Conformations of *trans*-1,2-Disubstituted-1-trimethylsilylcyclohexanes in Solution and in the Solid State. Crystal and Molecular Structure of 2-Trimethylsilyl-*trans*-2-methoxycyclohexanol

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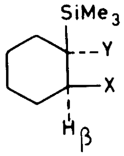
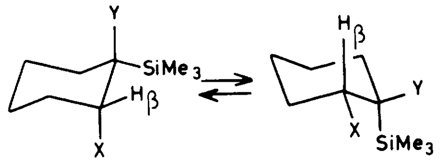
The ^{1}H n.m.r. spectra of a series of 14 *trans*-1,2-disubstituted-1-trimethylsilylcyclohexanes provided evidence for conformational equilibria favouring the conformer with the axial trimethylsilyl group in those compounds in which an intramolecular hydrogen bond can exist between the two electronegative substituents. Where such a bond is absent the conformation with an equatorial trimethylsilyl group is highly preferred. An *X*-ray diffraction study on 2-trimethylsilyl-*trans*-2-methoxycyclohexanol has shown that this molecule exists in the crystal in the conformation with an equatorial trimethylsilyl group, owing to stabilization by a strong intermolecular hydrogen bond between the axial hydroxy and methoxy groups of neighbouring molecules.

Organosilicon derivatives have been investigated extensively during the last two decades owing to their peculiar reactivities, which differ in many aspects from those of corresponding carbon derivatives, making them very useful agents for synthesis.[1]

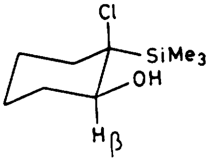
During the course of a study on the stereo- and regiochemistry of the reactions of 1-(trimethylsilyl)cyclohexene with several electrophiles and of the corresponding epoxide with different nucleophiles under acidic conditions,[2] we prepared many compounds of the general formula (**1**), *e.g.*, compounds (**2**)—(**15**) of Table 1, and observed that the n.m.r. multiplets (in $CDCl_3$) for the tertiary proton β to silicon (H_β) exhibited half-band widths ($W_{\frac{1}{2}}$) that ranged between 6.0 and 14.3 Hz, pointing to significantly different contributions from alternative conformers to the conformational equilibria in the compounds of this group. For instance, the diol (**2**) exhibited a quartet in $CDCl_3$ for the X part of the ABX system, corresponding, as confirmed by decoupling experiments, to J_{AX} of 7.4 Hz and a J_{BX} of 3.0 Hz in accordance with a high contribution of the conformer with an axial Me_3Si group. On the other hand, the corresponding signals for compounds (**8**)—(**15**) were narrow, ill-defined apparent triplets with $W_{\frac{1}{2}}$ ranging between 6.0 and 7.5 Hz, pointing to small J_{AX} and J_{BX} values and probably also to a small long-range coupling of the '*W* type,' in accordance with what was expected for purely equatorial protons. This observation led to the conclusion that in compounds of type (**1**) the difference in energy between conformers (**1e**) and (**1a**) may not be very high and that the preference for one or the other could depend on the nature of X and Y.



(**1**)



(**1e**) (**1a**)



(**16**)

Table 1 shows the $W_{\frac{1}{2}}$ values for the H_β signals of the compounds that were examined. For all those compounds that have no free hydroxy, and therefore cannot form an intramolecular hydrogen bond, (**8**)—(**15**), the $W_{\frac{1}{2}}$ value for H_β is small, in accordance with conformation (**1e**) if one excludes unlikely non-chair conformations. On the other hand, in the spectra in $CDCl_3$ of compounds having at least a free hydroxy, (**2**)—(**7**), and therefore capable of forming an intramolecular hydrogen bond in conformation (**1a**), $W_{\frac{1}{2}}$ for H_β is higher indicating a substantial contribution of the conformer with an axial Me_3Si group. The $W_{\frac{1}{2}}$ for an axial H_β signal can be estimated by taking as reference the *cis* compound (**16**), which should be entirely in the indicated conformation and has $W_{\frac{1}{2}}$ 16.5 Hz for H_β.[2] The contribution of conformer (**1a**) can be roughly assessed if one assumes a linear variation of $W_{\frac{1}{2}}$ values with the conformer ratio and takes 6.0 and 16.5 Hz, respectively, as the $W_{\frac{1}{2}}$ values for conformers (**1e**) and (**1a**). On the basis of equations (i) and (ii) where x_e and x_a are the mole fractions of

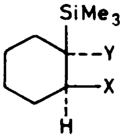
$$6.0x_e + 16.6x_a = W_{\frac{1}{2}} \qquad \text{(i)}$$

$$x_e + x_a = 1 \qquad \text{(ii)}$$

(**1e**) and (**1a**), in $CDCl_3$ compound (**3**) should exist as an equilibrium between (**1a**) and (**1e**) conformers in a ratio of about 8:2. This estimation is of course extremely rough, owing to the dependence of coupling constants on substituent electronegativities and on the uncertainty in measuring $W_{\frac{1}{2}}$ instead of coupling constants, but we believe it definitely shows a preponderance of conformer (**1a**) in (**3**), (**4**), and (**5**).

The preference for conformation (**1a**) for some of the compounds capable of forming intramolecular hydrogen bonds, although at first sight surprising in view of the large size of the trimethylsilyl groups, can be accounted for by its relatively small 'effective size.' A recently reported determination[3] sets the conformational energy at 2.4—2.6 kcal mol^{-1} ($A = -\Delta G$), which is much smaller than that for the analogous t-butyl group. Evidently the longer C–Si bond distances reduce the steric repulsion between an axial Me_3Si group and *syn*-axial hydrogen atoms. If one considers that the preference of the X and Y substituents for the diequatorial disposition should be

Table 1. ^1H N.m.r. and i.r. data of significance for conformation assignment



			^1H N.m.r.^{a}		I.r. (CCl_4) (cm^{-1})	
X	Y	Compound	δ	$W_{\frac{1}{2}}$	Free OH	Bonded OH
OH	OH	(**2**)	3.63	14.0	3 620	3 594^b
			3.70	8.4^c		
			3.70	7.6^d		
OH	OMe	(**3**)	3.97	14.3	3 621	3 592^b
			4.10	9.4^c		
			4.10	7.5^d		
OH	OEt	(**4**)	3.85	14.0	3 619	3 592^b
OH	Br	(**5**)	4.10	9.7	3 615	3 580^e
OH	Cl	(**6**)	3.90	9.0	3 618	3 593^e
Cl	OH	(**7**)	4.03	11.8		
$OCOC_6H_4NO_2(p)$	Br	(**8**)	5.63	6.2		
$OCOC_6H_4NO_2(p)$	Cl	(**9**)	5.47	6.0		
OMe	Br	(**10**)	3.55	7.2		
OMe	Cl	(**11**)	3.57	7.5		
Br	OMe	(**12**)	4.85	7.3		
Br	Br	(**13**)	4.68	7.3		
OMe	HgBr	(**14**)	3.97	5.9		
OMe	HgCl	(**15**)	3.88	6.0		

^{a} All spectra in $CDCl_3$, unless indicated otherwise; chemical shifts refer to signals for proton geminal to the X substituent. ^{b} Strong. ^{c} In DMSO. ^{d} In DMSO–D_2O. ^{e} Weak.

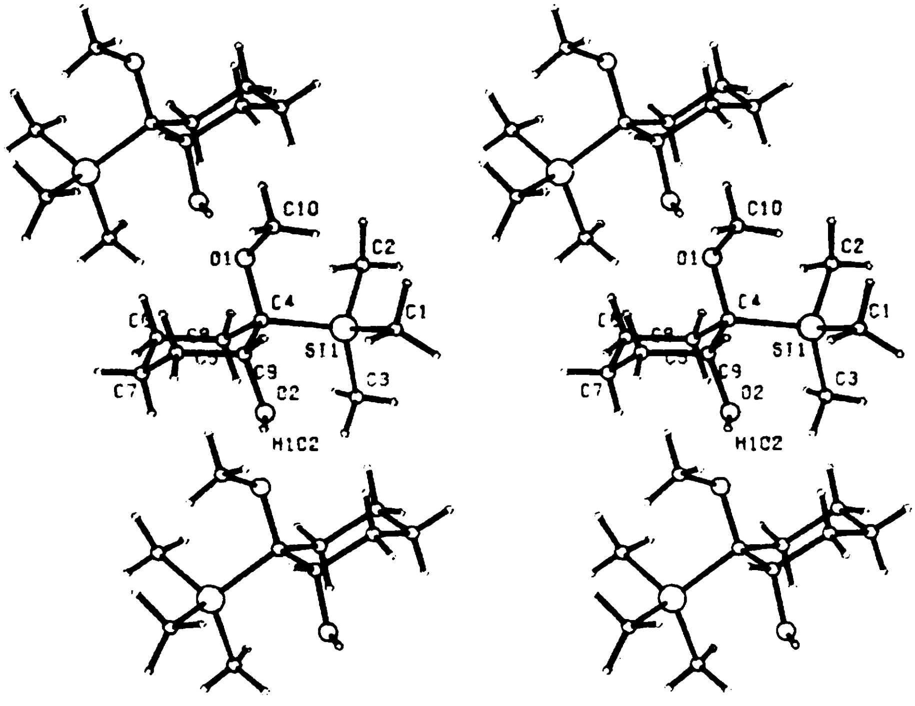


Figure. Stereopair showing the packing of the molecules of compound (**3**) as viewed along the 010 axis

somewhere between 1.2 and 1.6 kcal mol^{-1},[4] one can understand that a further stabilization through formation of the intramolecular hydrogen bond (*ca.* 1.0—1.3 kcal mol^{-1}), possible for conformers (**1a**), but not for (**1e**), could offset the conformational equilibrium in favour of the former. It may also be mentioned that 1-phenylcyclohexane analogues of (**2**) and (**3**) (phenyl in place of Me_3Si) exist essentially in the conformation with equatorial phenyl [an analogue of (**1e**)].[5] This could not be understood on the basis of the *A* value of 2.87 kcal mol^{-1} reported for phenyl in a phenylcyclohexane without geminal or vicinal substituents,[6] since a difference of only *ca.* 0.5 kcal mol^{-1} with respect to the *A* value for Me_3Si could not

Table 2. Atomic fractional co-ordinates (× 10^4) and thermal parameters (× 10^4 Å^2) with their estimated standard deviations in parentheses, and *B*-equiv

	X/*a*	*Y*/*b*	*Z*/*c*	*U*(11)	*U*(22)	*U*(33)	*U*(12)	*U*(13)	*U*(23)	*B*-equiv
Si(1)	6 231(1)	6 150	2 880(1)	507(4)	408(4)	427(4)	54(2)	31(2)	24(2)	3.570
O(1)	5 366(2)	7 165(1)	4 713(1)	510(9)	563(9)	293(7)	−69(7)	26(6)	6(6)	3.628
O(2)	4 003(3)	7 481(1)	1 448(1)	632(11)	746(12)	298(8)	175(9)	−70(7)	−17(7)	4.536
C(1)	3 875(4)	5 537(2)	2 373(3)	730(18)	549(14)	787(18)	−131(13)	53(13)	−120(13)	5.496
C(2)	7 925(6)	5 662(2)	4 186(3)	838(22)	619(17)	734(20)	216(16)	−44(16)	156(14)	5.913
C(3)	7 704(6)	6 220(2)	1 570(3)	815(21)	713(18)	699(18)	177(15)	327(16)	−35(15)	5.683
C(4)	5 595(3)	7 177(1)	3 434(2)	405(10)	416(10)	285(9)	−10(8)	3(7)	25(7)	2.956
C(5)	7 496(3)	7 719(1)	3 414(2)	431(11)	499(11)	440(12)	−51(9)	25(9)	69(9)	3.644
C(6)	7 071(5)	8 557(1)	3 790(3)	668(16)	476(13)	646(16)	−111(12)	−26(12)	15(11)	4.824
C(7)	5 158(5)	8 893(2)	2 993(3)	888(21)	411(13)	727(19)	16(12)	−67(15)	50(12)	5.502
C(8)	3 281(4)	8 381(1)	3 032(2)	635(15)	545(14)	518(14)	173(11)	−40(11)	−45(10)	4.583
C(9)	3 648(3)	7 540(1)	2 681(2)	452(12)	451(11)	339(11)	46(9)	−14(8)	−24(8)	3.336
C(10)	3 700(5)	6 715(2)	5 027(3)	675(16)	771(18)	472(14)	−128(14)	210(12)	31(13)	4.946
H(1O2)	3 206(57)	7 559(20)	1 068(34)	644(111)						
H(11)	3 838(64)	5 118(24)	1 646(34)	1 741(100)						
H(12)	2 562(64)	5 929(24)	2 172(34)	1 741(100)						
H(13)	3 797(64)	5 232(24)	3 212(34)	1 741(100)						
H(21)	7 268(66)	5 508(26)	4 971(45)	1 143(134)						
H(22)	9 197(68)	6 040(23)	4 388(36)	962(117)						
H(23)	8 636(62)	5 200(27)	4 015(37)	1 155(126)						
H(31)	7 843(75)	5 769(26)	1 278(43)	1 771(149)						
H(32)	6 626(45)	6 512(19)	822(26)	970(94)						
H(33)	9 137(51)	6 449(23)	1 917(31)	1 211(114)						
H(51)	7 771(48)	7 691(17)	2 572(29)	660(81)						
H(52)	8 525(44)	7 515(16)	4 000(26)	599(74)						
H(61)	8 193(61)	8 869(21)	3 685(35)	979(113)						
H(62)	6 831(41)	8 597(16)	4 628(27)	517(69)						
H(71)	4 910(45)	9 430(19)	3 235(25)	679(81)						
H(72)	5 599(56)	8 910(19)	2 199(34)	796(99)						
H(81)	2 012(45)	8 515(17)	2 437(25)	604(69)						
H(82)	2 921(42)	8 422(17)	3 829(28)	603(76)						
H(91)	2 409(36)	7 249(12)	2 774(19)	340(50)						
H(101)	3 409(44)	6 221(15)	4 641(24)	784(80)						
H(102)	3 952(46)	6 703(19)	5 908(27)	954(93)						
H(103)	2 394(73)	7 001(27)	4 911(45)	1 751(152)						

justify a shift from an 8:2 ratio (**1a**) to (**1e**) for (**2**) to one of at most 1:9 for the phenyl analogue. It therefore appears that the *A* value for phenyl must be considerably higher in a *trans*-1,2-disubstituted-1-phenylcyclohexane; this can be explained by the fact that, in any of its rotameric positions, an axial phenyl interferes either with the geminal substituent and *syn*-axial hydrogens, or with the vicinal *cis*-substituent, thus increasing the free-energy difference between the two chair conformers; this difference should be much less pronounced in (**2**), due to the longer C–Si bonds, as stated above.

The importance of hydrogen bonding in determining the conformational equilibrium can be further substantiated by additional experimentation. When the n.m.r. spectra of (**2**) and (**3**) were taken in [$^2H_6$]DMSO the half-band widths of the H_β signal decreased from 14.0 and 14.3 Hz to 8.4 and 9.4 Hz, and after exchange with D_2O, to 7.6 and 7.5 Hz respectively. As expected, intermolecular hydrogen bonding with the solvent disrupts the intramoleclar bonds and favours conformation (**1e**). The further decrease in band width on exchange with D_2O is due to the elimination of the C*H*–O–*H* coupling present in DMSO (*J* = *ca.* 4.5 Hz as judged from the OH doublet that collapses to a singlet after addition of D_2O). Furthermore, i.r. OH stretching frequencies of dilute solutions in CCl_4 (Table 1) give evidence for intramolecular hydrogen bonding with O–H stretching bands around 3 590 cm^{-1},[7,8] which are particularly strong in those compounds that have the broadest H_β signals in the n.m.r. spectra (Table 1).

In order to gain a better insight into the conformation we thought it worth while to determine the structure of one of our trimethylsilyl derivatives by *X*-ray diffraction, and also in view of the fact that, as far as we could ascertain, no structural data are available on any trimethylsilylcyclohexane, and only very few structural data are available on cyclohexylsilane.[9] Such data could also be interesting for a comparison with the structures of analogous t-butylcyclohexanes, for which several diffractometric structures are known.[10] We chose the methoxy derivative (**3**), for which the ^1H n.m.r. data mentioned above indicated the highest preference for conformation (**1a**) in $CDCl_3$ solution, since there was some possibility that such a conformation could also be found in the crystal.

A stereoview of the crystal packing, together with the numbering scheme of molecule (**3**), is given in the Figure. Relevant structural parameters are collected in Tables 2—5 (atomic fractional co-ordinates, bond distances and angles, torsion angles, and distances to atoms in adjacent unit cells). It can be seen that (**3**) exists in conformation (**1e**) and the packing arrangement shows that this preference must be due to a favourable situation for strong intermolecular hydrogen bonds between the hydroxy and methoxy groups of neighbouring molecules. Molecules of alternative chirality are thus stacked one upon another with the bulky Me_3Si group pointing in the opposite direction in order to have minimal mutual interaction. No such favourable packing would be possible in the alternative (**1a**) conformation. The existence of a strong intermolecular hydrogen bond is also proven by the good alignment between the methoxy oxygen [O(1)] of one molecule and the hydroxy hydrogen H(1O2) and oxygen [O(2)] of the other: O(2) · · · O(1)^{II} = 2.874(4) Å; O(2)–H(1O2)^{O} = 0.63(3) Å, O(2)–H(1O2) · · · O(1)^{II} 179.9(4.0)° (see Table 5) and by the short contact between O(1) · · · H(1O2) which is found to be 2.244(35)

Table 3. Bond distances and angles

(a) Bond distances (Å)

Si(1)–C(1)	1.869(3)	O(2)–H(1O2)	0.630(34)
Si(1)–C(2)	1.879(4)	C(4)–C(5)	1.528(3)
Si(1)–C(3)	1.878(4)	C(4)–C(9)	1.535(3)
Si(1)–C(4)	1.929(2)	C(5)–C(6)	1.526(3)
O(1)–C(4)	1.461(3)	C(6)–C(7)	1.523(5)
O(1)–C(10)	1.418(4)	C(7)–C(8)	1.509(4)
O(2)–C(9)	1.437(3)	C(8)–C(9)	1.520(3)

(b) Bond angles (°)

C(3)–Si(1)–C(4)	110.8(1)	Si(1)–C(4)–C(9)	113.1(3)
C(2)–Si(1)–C(4)	106.5(1)	Si(1)–C(4)–C(5)	109.7(2)
C(2)–Si(1)–C(3)	109.0(2)	C(5)–C(4)–C(9)	109.4(2)
C(1)–Si(1)–C(4)	113.6(2)	C(4)–C(5)–C(6)	113.6(2)
C(1)–Si(1)–C(3)	107.2(2)	C(5)–C(6)–C(7)	110.4(2)
C(1)–Si(1)–C(2)	109.7(2)	C(6)–C(7)–C(8)	110.7(3)
C(4)–O(1)–C(10)	116.8(2)	C(7)–C(8)–C(9)	112.4(3)
C(9)–O(2)–H(1O2)	113.0(34)	C(4)–C(9)–C(8)	113.0(2)
Si(1)–C(4)–O(1)	111.2(1)	O(2)–C(9)–C(8)	111.7(2)
O(1)–C(4)–C(9)	109.8(2)	O(2)–C(9)–C(4)	104.6(2)
O(1)–C(4)–C(5)	103.2(2)		

Table 4. Relevant torsion angles (°)

C(3)–Si(1)–C(4)–C(5)	−40.1(2)
C(2)–Si(1)–C(4)–C(5)	78.3(2)
C(1)–Si(1)–C(4)–C(5)	−160.8(2)
C(3)–Si(1)–C(4)–C(9)	82.4(2)
C(2)–Si(1)–C(4)–C(9)	−159.2(2)
C(1)–Si(1)–C(4)–C(9)	−38.3(2)
C(3)–Si(1)–C(4)–O(1)	−153.5(2)
C(2)–Si(1)–C(4)–O(1)	−35.1(2)
C(1)–Si(1)–C(4)–O(1)	85.8(2)
C(10)–O(1)–C(4)–Si(1)	−63.9(3)
C(10)–O(1)–C(4)–C(9)	62.1(3)
C(10)–O(1)–C(4)–C(5)	178.6(2)
H(1O2)–O(2)–C(9)–C(4)	169.2(36)
H(1O2)–O(2)–C(9)–C(8)	−68.2(36)
Si(1)–C(4)–C(9)–O(2)	−52.1(2)
O(1)–C(4)–C(9)–O(2)	−177.0(2)
C(5)–C(4)–C(9)–O(2)	70.5(2)
O(1)–C(4)–C(9)–C(8)	61.3(3)
Si(1)–C(4)–C(9)–C(8)	−173.9(2)
O(1)–C(4)–C(5)–C(6)	−63.8(3)
Si(1)–C(4)–C(5)–C(6)	177.7(2)
C(5)–C(4)–C(9)–C(8)	−51.3(3)
C(9)–C(4)–C(5)–C(6)	53.0(3)
C(4)–C(5)–C(6)–C(7)	−56.2(3)
C(5)–C(6)–C(7)–C(8)	55.9(3)
C(6)–C(7)–C(8)–C(9)	−55.7(3)
C(7)–C(8)–C(9)–C(4)	54.1(3)
C(7)–C(8)–C(9)–O(2)	−63.6(3)

Table 5. Inter- and intra-molecular contacts

(a) Intermolecular contacts less than 3.9 Å (Å)[a]

C(2)–C(2)$^{\mathrm{I}}$	3.763(6)	C(5)–O(2)$^{\mathrm{III}}$	3.398(4)
O(2)–O(1)$^{\mathrm{II}}$	2.874(4)	C(6)–O(2)$^{\mathrm{III}}$	3.517(4)
C(9)–O(1)$^{\mathrm{II}}$	3.682(5)	C(10)–O(2)$^{\mathrm{III}}$	3.816(6)
C(4)–O(2)$^{\mathrm{III}}$	3.772(5)		

(b) Intramolecular contacts around the silyl group (Å)

C(1)–C(10)	3.604(5)	C(2)–C(10)	3.537(6)
C(1)–O(2)	3.487(4)	C(2)–O(1)	3.169(4)
C(1)–O(1)	3.838(4)	C(3)–O(2)	3.219(5)

[a] Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z: I, $2-x, 1-y, 1-z$; II, $-\frac{1}{2}+x, 3/2-y, -\frac{1}{2}+z$; III, $\frac{1}{2}+x, 3/2-y, \frac{1}{2}+z$.

Å, that is about 0.2 Å less than the sum of the van der Waals radii of oxygen and hydrogen (*ca.* 2.50 Å).[11] It is therefore not surprising that the conformation in the crystal lattice is different from that prevailing in solution, where intramolecular hydrogen bonding becomes predominant. A Dreiding model of a molecule of **(3)** in its completely staggered **(1e)** conformation shows that the closest contacts between non-bonded atoms are those involving the hydroxy group and 3-methyl of the trimethylsilyl group, and the methoxy and 1- and 2-methyls. In the actual conformation, as deduced from the diffractometric data, these steric interactions are reduced by a rotation (*ca.* 20°) of the trimethylsilyl group from the staggered conformation whereas the O(1)–C(10) bond is perfectly staggered with respect to the C(4)–Si and C(4)–C(9) bonds. All contacts involving methyl carbons are greater than 3 Å (see Table 5). The cyclohexane ring is slightly flattened around the C–Si bond: the mean value of the internal torsion angle is 54.4°, lower than that found in unsubstituted cyclohexane (55.9°),[12] the deformation being largest for the C(8)–C(9)–C(4)–C(5) torsion angle; the puckering parameters[13] are: $q_2 = 0.028(3)$, $q_3 = -0.553(3)$ Å, $\varphi_2 = -34.9(5.5)$, $\theta_2 = 177.2(3)°$, indicating a chair conformation eventually of type $^4C_1$.[14] Similar flattening of the cyclohexane ring has been observed for t-butylcyclohexanes.[15] Other bond angle deformations contribute to diminishing repulsive interactions, such as the increase of the C(4)–O(1)–C(10) angle to 116.8(2)° that removes the methoxy group away from 1- and 2-methyl.

In conclusion, one can say that the long C–Si bonds, ranging between 1.869 Å for Si–C(1) and 1.929 Å for Si–C(4), allow for a conformation of type **(1e)** of compound **(3)** that is relatively devoid of strain, and that is stabilized by strong intermolecular hydrogen bonding in the crystal. The n.m.r. and i.r. evidence presented in the first part of this paper on the other hand strongly points to a high contribution of conformer of type **(1a)** in $CDCl_3$ solution where intramolecular hydrogen bonding becomes more important. The conformation with an axial Me_3Si group **(1a)** must evidently be of sufficiently low energy to be competitive with the alternative one.

Experimental

The preparation of all compounds in Table 1 has been reported elsewhere.[2] Crystals of 2-trimethylsilyl-*trans*-2-methoxycyclohexanol **(3)** suitable for *X*-ray analysis, m.p. 83—86 °C, were obtained by slow evaporation of a solution in light petroleum (b.p. 60—80 °C). ^{1}H N.m.r. spectra were determined in a JEOL C60 HL and on a Varian XL-100 spectrometer in deuteriochloroform, unless indicated otherwise; $CHCl_3$ was used as internal standard due to the presence of an Me_3Si group in all compounds. I.r spectra for the determination of OH stretching bands were taken with a Perkin-Elmer 257 double-beam grating spectrometer in dried (P_2O_5) CCl_4 using the indene band at 3 110 cm^{-1} as the calibration standard; a quartz cell of 2 cm optical length was employed and the concentration of the solutions was 5×10^{-3}M or lower to prevent intermolecular associations.

Crystal Data.—$C_{10}H_{22}O_2Si$, $M = 202.4$. Monoclinic, $a = 6.505(7)$, $b = 17.104(7)$, $c = 11.181(8)$ Å, $\beta = 99.2(1)°$, $U = 1\,228.0(1.7)$ Å^3, $Z = 4$, $D_c = 1.095$ g cm^{-3}, $F(000) = 448$. Space group $P2_1/n$. Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 14.6 cm^{-1}.

A crystal of dimensions 0.28 × 0.19 × 0.62 mm was used for the measurement of cell constants and data collection. The cell parameters were obtained by least-squares fitting of the setting of four angles of 27 reflections on a on-line Siemens diffractometer. The intensity data were collected using a scintillation counter with a pulse-height analyser, $\theta - 2\theta$ scan technique, five point method; one standard reflection every 50 was monitored. 1 723 independent data with $I > 2\sigma(I)$ remained after averaging the 3 273 symmetry-related reflections and were used in the analysis (the total number of independent reflections before and after the averaging was 4 550 and 2 327, respectively). Lorentz and polarization, but not absorption, corrections were applied.

The structure was solved by direct methods[16] using normalised structure factors with $E > 1.2$; the first E-map gave the positions of all non-hydrogen atoms.

All the hydrogens came out from a subsequent difference map, but those of C(1) methyl group were put in calculated positions. Full-matrix least-squares refinement[16] of atomic co-ordinates and anisotropic thermal parameters from the non-hydrogen atoms and isotropic for the hydrogens gave $R = 4.5\%$ ($R_w = 5.3\%$), $w = 1/[\sigma^2(F) + 0.02F^2)]$ for 1 723 observed reflections. Scattering factors were those from volume 4 of reference 17. All calculations were carried out on a CYBER 76 computer of Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio, Bologna. Atomic final co-ordinates with thermal parameters and structure factors for observed reflections are deposited as Supplementary Publication No. SUP 56068 (36 pp.).*

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* For details of the Supplementary Publication Scheme see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.