Determination by Electron Diffraction of the Molecular Structure of Tris(trimethylsilyl)methylphosphine in the Gas Phase

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The molecular structure of $(Me_3Si)_3CPH_2$ in the gas phase has been determined by electron diffraction. Important bond lengths (r_a) are Si–C 194.1(5), Si–Me 188.3(2), and P–C 180.8(9) pm. Steric strain within the tris(trimethylsilyl)methyl group is relieved by (*a*) compression of the methyl groups within each trimethylsilyl group, so that the Me–Si–Me angles are only 104.3(4)°, (*b*) tilting of the trimethylsilyl groups by 7.3(15)° away from each other, and (*c*) twisting of the trimethylsilyl groups by 21.2(4)° away from the fully staggered conformation.

The discovery of the lithium reagent, $(Me_3Si)_3CLi$, by Eaborn and co-workers [1] paved the way for the attachment of the tris(trimethylsilyl)methyl ('trisyl') substituent to a wide variety of other elements including B,[2] C,[2] Si,[1,3] Ge,[4] Sn,[5] P,[6] As,[7] Zn,[8] Cd,[8] Hg,[9] and Ni.[10] Interest in trisyl substitution has been generated by the fact that this very bulky group is responsible for some unusual patterns of reactivity. For example, the primary alkyl phosphine, $(Me_3Si)_3CPH_2$, is air-stable,[6] and the trichlorosilane, $(Me_3Si)_3CSiCl_3$, is unreactive towards methanol or alcoholic $AgNO_3$.[3a] A further consequence of trisyl substitution is to increase significantly the thermal stabilities of metal alkyls, bis(trisyl) compounds of Zn, Cd, and Hg, for instance, being stable to approximately 570 K.[8,9] The trisyl group has also found significant utility for the kinetic stabilisation of phosphorus–phosphorus double bonds in, for example, $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ and $(Me_3Si)_3CP{=}P(C_6H_2Bu^t{}_3\text{-}2,4,6)$.[11]

Given the foregoing facts, it is of importance to probe the structural details of compounds featuring the trisyl substituent. We report herein an electron diffraction study of $(Me_3Si)_3CPH_2$ which, along with a single-crystal *X*-ray diffraction study of $(Me_3Si)_3CP{=}PC(SiMe_3)_3$,[11d] provides the first structural information for a Group 5 trisyl compound. Previous structural work is confined to an electron diffraction study of the parent hydrocarbon, $(Me_3Si)_3CH$,[12] and single-crystal *X*-ray studies of $(Me_3Si)_3CSiMe_2Ph$,[13] $[(Me_3Si)_3C]_2Hg$,[9b] and $(Me_3Si)_3CB(Ph)[O(CH_2)_4C(SiMe_3)_3]$.[2]

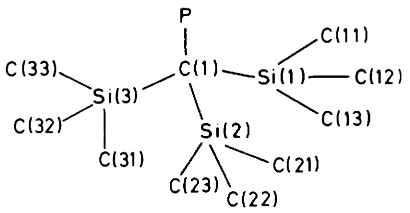
Experimental

Tris(trimethylsilyl)methylphosphine was prepared as described in the literature.[6]

Electron diffraction data were recorded in Oslo on Kodak Electron Image plates using a Balzers' Eldigraph KD.G2 apparatus.[14] Nozzle-to-plate distances were 497.81 and 247.85 mm, the accelerating voltage was 42 kV, and the nozzle temperature *ca.* 390 K. Electron wavelengths were determined from the scattering patterns of gaseous benzene. Data were obtained in digital form using the automatic Joyce-Loebl MDM6 microdensitometer at the S.E.R.C. Laboratory, Daresbury.[15] Calculations were carried out on ICL 2972 computers using established data-reduction [15] and least-squares refinement [16] programs, modified to take into account the appropriate sector and blackness corrections for the Oslo apparatus. Weighting points, used in setting up the off-diagonal weight matrices, are listed in Table 1 together with correlation parameters, scale factors, and the electron wavelengths. In all calculations the complex scattering factors of Schäfer *et al.*[17] were used.

Results

Molecular Model.—There was assumed to be three-fold symmetry at each methyl group, at each silicon atom, and also at the central carbon atom (disregarding the PH_2 group). The CPH_2 group had C_s symmetry. All the trimethylsilyl groups were therefore presumed to be identical. Two types of Si–C bonds are described by r_3(Si–C)(mean) and r_4(Si–C)(difference), as defined in Table 2. The atom-numbering scheme employed for the heavy atoms is shown below.



The structure was then defined by three more bonded distances r_1(C–P), r_2(P–H), and r_5(C–H), five valence angles [P–C–Si, C(11)–Si(1)–C(12), Si–C–H, C–P–H, and H–P–H],

Table 1. Weighting functions, correlation parameters, scale factors, and wavelengths

Camera height mm	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$	Correlation parameter	Scale factor	Wavelength/pm
	nm^{-1}							
250	4	60	90	250	296	−0.346	0.923(13)	5.895
500	2	20	40	120	146	0.401	0.866(10)	5.895

Table 2. Molecular parameters [a] for $(Me_3Si)_3CPH_2$

(*a*) Independent parameters

r_1(C–P)/pm	180.8(9)
r_2(P–H)/pm	140.1(28)
r_3(Si–C)(mean) [b]/pm	189.8(2)
r_4(Si–C)(difference) [c]/pm	5.8(5)
r_5(C–H)/pm	110.3(4)
Angle 1 (P–C–Si)/°	111.9(13)
Angle 2 [C(11)–Si(1)–C(12)]/°	104.3(4)
Angle 3 (Si–C–H)/°	110.6(6)
Angle 4 (C_3Si tilt)/°	−7.3(15)
Angle 5 (CH_3 twist)/°	65.0 (fixed)
Angle 6 (C_3Si twist)/°	81.2(4)
Angle 7 (C–P–H)/°	100.0 (fixed) [d]
Angle 8 (PH_2 twist)/°	0.0 (fixed) [d]
Angle 9 (H–P–H)/°	97.0 (fixed)

(*b*) Distances [e]

	Distance/pm	Amplitude/pm
d_1 (C–P)	180.8(9)	5.6 (fixed)
d_2 (P–H)	140.1(28)	8.5 (fixed)
d_3 [Si(1)–C(1)]	194.1(5)	5.6 (fixed)
d_4 [Si(1)–C(11)]	188.3(2)	5.6 (fixed)
d_5 (C–H)	110.3(4)	8.1(4)
d_6 (P···Si)	310.8(25)	11.9(4)
d_7 [C(1)···C(11)] [f]	333.0(25)	
d_8 [C(1)···C(12)] [f]	310.5(15)	
d_9 [C(1)···C(13)] [f]	318.9(7)	
d_{10} (Si···Si)	311.9(19)	
d_{11} [C(11)···C(12)]	297.3(10)	
d_{12} [Si(1)···C(21)]	363.4(20)	20.3(28)
d_{13} [Si(1)···C(33)]	352.1(13)	
d_{14} [P···C(12)]	340.0(18)	
d_{15} [Si(1)···C(22)]	397.4(17)	15.0(13)
d_{16} [Si(1)···C(31)]	413.2(19)	
d_{17} [P···C(13)]	398.1(24)	
d_{18} [Si(1)···C(23)]	479.3(19)	13.4(10)
d_{19} [Si(1)···C(32)]	474.4(20)	
d_{20} [P···C(11)]	482.6(33)	
d_{21} [C(11)···C(21)]	386.9(34)	8.6(21)
d_{22} [C(13)···C(21)]	366.3(25)	
d_{23} [C(13)···C(22)]	356.0(17)	
d_{24} [C(11)···C(22)]	534.2(17)	16.6(18)
d_{25} [C(11)···C(23)]	562.6(26)	
d_{26} [C(12)···C(21)]	550.8(22)	
d_{27} [C(12)···C(22)]	533.9(23)	
d_{28} [C(12)···C(23)]	627.7(20)	
d_{29} [C(13)···C(23)]	540.2(15)	
d_{30} (Si···H)	249.5(8)	13.7(7)

[a] Errors quoted in parentheses are estimated standard deviations, obtained in least-squares analyses, increased to allow for systematic errors. [b] $\{r[C(1)–Si(1)] + 3r[Si(1)–C(11)]\}/4$. [c] $r[C(1)–Si(1)] - r[Si(1)–C(11)]$. [d] See text. [e] Many non-bonded P···H, Si···H, C···H, and H···H distances were also included in the refinement but are not listed here. [f] Angles C(1)–Si–C(11), C(1)–Si–C(12), and C(1)–Si–C(13) were 121.1, 108.5, and 133.0° respectively.

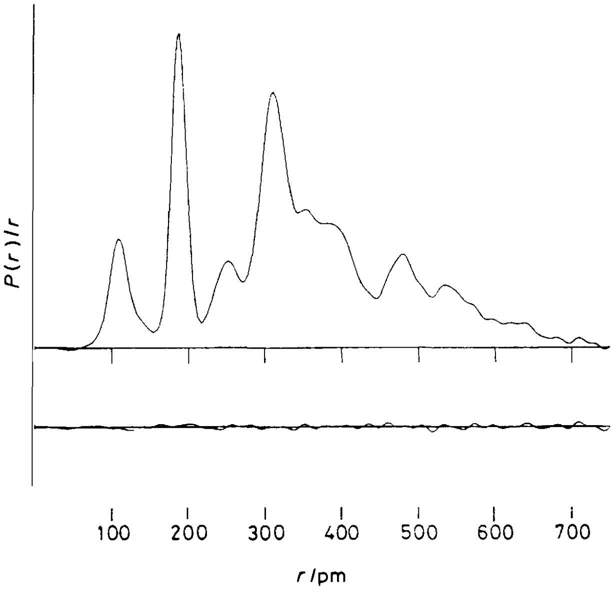


Figure 1. Radial distribution curve, $P(r)/r$, for $(Me_3Si)_3CPH_2$. Before Fourier inversion the data were multiplied by $s.\exp[-0.000\,02\,s^2/(Z_P - f_P)(Z_C - f_C)]$

the twist of the PH_2 group, the twist of the methyl substituents, and the twist and tilt of the trimethylsilyl groups. The twist angles were defined as positive for clockwise rotations, when viewed from P to C(1), C(11) to Si(1), and Si to C(1), respectively. The zero position for the PH_2 twist was that in which the PH_2 bisector was *anti* to one C(1)–Si bond, while zero positions for the other two twist angles in each case represented the eclipsed positions. The SiC_3 tilt was taken to be the angle between the three-fold axis of the SiC_3 group and the Si–C(1) bond and defined to be positive when the SiC_3 groups moved closer together. The molecular geometry was thus described by fourteen parameters, as listed in Table 2, which also contains dependent distances.

Refinement.—The refinement of the structure of a molecule as complex as tris(trimethylsilyl)methylphosphine is an undertaking not to be entered into lightly. The radial distribution curve (Figure 1) first shows a clear peak arising from the 27 C–H bonds (which we have assumed to be of equal length) together with the hint of a shoulder corresponding to the P–H bonded distance, which refined satisfactorily in the later stages of the work. The second peak, at *ca.* 185 pm, contains contributions from two different Si–C distances, even with the restrictions of the molecular model used, plus the P–C distance, and it is clearly impossible to distinguish these distances on the basis of this peak alone. The third peak is due to the Si(C)H atom pairs, and this defines the Si–C–H angle, but the next peak, at just over 300 pm, contains contributions from all the heavy-atom two-bond distances, as the bond lengths involved are approximately equal and the valence angles are all roughly tetrahedral. However, the region beyond 300 pm in the radial distribution curve has a complicated envelope, and yields a great deal of information about the structure.

With the exception of the twist angle for the methyl groups (which refined to 63.8 ± 5.0° and was subsequently fixed at 65°) all geometrical parameters relating to the $(Me_3Si)_3CP$ group could be refined, together with eight amplitudes of vibration. The results were, to us, somewhat unexpected, most notably in the length of the P–C bond, which was no greater than normal, and in the angles at the central carbon atom, being less than the tetrahedral angle between the Si–C bonds. These parameters were therefore changed to the expected values, but each time the refinements returned to the same minimum. One important constraint in these refinements was the fixing of the amplitudes of vibration for the bonded Si–C and P–C atom pairs to 5.6 pm. When these amplitudes were refined as a group they went to 6.5 pm, and the P–C distance changed to 193 pm, with all the Si–C distances 188 pm. Thus there is some uncertainty in the results, arising from correlations between this amplitude of vibration and various

Table 3. Portion of least-squares correlation matrix for $(Me_3Si)_3CPH_2$ showing all elements $\geqslant 50\%$

r_5	Angle 1	Angle 2	Angle 4	u_{12}	u_{15}	u_{18}	k_1	
							-59	r_1
58								r_2
							50	r_3
	71	-56	-75				56	r_4
		-79	-87		52	-60		Angle 1
		73			-65	63		Angle 4
				54				Angle -6
				50				u_6

geometrical parameters. However, we prefer the refinements with the fixed amplitude, as all other refined vibrational parameters are very close to expected values. Other correlations (shown in Table 3) are remarkably small; the most significant ones are between the angles of the skeleton.

The only parameter relating to the PH_2 group that refined satisfactorily was the P–H distance. The CPH angle refined to 100 ± 10°, and changing the PH_2 twist angle from 0 to 180° increased the *R* factor insignificantly.

The final parameters, for which R_G was 0.055, are listed in Table 2. The observed and final weighted difference intensity data are shown in Figure 2, and two views of the molecule in Figure 3.

Discussion

The P–H and P–C bond lengths in $(Me_3Si)_3CPH_2$ are 140.1(28) and 180.8(9) pm, respectively. Interestingly, these bond lengths are slightly shorter than those reported for the unencumbered alkylphosphine, $MePH_2$ [for which $r(P-H) = 142.3(7)$ and $r(P-C) = 185.8(3)$ pm].[18] How then is the steric strain distributed in $(Me_3Si)_3CPH_2$? Non-bonded P · · · Si distances are typically *ca.* 310 pm, and hence with a normal P–C bond length one predicts that the inner * C–Si [*i.e.*, C(1)] bond lengths should increase and the Si–C(1)–Si bond angles should close somewhat. The Si–C(1)–Si bond angles, 106.9(13)°, are, in fact, less than the tetrahedral angle; however the major effect is that the inner C–Si bond lengths [194.1(5) pm] are considerably larger than the normal value of 187 pm for this bond.[19] Steric strain is also manifested by twisting of the Me_3Si groups by 21.2(4)° away from the fully staggered conformation and by closing up of the angles within each Me_3Si group [the Me–Si–Me angles are 104.3(4)° and the mean outer C(1)–Si–Me angle is therefore 114.3°]. There are, however, no significant increases in the outer C–Si bond lengths which are 188.3(2) pm. A final indication of the steric strain, which has only been defined explicitly in one [12] of the previous structural studies (see above), is the tilt of the Me_3Si groups away from each other and towards the phosphorus atom. This tilt angle, which is 7.3(15)°, causes the shortest P · · · C contact to be 340 pm, which is approximately the sum of the van der Waals radii (350 pm),[20] and the outer C(1)–Si–Me angles to range from 108.5 to 121.1°. In the much less crowded $(Me_3Si)_3CH$ [12] the twist angle of the Me_3Si groups is 80.5(3)° from the eclipsed position (20.5° from staggered), but the tilt angle is small, only 1.9(6)°.

Reference to Table 4 reveals several distinct trends in the structural parameters for trisyl compounds. In the less sterically hindered molecules, $(Me_3Si)_3CH$ and $[(Me_3Si)_3C]_2Hg$, the steric strain within the trisyl group is relieved by widening of the Si–C–Si angles and there is very little elongation of the inner C–Si bonds. In the more sterically encumbered molecule, $(Me_3Si)_3CSiMe_2Ph$ {and to a lesser extent $(Me_3Si)_3CB(Ph)[O(CH_2)_4C(SiMe_3)_3]$} the trisyl substituent is attached to a larger moiety. In these cases, the Si–C–Si angles are much closer to tetrahedral and steric strain is relieved principally by elongation of the inner C–Si bond lengths. In $(Me_3Si)_3CPH_2$ the P · · · Si two-bond distances should be *ca.* 310 pm, causing the Si–C–Si angles to be less than tetrahedral; however, in other respects the PH_2 group is not particularly sterically demanding and the strain within the trisyl group is relieved by extensive twisting and tilting of the Me_3Si groups. Note that for all the molecules, the C–Si–C angles of the Me_3Si groups are small, and that this effect is most marked in those compounds with the narrowed Si–C–Si angles. Increases are observed for the C–Si, C–Hg, and C–C, but not for C–B and C–P bonds. The factors influencing these changes are not completely clear, but increases are most marked when the substituent (X) bears additional large groups.

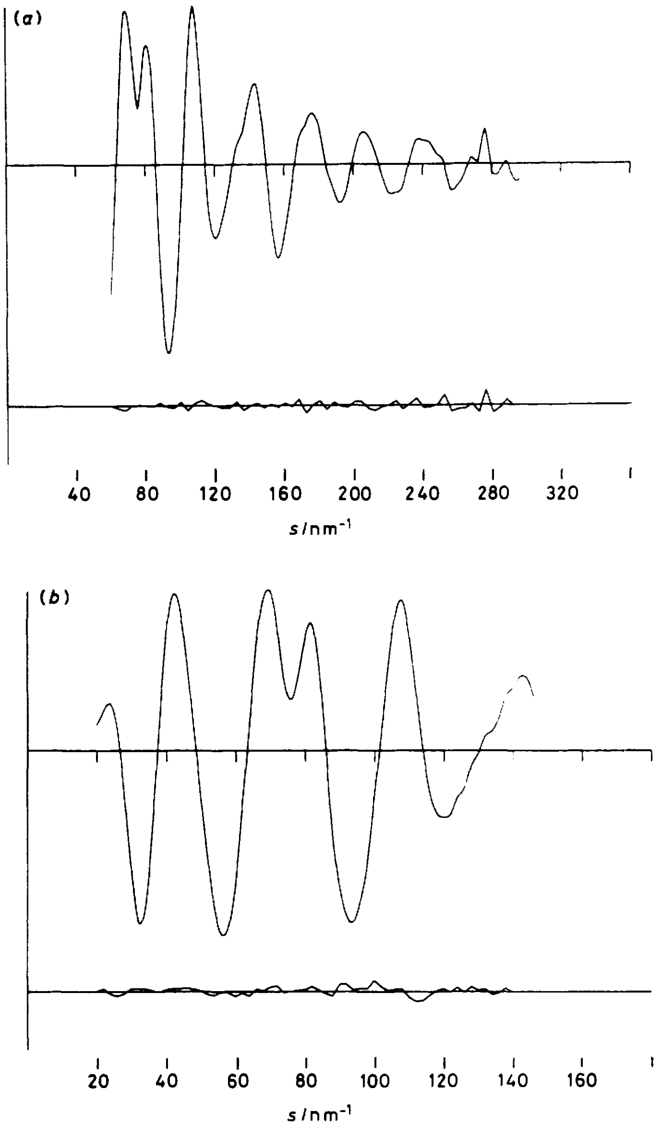


Figure 2. Observed and final weighted difference molecular scattering intensity curves for nozzle-to-plate distances of (*a*) 248 and (*b*) 498 mm

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* For the definition of inner and outer bond lengths see diagram in Table 4.

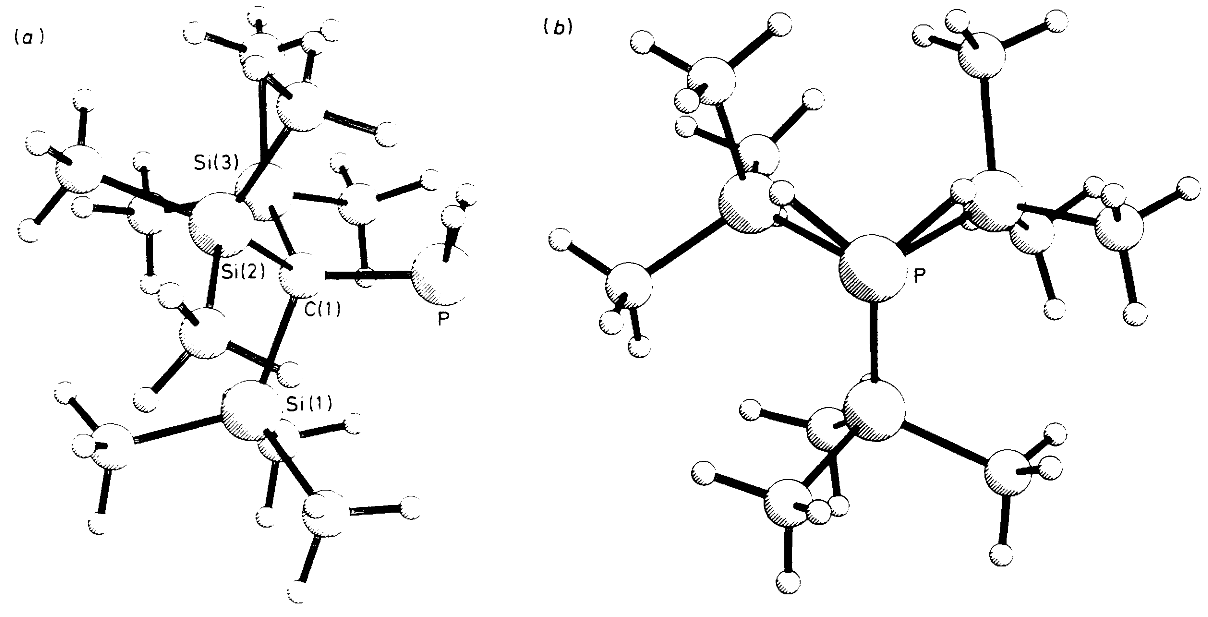
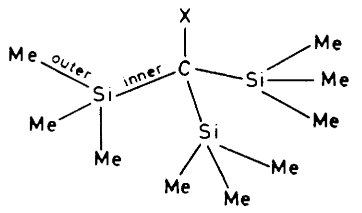


Figure 3. Perspective views of $(Me_3Si)_3CPH_2$ (*a*) perpendicular to the C(1)–P bond, and (*b*) viewed from P to the central carbon atom

Table 4. Average bond lengths (pm) and angles (°) for trisyl compounds, $(Me_3Si)_3CX$



Compound	inner C–Si	outer C–Si	Si–C–Si	C–Si–C(methyl)	C–X	Normal C–X [a]
$(Me_3Si)_3CPH_2$ [b]	194.1(5)	188.3(2)	106.9(13)	114.3(4)	180.8(9)	184
$(Me_3Si)_3CSiMe_2Ph$ [c]	192.0(6)	189.9(26)	109.5(10)	113.5(13)	192.6(8)	184
$(Me_3Si)_3CP{=}PC(SiMe_3)_3$ [d]	192(1)	187(1)	111.1(5)	112.5(5)	186(1)	184
$(Me_3Si)_3CB(Ph)[O(CH_2)_4C(SiMe_3)_3]$ [e,f]	190.0(12)	186.7(15)	110.4(3)	113.0(13)	156.7(11)	156
$(Me_3Si)_3CB(Ph)[O(CH_2)_4C(SiMe_3)_3]$ [g]	190.0(12)	186.7(15)	110.8(7)	113.0(13)	158.8(9)	154
$[(Me_3Si)_3C]_2Hg$ [h]	188.7(4)	187.1(3)	112.6(2)	113.0(11)	214.2(4)	207
$(Me_3Si)_3CH$ [i]	188.8(6)	187.3(2)	117.5(4)	112.8(3)	*j*	109

[a] All data taken from ref. 19. [b] This work. [c] Ref. 13. [d] Ref. 11*d*. [e] Ref. 2. [f] Data refer to $(Me_3Si)_3C$ group on boron. [g] Data refer to $(Me_3Si)_3C$ group on carbon. [h] Ref. 9*b*. [i] Ref. 12. [j] Not refined.

In summary, strain within trisyl compounds can be relieved in three general ways. In $(Me_3Si)_3CH$ the CH hydrogen is not very sterically demanding and strain within the trisyl group is relieved mainly by narrowing of the Si–C–H angles. When hydrogen is replaced by a PH_2 group, the two-bond Si · · · P contacts lead to widening of the Si–C–P angles. Thus strain within the trisyl group is most easily accommodated by tilting of the Me_3Si groups, which can be visualised as a slippage of the CH umbrella on the silicon atom. Lastly, when the X substituent also features an umbrella, as in $(Me_3Si)_3CSiMe_2Ph$, tilting of the Me_3Si groups is no longer possible. The angles at the central carbon therefore return to tetrahedral, and the strain is now relieved primarily by elongation of all the bonds to the central carbon atom.

Bulky groups are generally regarded as large inflexible objects. However, on the basis of the limited data available, it is clear that the trisyl group is quite deformable, and parameters change to accommodate the demands of the other ligands.

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