Journal of Organometallic Chemistry, 462 (1993) 31–37

JOM 24022

Structures of sterically overcrowded or charge-perturbed molecules XXVIII *. $[(H_3C)_3Si]_3C{-}C{\equiv}C{-}C[Si(CH_3)_3]_3$ – a π-system concealed by a hydrocarbon veil **

Hans Bock, Jochen Meuret and Klaus Ruppert

Institute of Inorganic Chemistry, University of Frankfurt, Niederurseler Hang, W-6000 Frankfurt am Main 50 (Germany)

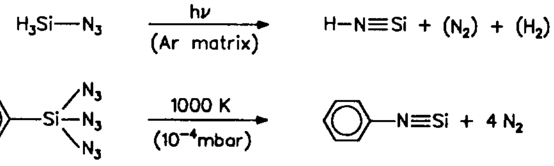
(Received February 16, 1993)

Abstract

The kinetically shielded di(tris(trimethylsilyl)methyl)acetylene crystallizes in the triclinic space group $P\bar{1}$ with 1 molecule per unit cell in rather dense lattice packing. Its staggered skeletal conformation of close to D_{3d} symmetry represents a sterically advantageous cogwheel gearing of the inner methyl groups of the half-shells of both substituents. The shortest nonbonded $C \cdots C$ distances of 400 pm between them equal the sum of the van der Waals radii of two H_3C groups. A space-filling representation of the molecular structure shows the acetylenic π-system to be almost completely covered by the peripheral HC skin, in keeping with its unusual unreactivity, *e.g.* towards catalytic hydrogenation. The spatial and electronic effects of the bulky substituents are discussed in terms of structural comparisons with chemically related compounds such as $[(H_3C)_3Si]_3Si{-}Si[Si(CH_3)_3]_3$, $[(H_3C)_3C]_3Si{-}Si[C(CH_3)_3]_3$ or $[(H_3C)_3Si]_3C{-}C_6H_4{-}C[Si(CH_3)_3]_3$, which also adopt staggered conformations of their sterically congested $[(H_3C)_3X]_3Y$-half shells along substituent axes of C_3-symmetry at different distances $Y \cdots Y$.

1. Introduction

Numerous novel unsaturated silicon molecules, for instance those containing a singly coordinated, triply-bonded Si center, are so reactive that they can only be prepared from appropriate precursors under conditions close to unimolecular, such as noble gas matrix photolysis [5] or flash vacuum pyrolysis [6–8]:



(1)

For unsaturated molecules with Si centers of higher coordination number, kinetic stabilization [9] can often be brought about through steric shielding by bulky inert substituents [10]. At the same time, however, more or less severe structural distortions are introduced owing to steric overcrowding [3,10–13] as in the extreme case of hexakis(tert-butyl)disilane [11] (Fig. 1(A)), in which the Si–Si bond is stretched by 36 pm to 270 pm length, or owing to electronic substituent effects [15], as, for instance, in 1,4-di(tris(trimethylsilyl)methyl)benzene [1,3,16] (Fig. 1(B)), in which the ipso ring angles [2,17] are contracted by 6° to 114° predominantly because of the donor properties of $[(H_3C)_3Si]_3C$ [1,3,8,15,16].

The space-filling models, drawn on the basis of structural data [11,16], also show that the disilane molecule is in effect a hydrocarbon ellipsoid with a SiSi backbone, and that in the benzene derivative, in which the bulky silahydrocarbon half-shells are approximately 220 pm apart [1], the benzene π-system is only partly visible through a small slit.

The distance between the two $[(H_3C)_3Si]_3C$ half-shells (Fig. 1(B)) can be further reduced by connecting

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Correspondence to: Prof. Dr. H. Bock.

* For Part XXVII *cf.* ref. 1, *cf.* also refs. 2–4.

** Dedicated to Professor M.F. Lappert on the occasion of his 65th birthday.

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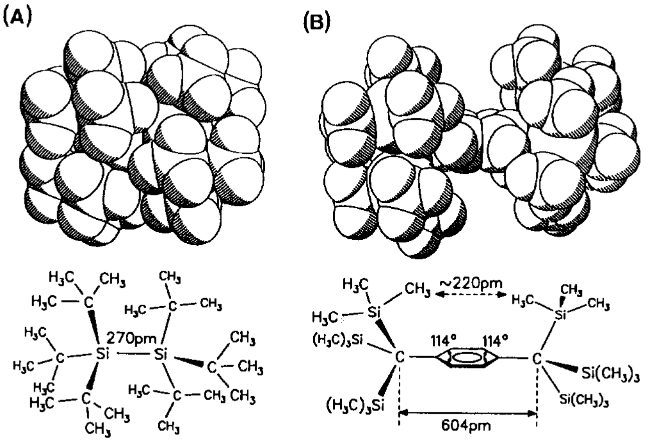
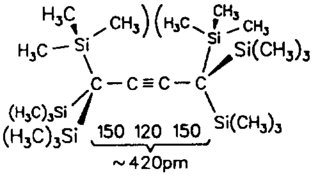


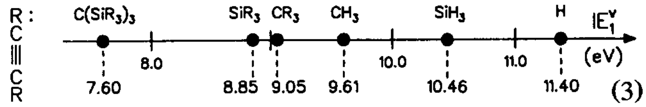
Fig. 1. Space-filling structures of hexakis(tert-butyl)disilane [11] (A) and of 1,4-di(tris(trimethylsilyl)methyl)benzene [16] (B) with selected bond lengths and angles (*cf.* text).

them through a shorter "π-link" such as that provided by an acetylene unit, as in $[(CH_3)_3Si]_3C{-}C{\equiv}C{-}C[Si(CH_3)_3]_3$, (cf. (2)).



(2)

The compound was first synthesized in 1968 by treatment of a mixture of hexachlorobutyne-2 and dimethylchlorosilane with lithium [18] (see Experimental section) and, owing to the steric shielding of the central π-system [19], in reactivity it rather resembles an alkylsilane: for instance, its C≡C bond cannot be hydrogenated at 200°C/50 atm in the presence of a palladium–charcoal catalyst in cyclohexane [18]. Other molecular properties are also surprising; thus its first vertical ionization energy of only 7.60 eV [8,19,21] is the lowest measured so far for an alkyl or silyl substituted acetylene [8,15,20] and is shifted relative to that of the parent acetylene [20] by 3.8 eV.



(3)

Because of its low first ionization energy the compound can be oxidized with $AlCl_3/H_2CCl_2$ [22], but the resulting radical cation characterized by ESR is that of the corresponding butatriene, $[(H_3C)_3Si]_2C{=}C^{\cdot}{=}^{\oplus}C{=}C[Si(CH_3)_3]_2$ [19,21]. Furthermore, slow reduction at a potassium metal mirror in a [2.2.2]cryptand DME solution gives finally the butatriene radical anion $[(H_3C)_3Si]_2C{=}C^{\cdot}{=}^{\ominus}C{=}C[Si(CH_3)_3]_2$, which has lost two R_3Si groups[21].

The single crystal structure determination reported here, was prompted by questions such as whether the lattice of the title acetylene would be as densely packed as those of other organosilicon species with a hydrocarbon skin [1–3,10,16], whether any skeletal distortions due to steric overcrowding or electronic substituent effects could be detected [1–3,15] and, especially, whether structural comparison with related compounds also containing bulky, half-shell groups along a C_3 substituent axis $(R_3X)_3Y \cdots Y(XR_3)_3$ (X, Y = C, Si) in staggered conformation but at varying distances Y ··· Y [1,3], would provide additional information on the ground state electron distributions [15].

2. Experimental section

2.1. *Hexakis(trimethylsilyl)-2-butyne [18]*

In a three-necked flask equipped with stirrer, dropping funnel and reflux condensor, to a mixture of 3.2 ml (5.4 g, 20.6 mmol) of hexachlorobutadiene and 26 ml (22.4 g, 204 mmol) of trimethylchlorosilane in 100 ml THF under Ar was added during 2 h 3.0 g (432 mmol) of lithium powder, the temperature being kept between −10 and +5°C. The red brown suspension was stirred for 22 h at room temperature, the surplus Li filtered off, and the solution hydrolysed with 2 N HCl. The yellow aqueous layer was extracted three times with diethyl ether and the combined extracts were dried over Na_2SO_4 and filtered, and the solvents were distilled off. The white residue was washed with ethanol, recrystallized from acetone, and dried at 10^{-2} mbar to give 5.8 g (58%) of white flaky crystals, m.p. 276°C. ^1H NMR (CD_2Cl_2, TMS): δ 0.21 ppm (s, 18H) at 300 K and $\delta = 0.07$ ppm (s, 18H) at 190 K. MS:

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement factors (atoms for which no data appear are symmetry related to those shown, *e.g.*: Si(1), Si(2) and Si(3) to Si(6), Si(5) and Si(4), respectively)

Atom	x	y	z	U_{eq}
Si(1)	3956(2)	7366(2)	2074(1)	44(1)
Si(2)	1379(2)	3527(2)	2083(1)	46(1)
Si(3)	518(2)	6417(2)	2780(1)	44(1)
C(1)	1530(6)	5606(6)	1818(4)	33(2)
C(2)	447(6)	5188(5)	527(4)	29(2)
C(11)	5642(9)	7555(9)	3531(6)	74(4)
C(12)	4552(9)	6876(9)	712(6)	67(3)
C(13)	4279(9)	9565(8)	2230(7)	68(3)
C(21)	2094(12)	3668(10)	3745(6)	83(5)
C(22)	−995(9)	1638(8)	1286(6)	69(3)
C(23)	2836(10)	2988(9)	1459(7)	73(4)
C(31)	2128(10)	7653(10)	4381(5)	74(4)
C(32)	−103(11)	7902(10)	2109(7)	72(5)
C(33)	−1618(9)	4603(9)	2846(6)	71(4)

$m/e = 487$ ($M^{\oplus}$), 472 ($M^{\oplus} - CH_3$), 457 ($M^{\oplus} - 2\ CH_3$), 442 ($M^{\oplus} - 3\ CH_3$), 414 ($M^{\oplus} - Si(CH_3)_3$), 73 ($Si(CH_3)_3^{\oplus}$).

Single crystals were grown from a solution of 1 g in 20 ml CH_2Cl_2 after careful layering with isopropanol.

2.2. *Crystal structure determination of hexakis(trimethylsilyl)-2-butyne*

$C_{22}H_{54}Si_6$ (MW 487.16), triclinic, space group $P\bar{1}$ (No. 2 Int. Tab.), $Z = 1$, $a = 905.14(80)$, $b = 920.17(90)$, $c = 1187.45(90)$ pm, $\alpha = 96.86(7)$, $\beta = 105.28(7)$, $\gamma = 118.32(6)°$, V (293 K) $= 804.31 \cdot 10^6 pm^3$, $\rho_{calc.} = 1.006$ g cm^{-3}, $\mu(Mo\text{-}K\alpha) = 0.27\ mm^{-1}$, Siemens AED II four-circle diffractometer with graphite monochromator, $3° < \theta < 56°$, ω-scan, 4104 measured reflections of which 2553 are independent with $I > 2\sigma(I)$. Direct methods (SHELXTL-PLUS), $N = 2553$, $NP = 128$, $R = 0.088$, $R_W = 0.09$, $w = 1/\sigma^2\ (F) + 0.003\ F^2$, GOOF = 1.867, $+0.72/-0.91$ e/Å^3; Si- and C-atoms anisotropically refined, H-atoms not detected. The molecule lies

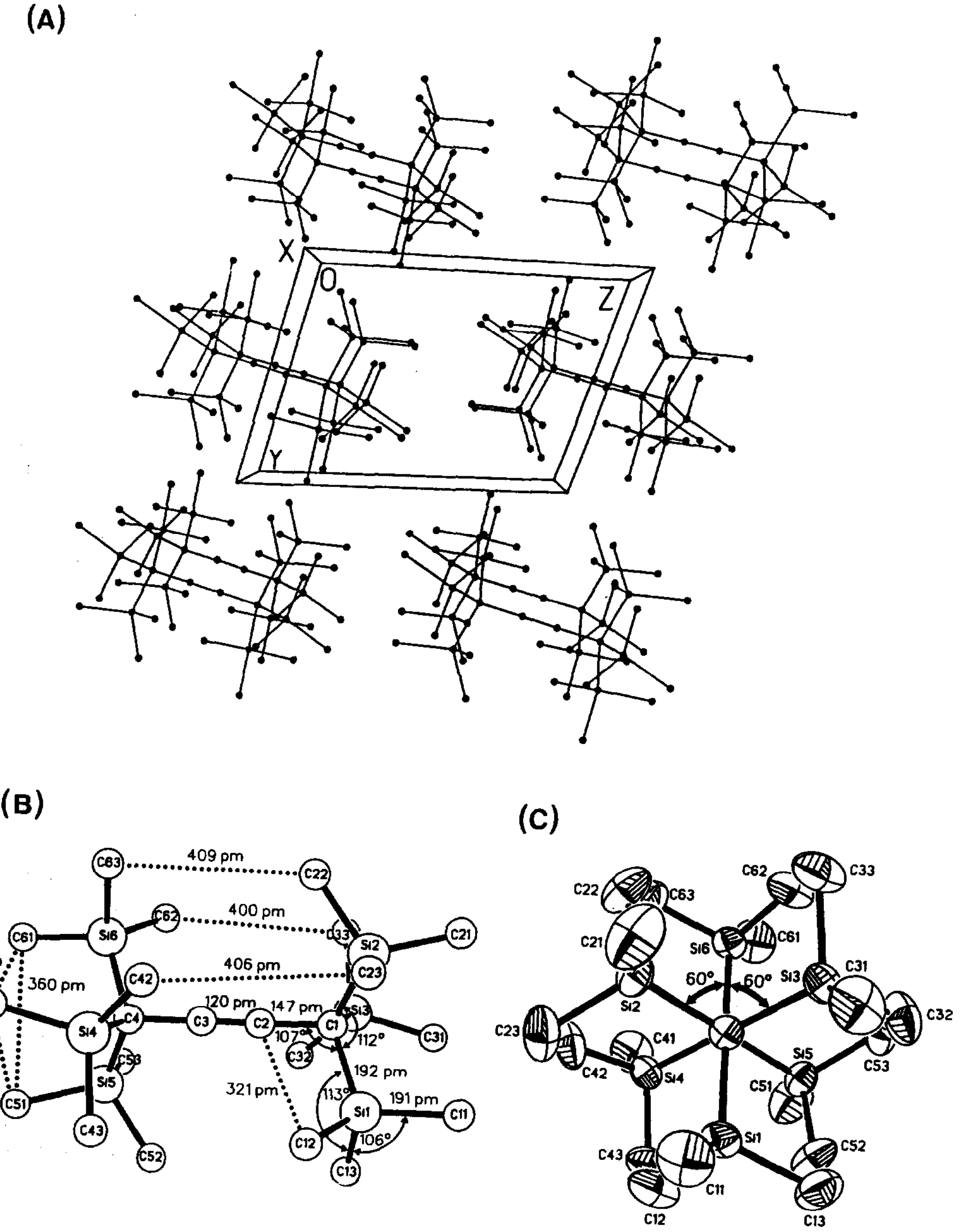


Fig. 2. Single crystal structure of hexakis(trimethylsilyl)-2-butyne: (A) lattice packing with unit cell ($P\bar{1}$, $Z = 1$); (B) side view with numbering of the centers, some selected bond lengths and angles (Table 2), and nonbonded distances between methyl group C centers; and (C) CC axial view of the molecular skeleton (50% thermal ellipsoids).

around a centre of inversion (Table 1). A complete list of bond lengths and angles, and parameters and hydrogen atom coordinates, and structure factors are available from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the deposition number CSD-57680, the authors, and the full journal citation.

3. Results and discussion

3.1. Crystal lattice packing

The title compound crystallizes in triclinic unit cells each containing only one molecule (Fig. 3(A)). As expected for ellipsoids with hydrocarbon surfaces, there is no stacking as a result of π-interactions: the linear C–C≡C–C chains are arranged parallel both in x and z directions, with comparable intermolecular distances between their centers of 905 pm in the x- and 920 and 935 pm in the z-direction. Nevertheless, the shortest nonbonded intermolecular C ··· C distance is only 391 pm: since the sum of the van der Waals radii of two methyl group interference is 400 pm [11], the molecules partly interlock, presumably due to some van der Waals bonding between the penetrating hydrocarbon spheres. Structurally related molecules such as $[(H_3C)_3Si]_3Si-Si[Si(CH_3)_3]_3$ or $[(H_3C)_3Si]_3C-C_6H_4-C[Si(CH_3)_3]_3$ with analogous HC-covered half-shell substituent groups also exhibit comparable intermolecular C ··· C distances of only 389 pm [12] or 382 pm [16]. The resulting, seemingly attractive, lattice packing is possibly promoted by the silicon-induced polarization $>Si^{\delta\oplus}-C^{\delta\ominus}-H^{\delta\oplus}$ in the molecular surface skins.

TABLE 2. Selected structural parameters for hexakis(trimethylsilyl)-2-butyne (numbering Fig. 3(C))

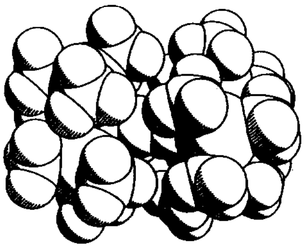
Selected bond lengths (pm)			
C(1)–C(2)	147.3(6)	Si(1)–C(13)	188.0(8)
C(2)–C(3)	119.9(8)	Si(2)–C(21)	187.6(7)
C(1)–Si(1)	192.1(4)	Si(2)–C(22)	187.8(6)
C(1)–Si(2)	192.2(6)	Si(2)–C(23)	189.3(11)
C(1)–Si(3)	192.2(6)	Si(3)–C(31)	186.6(5)
Si(1)–C(11)	190.7(7)	Si(3)–C(32)	189.0(11)
Si(1)–C(12)	190.4(9)	Si(3)–C(33)	189.2(7)
Selected bond angles (°)			
C(1)–C(2)–C(3)	178.7(7)	Si(1)–C(1)–Si(2)	111.7(3)
C(2)–C(1)–Si(1)	106.6(3)	Si(1)–C(1)–Si(3)	111.7(2)
C(2)–C(1)–Si(2)	107.1(3)	Si(2)–C(1)–Si(3)	111.9(3)
C(2)–C(1)–Si(3)	107.4(4)	C(11)–Si(1)–C(12)	110.0(4)
C(1)–Si(1)–C(11)	111.4(3)	C(11)–Si(1)–C(13)	106.2(3)
C(1)–Si(1)–C(12)	109.8(2)	C(12)–Si(1)–C(13)	106.4(4)
C(1)–Si(1)–C(13)	112.9(3)	C(21)–Si(2)–C(22)	108.4(3)
C(1)–Si(2)–C(21)	111.8(3)	C(21)–Si(2)–C(23)	106.9(5)
C(1)–Si(2)–C(22)	110.3(3)	C(22)–Si(2)–C(23)	106.2(3)
C(1)–Si(2)–C(23)	112.9(3)	C(31)–Si(3)–C(32)	107.1(4)
C(1)–Si(3)–C(31)	112.3(4)	C(31)–Si(3)–C(33)	107.5(3)
C(1)–Si(3)–C(32)	110.6(4)	C(32)–Si(3)–C(33)	106.5(4)
C(1)–Si(3)–C(33)	112.6(3)		

3.2. Molecular structure

The doubly tris(trimethylsilyl)methyl-substituted acetylene (Fig. 2(B) and (C)) has an almost linear inner C_4 chain with a normal C≡C triple bond length [23] of 120 pm and shortened CC single bonds each of 147 pm. The latter are consistent with some hyperconjugative $\sigma_{CSi3} \rightarrow \pi_{CC}$ electron delocalization, which would increase the electron density around the σ_{CC} bond. Overall, a shorter than expected (*cf.* (1)) C_4 chain with a length of only 414 pm results. With respect to this CC axis, the bulky half-shell substituents are arranged in a staggered conformation of close to C_3 symmetry (Fig. 2(C)), which implies nearly identical dihedral angles. All of their formally tetrahedral centers are considerably distorted, with angles around C1 and C4 between 107 and 112° and around Si1 to 6 between 106 and 113° (Table 2). Some explanation of these distortions can be derived by looking first at the sterically most congested outer H_3C sphere, in which there are three nonbonded C ··· C distances between 360 pm (C21 ··· C11) and 364 pm (C21 ··· C31) (Fig. 2(B)). These are all well within the sum of van der Waals radii of 400 pm for two CH_3 groups, and although the axial view (Fig. 2(C)) clearly shows relieving cogwheel-like gearing, the resulting compression could be responsible for the observed distortions. One feature of the distortion (Fig. 2(B) and Table 2) is that the two angles C13–Si1–C1 and Si1–C1–Si2 are widened to about 113 and 112°, whereas others such as Si1–C1–C2 are narrowed to about 107°. Between the inner sides of the two half-shells, there are nonbonded C ··· C distances ranging from 400 to 433 pm (Fig. 2(B)). Although all of them are either equal to or larger than the sum of two CH_3 interference radii of 400 pm, adjacent angles such as C1–Si1–C13 are stretched to 113°, whereas the complementary angles such as C11–Si1–C13 are compressed to 106° (Fig. 2(B) and Table 2).

Puzzlingly, the nonbonded distances between the acetylene π-center C2 and methyl carbons such as C12, of only 321 pm (Fig. 2(B)), are rather short. If, as usual [24], the radius of a π-cloud is assumed to be about 170 pm and this is added to the H_3C interference radius of about 200 pm, then there must be considerable overlap and, consequently, some bonding interaction between the π-cloud and the CH_3 groups. This previously largely neglected aspect may play a considerable part in the stabilization of radical cation states such that from the title compound, and thus to its astoundingly low first ionization potential of only 7.60 eV, *i.e.* 3.8 eV (!) below that of the parent HC≡CH (2).

Overall, the doubly $[(H_3C)_3Si]_3C$-substituted acetylene has the shape of a hydrocarbon ellipsoid, as convincingly demonstrated by a space-filling representation (see (4)) based on the structural data (H-radii upscaled from 32 to 53 pm; H-positions calculated).



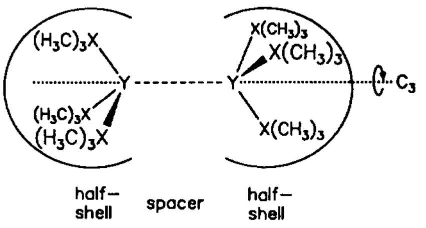
(4)

The acetylene backbone is hardly visible through the slit between the two half-shells of the bulky substituents, which touch each other, and this provides an explanation for the surprising unreactivity of the compound even towards H_2 attack [18]. The space-filling molecular model (4) also reveals the cogwheel-gearing of the two molecular halves in their staggered conformation along the C_4 chain, *i.e.* their C_3 symmetry axis, as well as of the H_3C groups within the same half-shell due to the short non-bonded distances (Fig. 2(C)) between them. In summary, di(tris(trimethylsilyl)methyl)-acetylene seems to be a molecule close to a limit, where steric overcrowding still can be relieved without severe skeletal distortions such as the very large ones observed in most congested molecules hexakis(tert-butyl)disilane [11] (Fig. 1(A)) and hexakis(trimethylsilyl)disilane so far observed [1–3].

3.3. *Criteria for steric overcrowding caused by bulky half-shell substituents*

Steric congestion in molecules containing space-filling substituents is a fascinating phenomenon that is at present undergoing extensive reinvestigation [2,25,26]. Some of the topics include prototype parent molecules such as ethylene [2,25,27,28], benzene [2,29,30] or trialkylamines [2,31], as well as prototype bulky substituents such as dimethylamino groups [2,28,32], mesityl and supermesityl [9,10] or tert-butyl and trimethylsilyl ligands [1,2,10–13,27,30]. Their space filling capacity is often defined by van der Waals radii [2,26], which, however, because of frequently aspherical electron density distributions around substituents and often restricted rotational degrees of freedom, must be used with some caution [12]. As concerns the skeletal distortions due to spatial overcrowding, usually as confirmed by quantum chemical [2] or force field calculations [33], angle changes are energetically preferred over those of bond lengths [2,34].

The most straightforward and informative way of discussing the complex effects of steric overcrowding is to compare the structures of closely related molecules. In the case of those with half-shell substituents $-Y[X(CH_3)_3]_3$ (X, Y = C, Si) in staggered conformation along a C_3 symmetry axis the spacer distances Y ··· Y can be varied considerably.

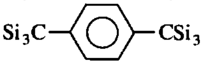


(5)

The molecules investigated within this series of organosilicon compounds [1,3,12] can be supplemented by selected examples taken from the literature with the same structural characteristics [11,13,35] to establish a satisfyingly congruent set (Table 3).

Starting with the most congested organosilicon compound, hexakis(tert-butyl)disilane, in which the disilane backbone is completely covered by the ellipsoidal hydrocarbon surface (Fig. 1(A)) and which also has one of the most densely packed lattices for alkylsilanes, with shortest intermolecular distances C ··· C of only 371 pm (!), very large skeletal distortions are observed (Table 3) [11]: thus, the Si–Si bond is stretched by 34

TABLE 3. Characteristic structural parameters of molecules containing bulky half-shell substituent groups $-Y[X(CH_3)_3]_3$ along C_3 symmetry axes fixed at varying distances Y ··· Y by various spacers (distances in pm, angles in °; values not reported –)

$[(H_3C)_3X]_3Y \cdots Y[X(CH_3)_3]_3$	[Lit.]	$d_{Y \cdots Y}$	d_{YX}	$\omega(X_3Y \cdots YX_3)$	$d_{C(H) \cdots (H)C'}$
$C_3Si—SiC_3$	[9]	270	199	45 + 75	⩾ 334
$Si_3Si—SiSi_3$	[10]	240	239	44 + 76	⩾ 352
$C_3Si—O—SiC_3$	[12]	333	195	$\begin{Bmatrix}43 + 77\\47 + 73\end{Bmatrix}$	⩾ 355
$Si_3C—C{\equiv}C—CSi_3$	[*]	414	192	60	⩾ 400
$Si_3Si—Zn—SiSi_3$	[35]	468	233	60	–
	[1]	604	192	60	⩾ 620

pm (!) to 270 pm relative to those of 236 pm in tetrakis(trimethylsilyl)silane $Si(Si(CH_3)_3)_4$ [36] and the Si–C bonds are elongated by 10 pm (!) relative to the fairly normal ones of 189 pm in the same tetrahedral pentasilane [36]. The shortest nonbonded C $\cdots$ C distance between two methyl groups of different half-shells is only 334 pm, and thus is about 17% below the sum of two H_3C van der Waals radii of 400 pm. All of this supports the proposed CH $\cdots$ HC van der Waals surface bonding [14], which may be needed to compensate for the considerably reduced Si–Si bond orders [1,3,11,13] in order to avoid dissociation into two silyl radicals. The compression within the molecule is also illustrated by the widened bond angles Si–Si–C and, above all, by the difference between the dihedral angles $\omega(C_3Si–SiC_3)$ of 75 and 45, *i.e.* 30° (Table 3), which clearly demonstrates that there is extreme cogwheel-like gearing between the two molecular halves.

Replacing the Si–C by longer Si–Si substituent bonds in hexakis(trimethylsilyl)disilane [1–3,12] releases some steric strain (Table 3), as illustrated by the almost normal length of the central Si–Si bond. Inversely, however, within the bulky substituent groups the angle changes become more dominant and, as also can be gathered from the still rather short nonbonded H_3C group minimum distances of 352 pm, there is still extreme meshing, as indicated by the differing dihedral angles $\omega(Si_3Si–SiSi_3)$ of 44 and 76° (Table 3). This structural parameter is thus proposed as the most significant criterion for steric overcrowding [1–3,12].

Another convincing example is provided by hexakis(tert-butyl)disiloxane [13] (Table 3), which contains a linear Si–O–Si backbone. Although the oxygen spacer increases the distance between the half-shells, it is the dense intramolecular packing of six tert-butyl substituents with Si–C bonds of only 195 pm length to the Si centers, which not only widens the central angle Si–O–Si but, in addition, results in different dihedral angles of 43° and 77° and of 47° and 73° for the two independent moieties in the unit cell [13]. Despite the relief of steric strain relative to that in hexakis(tert-butyl)disilane, the shortest nonbonded distance of 355 pm between methyl C centres in the different substituent half-shells is still considerably below the 400 pm sum of the van der Waals radii between two H_3C groups. Furthermore, analysis of its lattice packing [4], reveals the shortest intermolecular distances, of only 361 pm, so far found.

Argument along these lines indicates that all the other organosilicon compounds with two half-shell groups along a C_3 substituent axis (Table 3) no longer experience severe spatial overlap: accordingly, in the acetylene derivative reported in the present paper (Table 3, [*]), which shows a half-shell substituent spacing of 414 pm and shortest nonbonded C $\cdots$ C distances only slightly larger than the sum of two H_3C interference radii, there are no unusual distortions either in the bond lengths or bond angles (Fig. 2(A)). The same argument applies to the disilylzinc derivative with a linear Si–Zn–Si skeleton [35], and the 1,4-di(tris(trimethylsilyl)methyl)-substituted benzene [1,3,16] in which, because of the increased spacing, equal dihedral angles each of 60° are found. The criterion of the degree of overcrowding can be extended to cover some structures of unsymmetrically substituted silicon derivatives, which contain (nearly) C_3 substituent axes and sufficiently large spacers such as tris(tert-butoxy)zirconiumtris(trimethylsilyl)silyl [37], or the sterically less congested borimide derivative $[(H_3C)_3Si]_3Si–B{\equiv}N–C(CH_3)_3$ [38]. Both exhibit staggered conformations with equal dihedral angles, indicating almost negligible or no steric overcrowding.

4. Conclusions

The structural evidence presented supports the proposal that the novel criterion for sterical overcrowding based on the presence of different dihedral angles along C_3 symmetric substituent axes is a general one, which, therefore, may be modified for spatial arrangements of other symmetry and tested for a wide variety of compounds. The suggested intramolecular and attractive van der Waals contacts between $Si^{\delta\oplus}–C^{\delta\ominus}–H^{\delta\oplus}$ polarized methyl groups in organosilicon compounds, possibly contribute essentially to the bonding in molecules [14] such as hexakis(tert-butyl)disilane, in which the elongated Si–Si distance results in a drastically reduced bond order [11]. The intermolecular van der Waals bonding $C(H_3) \cdots (H_3)C$ suggested by the lattice packing of the ellipsoidal hydrocarbons with a silicon backbone [1,4], could have far-reaching consequences, extending from the viscosity of polysiloxane liquids to the self-organization of organosilicon molecules in solution and in crystals [39].

Acknowledgements

These investigations were sponsored by the Deutsche Forschungsgemeinschaft, the State of Hesse, and the Fonds der Chemischen Industrie.

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