

Sterically Congested Molecules. Part 4.¹ Front Strain along a C–C Double Bond in the Crystal Structure of [1-(1,1,3,3-Tetramethylindan-2-ylidene)-1-(trimethylsilyl)methyl] 2-Trimethylsilylphenyl Thioether

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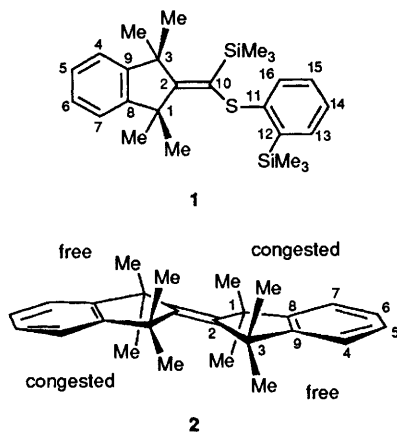
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The 1,1,3,3-tetramethylindan-2-ylidene moiety which occupies one end of the C–C double bond in the title molecule (**1**) exhibits only small deformations in the solid-state structure despite its repulsive interactions with the heteroatoms at the other end. Front strain along this double bond causes remarkable extensions of angles and bond lengths involving those heteroatoms. The exocyclic olefinic carbon atom is slightly pyramidalized but the C–C double bond is not elongated. The low flexibility of the former moiety is suggested to be a transferable property for the visualization of front strain.

E/Z Equilibrium constants² may be influenced by non-bonding interactions of bulky substituents in mutual *cis* positions at a double bond. While such repulsions can be qualified as a special kind of front strain,³ it is difficult to quantify this effect in energy terms (*i.e.*, by a single number) because the necessary choice of a reference system⁴ would be even more artificial than for total strain.^{5,6}

An alternative description^{5,6} of strain makes use of its geometrical consequences. For a polyatomic molecule, this can become quite cumbersome since many or all interatomic distances and angles may be distorted. Of course, such a distribution of total strain over numerous internal coordinates⁵ should also vitiate any proper comprehension of the relative importance of an individual strain component.

However, if some parts of a molecule are highly resistant to deformation, the geometrical consequences of a strain component might accumulate at the more deformable parts and thus allow for an immediate recognition (and, perhaps, quantification) in terms of only a few local distortions. We have met such a rare⁵ case during X-ray crystallographic analysis of the title compound **1**, which carries the hetero-atoms S and Si in acyclic connections at one end of the C–C double bond in opposition to the hardly deformable 1,1,3,3-tetramethylindan-2-ylidene group at the other end.



The rather limited flexibility of the latter moiety may be gleaned from an inspection of the published⁷ solid-state structure of octamethyl-2,2'-bisindanylidene (**2**). This highly strained alkene shows a stepped shape (by 0.77 Å) such that its four 'outer' methyl groups reside in partially free sites above and

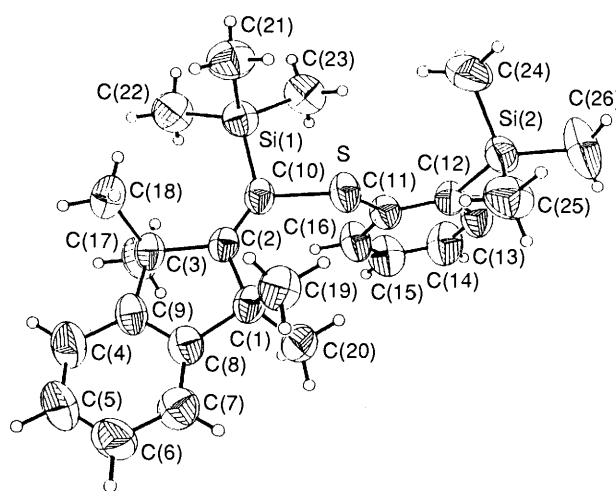


Fig. 1 ORTEP plot and crystallographic numbering of the alkene **1**, with thermal ellipsoids at 30% probability level

below the olefinic plane, whereas the four 'inner' ones are in a highly congested region imposed by the opposing half-molecule. Very close contacts of the latter methyl functions attest to this analysis, with shortest distances H...H approaching 1.89 Å and C...C 3.246 Å. These repulsive interactions are already minimized in **2** by the following deformations. The C(2)–C(10) double bond is not elongated but somewhat out of the aromatic plane and pulled farther away from the compressed C(8)–C(9) bond, causing a small decrease of the C(1)–C(2)–C(3) angle to 105.2(1)°. All eight methyl groups are bent back only weakly from their opposing partners in **2** such that the angles CH₃–C(quat.)–C(aromatic) average to 105.9(3)°. A similar folding and lateral compression of the five-membered ring together with back-bending of its methyl groups is also observed in a related octamethyltetrahydrofulvalene.⁸

Results and Discussion

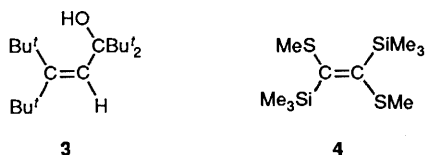
The molecule **1** is shown in Fig. 1 as an ORTEP plot and non-hydrogen atom co-ordinates are given in Table 1. Its *ortho*-substituted benzene rings are almost orthogonal (95.3°) to each other; both of them are planar but have their non-hydrogen substituents clearly out-of-plane. Yet, contrasting with **2**, the triangle spanned by C(1)–C(2)–C(3) is almost coplanar with the

Table 1 Final atomic co-ordinates for **1** at 20 °C, with estimated standard deviations in parentheses

Atom	x	y	z
S	0.2537(1)	0.7518(1)	0.1501(1)
Si(1)	0.2087(1)	0.8706(1)	-0.0083(1)
Si(2)	0.1979(1)	0.5182(1)	0.1502(1)
C(1)	0.3285(2)	0.9296(2)	0.2733(2)
C(2)	0.2852(2)	0.9445(2)	0.1743(2)
C(3)	0.2934(2)	1.0529(2)	0.1538(2)
C(4)	0.3691(3)	1.1939(3)	0.2596(3)
C(5)	0.4122(3)	1.2210(3)	0.3434(3)
C(6)	0.4288(3)	1.1553(3)	0.4094(3)
C(7)	0.4034(3)	1.0592(3)	0.3908(2)
C(8)	0.3607(2)	1.0304(2)	0.3063(2)
C(9)	0.3435(2)	1.0970(2)	0.2410(2)
C(10)	0.2451(2)	0.8766(2)	0.1146(2)
C(11)	0.1160(3)	0.7173(2)	0.1452(2)
C(12)	0.0939(2)	0.6173(2)	0.1479(2)
C(13)	-0.0140(3)	0.5922(2)	0.1479(2)
C(14)	-0.0959(3)	0.6595(3)	0.1449(3)
C(15)	-0.0722(3)	0.7557(3)	0.1421(3)
C(16)	0.0325(3)	0.7846(3)	0.1426(3)
C(17)	0.1776(3)	1.0961(2)	0.1164(2)
C(18)	0.3692(3)	1.0706(3)	0.0952(2)
C(19)	0.4320(3)	0.8650(3)	0.2996(2)
C(20)	0.2384(3)	0.8918(2)	0.3129(2)
C(21)	0.3415(3)	0.8365(3)	-0.0318(3)
C(22)	0.1476(3)	0.9781(3)	-0.0746(2)
C(23)	0.1045(3)	0.7750(3)	-0.0522(3)
C(24)	0.2517(4)	0.5205(3)	0.0544(3)
C(25)	0.3183(3)	0.5281(3)	0.2468(3)
C(26)	0.1277(4)	0.4010(3)	0.1538(4)

aromatic plane C(4)–C(9) (twist 1.2°) but tilted against the S–C(10)–Si(1) plane by 10.7°. The exocyclic olefinic carbon atom C(10) is slightly pyramidalized, protruding from the plane C(2)–Si(1)–S by 0.124 Å, such that the eight-carbon fragment C(1)/C(3)/C(4)–C(9) is geometrically very similar to that in **2**. On the other hand, back-bending is now much weaker than in **2**, as shown by the four angles CH₃–C(quat.)–C(aromatic) averaging to 109.3(8)° in **1**. The conclusion that local strain at C(2) is much less in **1** than in **2** gains support from the magnitude of the intra-annular angle C(1)–C(2)–C(3), 108.9(2)°, which is to be compared with those of cyclopentanones,^{9–11} 109–111°, and of cyclopent-3-enone,¹² 109(1)°.

Strain is mainly linked to the heteroatoms, as the shortest C–C distances occur for C(17)/C(22) (3.43 Å) and C(11)/C(23) (3.26 Å). Due to the small dihedral angle C(3)–C(2)–C(10)–Si(1) = 12.6(5)°, this silicon atom has close contacts with C(18) (3.57 Å) and C(3) (3.60 Å), in spite of a dramatic widening of the Si(1)–C(10)–C(2) angle to 135.5(2)° and an increased Si(1)–C(10) bond length of 1.919(4) Å. The normal bonding parameters are 121.5°^{13a} and 1.87 Å¹³ for silicon at a trigonal carbon atom. However, a much larger value, 143.8°, was reported¹⁴ for the corresponding angle at the CH function in **3**, showing once more that steric effects depend more on the effective shapes⁵ than on the relative sizes of bulky substituents, since a C–C bond is shorter than a C–Si bond.



The sulfur atom in **1**, pointing in between the pairs of methyl groups at C(1), Si(1) and Si(2), is circled at short distances by Si(1) (2.97 Å), C(1) (3.16 Å), C(19) (3.22 Å), C(20) (3.32 Å),

Table 2 Bond lengths/Å and selected angles/° for the alkene **1**, with estimated standard deviations in parentheses

S–C(10)	1.822(3)	S–C(11)	1.773(3)
Si(1)–C(10)	1.919(4)	Si(1)–C(21)	1.865(4)
Si(1)–C(22)	1.878(4)	Si(1)–C(23)	1.863(4)
Si(2)–C(12)	1.889(3)	Si(2)–C(24)	1.851(5)
Si(2)–C(25)	1.861(3)	Si(2)–C(26)	1.861(5)
C(1)–C(2)	1.560(4)	C(1)–C(8)	1.515(4)
C(1)–C(19)	1.540(4)	C(1)–C(20)	1.535(5)
C(2)–C(3)	1.552(4)	C(2)–C(10)	1.347(4)
C(3)–C(9)	1.511(4)	C(3)–C(17)	1.535(4)
C(3)–C(18)	1.534(5)	C(4)–C(5)	1.370(6)
C(4)–C(9)	1.398(5)	C(5)–C(6)	1.378(6)
C(6)–C(7)	1.388(5)	C(7)–C(8)	1.386(5)
C(8)–C(9)	1.378(5)	C(11)–C(12)	1.420(4)
C(11)–C(16)	1.396(5)	C(12)–C(13)	1.397(5)
C(13)–C(14)	1.381(5)	C(14)–C(15)	1.373(6)
C(15)–C(16)	1.370(5)		
C(10)–S–C(11)	105.7(1)	C(10)–Si(1)–C(21)	104.3(1)
C(10)–Si(1)–C(22)	120.2(2)	C(22)–Si(1)–C(23)	102.4(2)
C(12)–Si(2)–C(24)	112.2(2)	C(12)–Si(2)–C(25)	111.1(2)
C(2)–C(1)–C(8)	103.0(2)	C(8)–C(1)–C(19)	108.6(2)
C(8)–C(1)–C(20)	109.0(3)	C(1)–C(2)–C(3)	108.9(2)
C(1)–C(2)–C(10)	127.1(3)	C(3)–C(2)–C(10)	124.0(3)
C(2)–C(3)–C(9)	103.2(2)	C(9)–C(3)–C(17)	108.6(3)
C(9)–C(3)–C(18)	110.0(2)	C(5)–C(4)–C(9)	118.9(4)
C(4)–C(5)–C(6)	121.5(4)	C(5)–C(6)–C(7)	119.5(4)
C(6)–C(7)–C(8)	119.8(4)	C(1)–C(8)–C(7)	127.6(3)
C(1)–C(8)–C(9)	112.3(3)	C(7)–C(8)–C(9)	120.1(3)
C(3)–C(9)–C(4)	127.2(3)	C(3)–C(9)–C(8)	112.5(3)
C(4)–C(9)–C(8)	120.3(3)	S–C(10)–Si(1)	105.2(2)
S–C(10)–C(2)	117.5(2)	Si(1)–C(10)–C(2)	135.5(2)
S–C(11)–C(16)	117.4(2)	S–C(11)–C(12)	122.1(2)
C(12)–C(11)–C(16)	120.5(3)	Si(2)–C(12)–C(11)	125.1(2)
Si(2)–C(12)–C(13)	118.7(2)	C(11)–C(12)–C(13)	116.2(3)

Table 3 Selected torsional angles/° for **1**, with estimated standard deviations in parentheses

C(11)–S–C(10)–Si(1)	-84.7(2)
C(11)–S–C(10)–C(2)	108.2(3)
C(10)–S–C(11)–C(16)	-18.8(3)
C(22)–Si(1)–C(10)–C(2)	-35.9(4)
C(22)–Si(1)–C(10)–S	160.6(2)
C(26)–Si(2)–C(12)–C(11)	179.8(3)
C(8)–C(1)–C(2)–C(3)	-0.3(3)
C(8)–C(1)–C(2)–C(10)	-179.3(3)
C(2)–C(1)–C(8)–C(7)	179.1(3)
C(1)–C(2)–C(3)–C(9)	1.3(3)
C(10)–C(2)–C(3)–C(9)	-179.6(3)
C(1)–C(2)–C(10)–S	-6.4(4)
C(3)–C(2)–C(10)–Si(1)	12.6(5)
C(2)–C(3)–C(9)–C(4)	179.8(3)
S–C(11)–C(12)–Si(2)	-3.6(4)
Si(2)–C(12)–C(13)–C(14)	-178.9(3)

C(23) (3.32 Å), Si(2) (3.32 Å) and C(25) (3.48 Å). To account for similar close contacts to sulfur, the possibility of non-bonded attraction has been postulated.¹⁵ Front strain on sulfur along the C–C double bond is expressed by the widened angle C(1)–C(2)–C(10) = 127.1(3)° which permits an almost normal angle S–C(10)–C(2) as shown in Table 2. This implies a weak lateral displacement of the exocyclic C(10) atom as a further possibility of strain accommodation in front of the 1,1,3,3-tetramethylindan-2-ylidene fragment. Probably due to repulsion of S by both Si(1) and C(1), the S–C(10) bond length is abnormally extended to 1.822(3) Å. Except for the contracted angle Si(1)–C(10)–S = 105.2(2)°, the geometrical situation about C(10) is similar to that in the silylated ethylenebis(thioether) **4** whose bond lengths are less increased [C–Si = 1.905(4) Å and C–S = 1.797(2) Å]¹⁶ than in **1**.

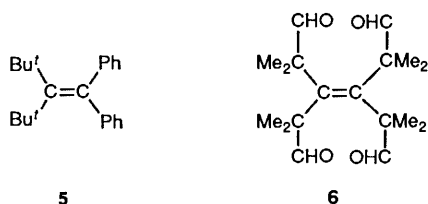
Beyond the olefinic region, the almost coplanar (Table 3) Z-arrangement of sulfur and Si(2) with the aromatic nucleus, C(11)–C(16), can be seen to have normal angles if the corresponding part of **4**¹⁶ is taken as a reference; but the S–C(11) and Si(2)–C(12) bond lengths (Table 2) match the standard values^{13b} of 1.773(9) Å and 1.868(14) Å, respectively, in accord with the slightly elongated bond C(11)–C(12) = 1.420(4) Å. Therefore, 'ortho-strain' between the S and Si(2) atoms is thought to be present but relatively weak in **1**; indeed, the intra-annular angles at C(11) and C(12) in Table 2 are close to their normal values^{13a} of 119.7(3)° and 117.0(2)°, respectively.

Conclusion

Front strain along the C–C double bond in **1** is expressed by distinct geometrical distortions outside of the 1,1,3,3-tetramethylindan-2-ylidene part of the molecule. This latter fragment might therefore be expected to provide a transferable abutment which may be useful for the immediate recognition and simple geometrical description of strain components in related substances with other substituents in place of the Si(1) and S atoms. Structural transferability must of course also be stipulated for direct comparisons within a series of compounds by other than geometrical properties, like the dependency of rates of reactions on front strain.

Other systems appear less suitable for this purpose. Thus, 1,1-bis(*tert*-alkyl)-substituents are more flexible⁵ and often show structural disorder or signs of additional alleviation of strain, as expressed by the spread of terminal (*tert*-C)–C–(*tert*-C) angles in **5**¹⁷ with 119.2° or in **6**¹⁸ with 114.2° and 112.5°. On the other hand, the corresponding angle in the six-membered ring of γ -pyrone imines¹⁹ and their iminium salts is also quite variable with reported values between 113.8° and 116.8°.

Comparing the Bu^t–C=C angles²⁰ in planar (*Z*)-1,2-di-*tert*-butylethylene (136.4°) and in the less planar (*Z*)-2,3-di-*tert*-butylbut-2-ene (131–132°), it is seen that buttressing methyl groups at both ends of the double bond can already reduce the angular sensitivity for front strain. We think that our model **1** provides for a simpler and, therefore, more convincing geometrical recognition of front strain by the accumulation of distortions at only one end of its C–C double bond.



Strain is a useful and important concept for the quantitative characterization of organic and organometallic substances in their ground states, as witnessed by the rapid evolution of molecular mechanics methods. It is also relevant for a proper comprehension of reactivity.^{3–6,21,22} Further progress in the calibration of force-fields should be facilitated by more experimental data from rigid²² compounds, like **1**, if these have little or no conformational ambiguity and focus geometrical distortions in certain molecular regions.

Experimental

[1-(1,1,3,3-Tetramethylindan-2-ylidene)-1-(trimethylsilyl)-methyl] 2-Trimethylsilylphenyl Thioether (**1**).—The crude

material was prepared by treatment of the corresponding dilithio compound (Li in place of SiMe₃)²³ with chlorotrimethylsilane and recrystallized from methanol; m.p. 110 °C, colourless²³ (Found: C, 71.3; H, 8.7; S, 7.3. C₂₆H₃₈SSi₂ requires C, 71.16; H, 8.73; S, 7.31).

Crystal data. C₂₆H₃₈SSi₂, *M* = 438.8, monoclinic, *P*2₁/*c* (no. 14), *a* = 12.533(4), *b* = 13.904(6), *c* = 16.192(4) Å, β = 105.74(2)°, *V* = 2716(2) Å³, *Z* = 4, *D*_x = 1.073 g cm⁻³, crystal size (mm) = 0.4 × 0.3 × 0.8, *F*(000) = 952, μ (Mo–K α) = 2.10 cm⁻¹, λ = 0.710 69 Å (Mo–K α , graphite monochromator, Nicolet R3m automated X-ray diffractometer).

Data collection. 20 °C, ω -scans, 2 control reflections monitored after every 48 intensity measurements, 2θ -range = 2–47° in *hk* ± *l*, scan speed = 2–29.3°/min, scan width = 0.8°, reflection-to-background-ratio = 1:0.5; 4885 reflections scanned, 3896 unique reflections, and 3157 considered as observed with *I* ≥ 2 σ (*I*).

Structure solution and refinement. The structure was solved by SHELXS-86²⁴ and refined by using the SHELXTL-Plus²⁵ program package. Corrections of reflection intensities to variations in the intensities of the control reflections (<1%), Lorentz and polarization corrections applied. Direct methods revealed the positions of all non-hydrogen atoms (Table 1). Anisotropic refinement of these and a difference Fourier synthesis led to all hydrogen positions except for those at C(22) and C(25). Methyl hydrogen atoms were included in the final refinement with fixed C–H distances (0.96 Å) in a riding model, with 262 variables in a full-matrix treatment, giving *R* = 0.056, *R*_w = 0.055, *w*⁻¹ = $\sigma^2(F) + 0.000 375F^2$; GOOF = 1.494, largest residual electron density 0.23 e/Å³.

Lists of anisotropic thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.*

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