Si(1)-C(11)	109.6(1)	N-Si(1)-C(12)	111.4(2)
C(11)-Si(1)-C(12)	108.1(2)	N-Si(1)-O′	107.6(1)
C(11)-Si(1)-O′	110.5(1)	C(12)-Si(1)-O′	109.6(1)
N-Si(2)-O	109.0(1)	N-Si(2)-C(21)	107.4(1)
O-Si(2)-C(21)	107.9(1)	N-Si(2)-C(25)	107.8(1)
O-Si(2)-C(25)	107.4(1)	C(21)-Si(2)-C(25)	117.1(1)
Si(1)-N-Si(2)	145.2(2)	Si(2)-O-Si(1′)	178.0(1)
Si(2)-C(21)-C(22)	112.6(2)	Si(2)-C(21)-C(23)	112.0(2)
C(22)-C(21)-C(23)	109.2(3)	Si(2)-C(21)-C(24)	107.7(2)
C(22)-C(21)-C(24)	107.3(3)	C(23)-C(21)-C(24)	107.8(3)
Si(2)-C(25)-C(26)	112.8(2)	Si(2)-C(25)-C(27)	107.3(2)
C(26)-C(25)-C(27)	107.9(3)	Si(2)-C(25)-C(28)	112.1(2)
C(26)-C(25)-C(28)	109.2(3)	C(27)-C(25)-C(28)	107.3(3)

TABLE 6

BOND LENGTHS (Å) AND ANGLES (°) FOR III

Si-N	1.720(3)	Si-C(1)	1.874(5)
Si-C(2)	1.900(4)	Si-N′	1.708(3)
C(1)-C(12)	1.544(7)	C(1)-C(11)	1.523(7)
C(2)-C(22)	1.530(8)	C(2)-C(21)	1.504(8)
N-Si-C(1)	110.9(2)	N-Si-C(2)	105.9(2)
C(1)-Si-C(2)	110.4(2)	N-Si-N′	110.9(2)
C(1)-Si-N′	106.6(2)	C(2)-Si-N′	112.3(2)
Si-N-Si′	139.1(2)	Si-C(1)-C(11)	115.8(3)
Si-C(1)-C(12)	111.6(3)	Si-C(2)-C(21)	115.1(3)
Si-C(2)-C(22)	111.5(4)		

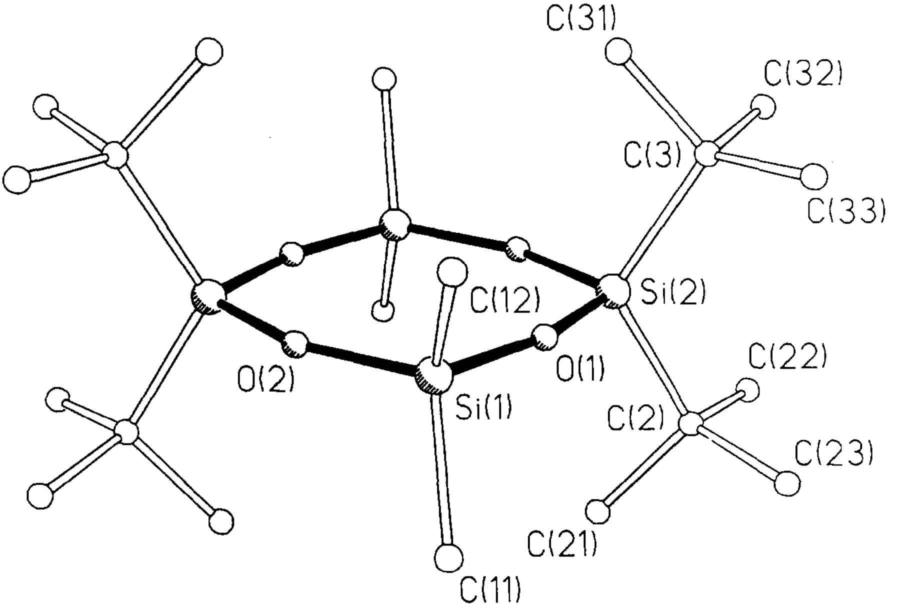


Fig. 1. Molecular structure of I with unique atoms labelled. Hydrogen atoms are omitted for clarity.

Final atomic coördinates are given in Tables 1–3 and bond lengths and angles in Tables 4–6. Structure factors, anisotropic thermal displacement parameters, and hydrogen coordinates may be obtained from the authors. Figures 1–3 show the molecular structures.

Results and discussion

After completion of the structure determinations it was realized that I and II are effectively isostructural, despite the very different bond angles at the NH and O ring members. Both rings lie on crystallographic inversion centres and are essentially planar; the mean deviations of the eight ring atoms from their mean plane is 0.003 Å in I and 0.010 Å in II. Planar eight-membered rings are rare, but octaphenyl-

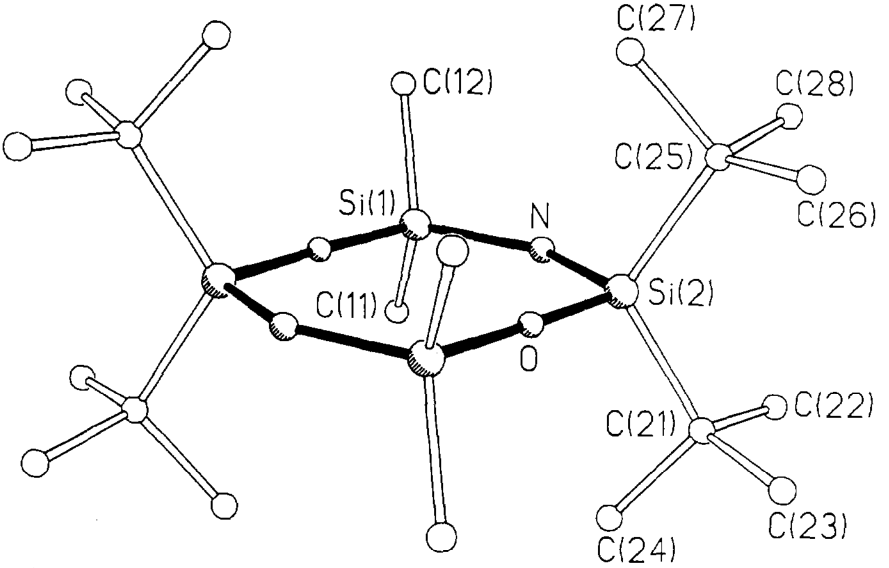


Fig. 2. Molecular structure of II with unique atoms labelled. Hydrogen atoms are omitted for clarity.

cyclotetrasiloxane is almost planar (mean deviation 0.10 Å) [8]. Particularly unusual features of II are the virtually linear Si–O–Si units in the ring (Si–O–Si 178.0(1)°); the Si–N–Si angle of 145.2(2)° and the Si–O–Si angles in I (156.0(1), 164.2(1)°) are more typical. The Si–O bonds in I and II (range 1.609–1.623 Å) and the Si–N bonds in II (1.670(3), 1.682(3) Å) are all short, consistent with some p_π–d_π

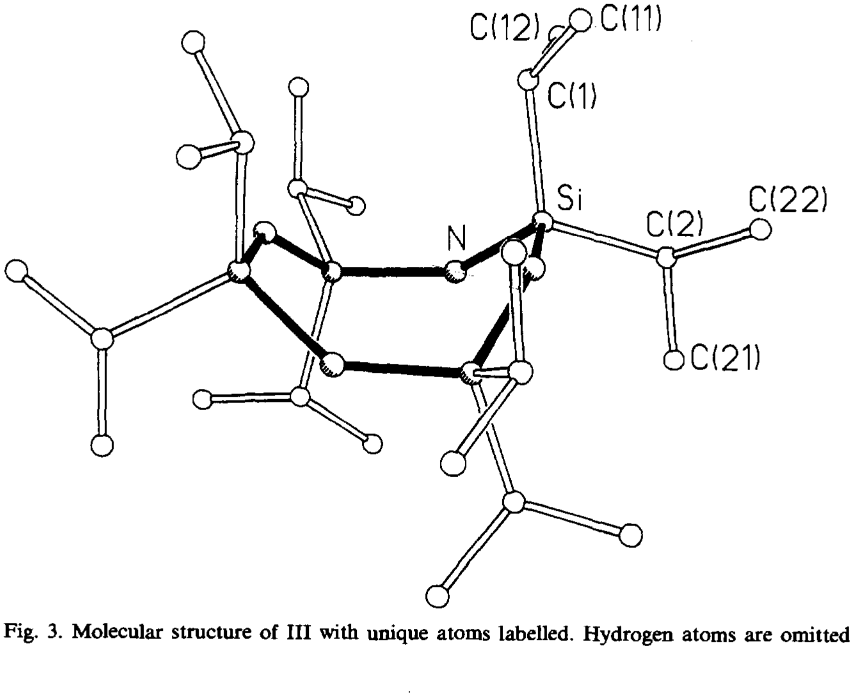


Fig. 3. Molecular structure of III with unique atoms labelled. Hydrogen atoms are omitted for clarity.

delocalisation in the planar rings. III adopts a tub conformation with $S_4(\bar{4})$ crystallographic symmetry; the Si atoms lie at ±0.51 and the N atoms at ±0.45 Å from the mean ring plane. The Si–N bonds are significantly longer (1.720(3), 1.708(3) Å), and the bond angle at nitrogen (139.1(2)°) is smaller. Still longer Si–N bonds and smaller ring nitrogen angles are observed in $[Me_2SiNH]_4$ (chair and cradle conformations; mean Si–N 1.728 Å, mean Si–N–Si 132.0° [9]) and $[Me_2SiNMe]_4$ (tub conformation; mean Si–N 1.735 Å, mean Si–N–Si 122.8° [10]).

Acknowledgements

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