Crystal and Molecular Structure of 1,8-Bis(trimethylsilyl)octatetrayne

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A structural analysis of 1,8-bis(trimethylsilyl)octatetrayne has been carried out by *X*-ray diffraction. Crystals are orthorhombic, space group *Pbcn*, $a = 11{\cdot}966(2)$, $b = 12{\cdot}544(3)$, $c = 22{\cdot}809(3)$ Å, $Z = 8$. The structure has been refined by least-squares to *R* 0·056 for 1093 reflections. The chain of carbon atoms comprising the conjugated triple bonds has a slight curve, and shows clear bond-length alternation: 1·20 for the formal triple-bonds and 1·38 Å for the formal single bonds, except for the central single bond which is significantly shorter, *viz.* 1·33 Å.

MOLECULES possessing a system of alternant single and triple bonds might be expected to exhibit properties consistent with delocalisation of the π-electron density along the carbon chain. However, structural evidence for molecules containing the butadiyne [1] and hexatriyne [2] systems has shown that, although the u.v. spectra [3] are consistent with this view, the bond lengths in such molecules are essentially the same as for isolated single and triple bonds. In order to ascertain whether or not bond alternation persists in more extended conjugated systems we have determined the crystal structure of the title molecule containing the octatetrayne unit. Bond-length data are available for one other tetra-acetylene, 1,8-bisphenyloctatetrayne.[4]

EXPERIMENTAL

Crystal Data.—$C_{14}H_{18}Si_2$, $M = 242{\cdot}49$, Orthorhombic, $a = 11{\cdot}966(2)$, $b = 12{\cdot}544(3)$, $c = 22{\cdot}809(3)$ Å, $Z = 8$, $U = 3423{\cdot}7$ Å^3, $D_c = 0{\cdot}94$ g cm^{-3}, $F(000) = 1040$. Cu-K_α radiation, $\lambda = 1{\cdot}54051$ Å; μ(Cu-K_α) = 16·3 cm^{-1}. Space group *Pbcn* (No. 60) from systematic absences: $0kl$ for k odd, $h0l$ for l odd, and $hk0$ for $h + k$ odd.

1,8-Bis(trimethylsilyl)octatetrayne, prepared by oxidative coupling of trimethylsilylbutadiyne as described elsewhere,[5] was crystallised from acidified ethanol as white translucent long thin needles. Two short sections *ca.* 0·4 mm long were cut from a crystal of cross-section *ca.* 0·26 × 0·13 mm for use in data collection. Preliminary cell dimensions were derived from precession and Weissenberg films. One crystal was mounted on a Hilger and Watts four-circle diffractometer and accurate measurements of Bragg angles (Cu-K_{α_1}) for twelve reflections at moderately high angle were used in a least-squares derivation of the cell parameters. This crystal was used for the collection of diffraction data for the positive quadrant, for θ 2—40°, with Cu-K_α radiation (graphite crystal monochromator). After every 100 reflections, three standard reflections (8,0,0; 0,2,0; 4,6,2) were remeasured and these showed an approximately linear loss of intensity with time, amounting to a total of 20%. A second crystal was used for the collection of diffraction data with θ values 35—50°. The standard reflections were used to apply a correction factor for fall off of intensities within each set, and also to scale together the two data sets. The usual corrections for Lorentz and polarisation factors were applied but no correction was made for absorption. Those intensities having $I < 3\sigma(I)$ (based on counting statistics) were classified as 'unobserved.' After averaging of equivalent reflection data, there were 1093 significant reflections out of a total of 1640 independent reflections measured.

Structure Determination.—The data were converted to normalised structure factor magnitudes ($|E|$) and the structure solved by direct determination of signs for reflections with $|E| > 1{\cdot}5$, by use of a symbolic addition [6] program written by one of us (P. B. H.). Three reflections (1,4,7; 4,2,13; 7,3,10) were assigned positive signs to define the origin and new signs accepted as valid if indicated with a probability >0·97. Signs for 198 reflections were derived without using any symbols, giving a unique solution for which the consistency index was 0·96. A Fourier synthesis based on these reflections gave the positions of the silicon and carbon atoms. Least-squares refinement of positional and isotropic temperature factors reduced *R* to 0·16. All significant reflections were included with unit weights. Continued refinement with anisotropic temperature factors converged at *R* 0·079. A difference-Fourier showed the

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[1] T. Taga, N. Masaki, K. Osaki, and T. Watanabe, *Bull. Chem. Soc. Japan*, 1971, **44**, 2981; A. V. Jones, *J. Chem. Phys.*, 1952, **20**, 860.

[2] G. A. Jeffrey and J. S. Rollett, *Proc. Roy. Soc.*, 1952, **A213**, 86.

[3] M. Beer, *J. Chem. Phys.*, 1956, **25**, 745.

[4] I. Nitta, *Acta Cryst.*, 1960, **13**, 1035.

[5] F. Waugh and D. R. M. Walton, *J. Organometallic Chem.*, 1972, **37**, 45.

[6] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

TABLE 1

Final position parameters, with estimated standard deviations in parentheses in the units of the last decimal place

(*a*) Non-hydrogen atoms

	x	*y*	*z*
Si(1)	−0·3683(2)	0·6734(2)	−0·0563(1)
Si(2)	0·2377(2)	0·1623(2)	0·2900(1)
C(1)	−0·2631(6)	0·6075(5)	−0·0116(3)
C(2)	−0·1959(6)	0·5622(5)	0·0187(3)
C(3)	−0·1219(6)	0·5078(6)	0·0550(3)
C(4)	−0·0615(6)	0·4608(5)	0·0878(3)
C(5)	0·0028(6)	0·4056(6)	0·1246(3)
C(6)	0·0561(5)	0·3539(6)	0·1590(3)
C(7)	0·1146(5)	0·2936(5)	0·1991(3)
C(8)	0·1663(5)	0·2427(6)	0·2350(3)
C(9)	0·1318(8)	0·0838(9)	0·3291(5)
C(10)	−0·3833(7)	0·5934(7)	−0·1222(3)
C(11)	−0·3164(9)	0·8062(6)	−0·0744(3)
C(12)	−0·4979(8)	0·6784(7)	−0·0127(4)
C(13)	0·3106(12)	0·2504(8)	0·3395(5)
C(14)	0·3347(12)	0·0797(12)	0·2524(5)

(*b*) Proposed positions of the hydrogen atoms

	x	*y*	*z*	Bonded to
H(1)	−0·438	0·604	−0·153	C(10)
H(2)	−0·420	0·528	−0·112	C(10)
H(3)	−0·298	0·580	−0·147	C(10)
H(4)	−0·388	0·858	−0·093	C(11)
H(5)	−0·260	0·810	−0·098	C(11)
H(6)	−0·310	0·846	−0·044	C(11)
H(7)	0·250	0·307	0·347	C(13)
H(8)	0·350	0·300	0·305	C(13)
H(9)	0·350	0·208	0·362	C(13)
H(10)	0·350	0·090	0·217	C(14)
H(11)	0·295	0·025	0·255	C(14)
H(12)	0·392	0·050	0·271	C(14)
H(13)	0·180	0·045	0·350	C(9)
H(14)	0·075	0·055	0·292	C(9)
H(15)	0·088	0·150	0·349	C(9)
H(16)	−0·490	0·694	0·028	C(12)
H(17)	−0·523	0·595	−0·034	C(12)
H(18)	−0·525	0·750	−0·021	C(12)

general positions of the hydrogen atoms, although the peaks were rather diffuse, presumably owing to the very high thermal motion of the methyl carbon atoms. Positions for the hydrogen atoms were estimated from the Fourier map and refinement of the structure continued including fixed contributions from the hydrogen atoms, each given an isotropic temperature factor of B 10·0 Å^2. Three cycles of refinement reduced R to 0·060.

An analysis of structure factors suggested a change in the weighting scheme. One reflection (1,0,4) had a much larger discrepancy than any other and was given a weight of zero. The remaining data were given a weight of 1 if $|F_o| < 35$ and a weight of $(35/|F_o|)^2$ if $|F_o| > 35$. Five cycles of refinement using this weighting scheme converged at R 0·056. At this point, the maximum parameter shift was $< 0{\cdot}02\sigma$.

The silicon and carbon final atom positions and their anisotropic temperature factors are listed in Tables 1 and 2 respectively. Figure 1 is an ORTEP drawing of the molecule showing the atom numbering and the 50% thermal vibration ellipsoids. The proposed positions of the hydrogen atoms are in Table 1. A list of bond lengths and angles is given in Table 3. Atomic scattering factors and dispersion corrections were taken from ref. 7. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21202 (7 pp., 1 microfiche).[†]

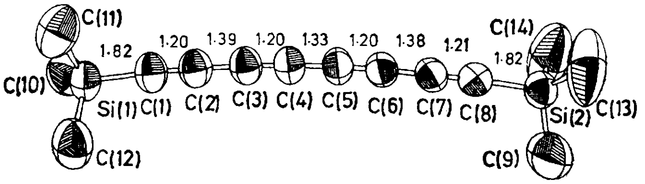

FIGURE 1 Perspective drawing of the molecule showing ellipsoids of thermal motion with 50% probability

DISCUSSION

The chain of triple-bonded atoms is not exactly linear. The atoms Si(1), C(1)—(8), and Si(2) lie in the same plane (maximum deviation 0·02 Å), and form a gentle curve such that atoms C(4) and C(5) are 0·5 Å from the straight line joining Si(1) and Si(2). Each of the angles subtended at carbon atoms C(1)—(8) are less than 3° from 180°. It is known [8] that acetylene molecules have a low force constant for bending of the molecule,

TABLE 2

Thermal parameters * (Å^2 × 10^4), with estimated standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si(1)	1073(15)	1106(15)	0882(12)	0244(13)	−0126(11)	0018(12)
Si(2)	0954(13)	0890(12)	1016(12)	0070(12)	−0180(11)	0110(11)
C(1)	1109(56)	1017(48)	0920(43)	0153(44)	−0183(43)	−0100(40)
C(2)	1064(53)	1053(51)	0858(45)	0059(44)	−0133(42)	−0110(41)
C(3)	0999(49)	1075(49)	0847(42)	0139(44)	−0103(41)	−0092(43)
C(4)	0953(47)	1047(50)	0860(43)	0155(42)	−0136(40)	−0038(41)
C(5)	0909(47)	1140(51)	0857(45)	0157(43)	−0127(40)	0045(42)
C(6)	0856(43)	1131(53)	0852(43)	0046(42)	−0066(39)	0007(41)
C(7)	0772(43)	1098(52)	0909(43)	0054(38)	−0071(37)	−0018(40)
C(8)	0848(46)	1132(50)	0966(47)	0023(41)	−0013(39)	0104(42)
C(9)	1478(78)	2252(106)	2724(121)	0008(79)	−0392(82)	1313(98)
C(10)	1230(60)	1696(71)	1205(55)	−0119(56)	−0256(48)	−0245(53)
C(11)	2208(97)	1115(57)	1448(63)	0365(67)	0011(65)	−0016(53)
C(12)	1636(81)	1776(79)	1472(66)	0623(69)	0022(60)	0007(64)
C(13)	3911(165)	1194(64)	2446(111)	0174(94)	−1950(121)	0491(76)
C(14)	2854(144)	3490(158)	1719(85)	1846(139)	0019(95)	0631(113)

* The anisotropic temperature factor has the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)$.

[†] See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[7] D. T. Cromer and J. A. Waber, *Acta Cryst.*, 1965, **18**, 104; D. T. Cromer, *ibid.*, p. 17; R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[8] P. Torkington, *Proc. Roy. Soc.*, 1951, **A206**, 17.

and bearing in mind the small deviation from linearity at any one atom, it seems probable that the curvature of the octatetrayne chain is due to crystal-packing forces rather than to any intrinsic property of the molecule. Figure 2 shows the packing of eight molecules in the unit cell, and Table 4 lists short contacts. It can be seen that there are several such contacts between the carbon atoms of the octatetrayne chain and the methyl groups on adjacent molecules, but none between the carbon atoms of two adjacent octatetrayne chains. This type of interaction is presumably excluded by the bulky end-groups, a contributory factor to the stability of such polyacetylenes.[9]

TABLE 3

Bond lengths (Å) and angles (°) in the molecule, with estimated standard deviations in parentheses

(*a*) Bonds			
Si(1)–C(1)	1·819(7)	C(1)–C(2)	1·203(10)
Si(1)–C(10)	1·816(8)	C(2)–C(3)	1·390(10)
Si(1)–C(11)	1·825(8)	C(3)–C(4)	1·196(10)
Si(1)–C(12)	1·844(9)	C(4)–C(5)	1·334(10)
Si(2)–C(8)	1·822(7)	C(5)–C(6)	1·200(10)
Si(2)–C(9)	1·836(11)	C(6)–C(7)	1·378(9)
Si(2)–C(13)	1·806(12)	C(7)–C(8)	1·209(9)
Si(2)–C(14)	1·776(14)		
(*b*) Angles			
C(1)–Si(1)–C(10)	106·4(3)	C(9)–Si(2)–C(14)	111·8(6)
C(1)–Si(1)–C(11)	107·9(4)	C(13)–Si(2)–C(14)	110·1(6)
C(1)–Si(1)–C(12)	107·2(3)	Si(1)–C(1)–C(2)	178·1(6)
C(11)–Si(1)–C(10)	110·5(4)	C(1)–C(2)–C(3)	177·7(8)
C(11)–Si(1)–C(12)	112·1(4)	C(2)–C(3)–C(4)	177·4(7)
C(10)–Si(1)–C(12)	112·5(4)	C(3)–C(4)–C(5)	177·8(8)
C(8)–Si(2)–C(9)	107·9(4)	C(4)–C(5)–C(6)	176·9(8)
C(8)–Si(2)–C(13)	108·6(4)	C(5)–C(6)–C(7)	178·4(7)
C(8)–Si(2)–C(14)	107·3(5)	C(6)–C(7)–C(8)	178·6(7)
C(9)–Si(2)–C(13)	111·0(5)	C(7)–C(8)–Si(2)	177·2(6)

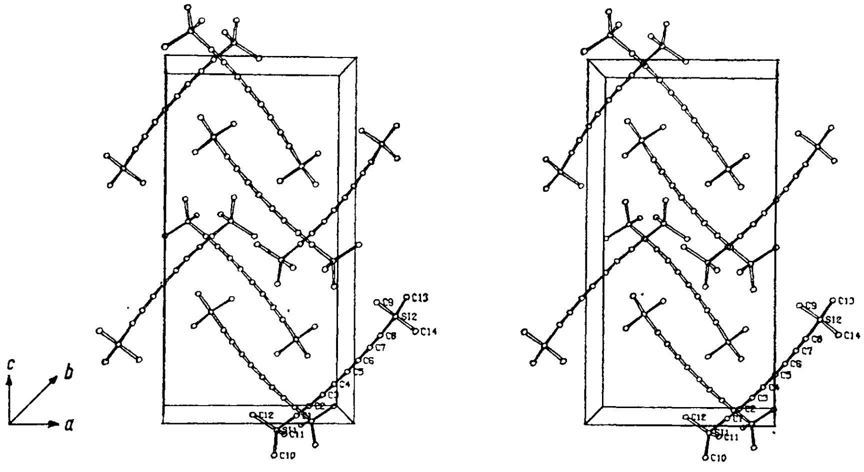

FIGURE 2 A stereoview of the eight molecules of one unit cell, viewed along the *b* axis

The carbon–carbon distances in the octatetrayne chain show clear bond-length alternation and are symmetrical with respect to the centre of the chain. All the formal triple bonds have a length of 1·20 Å, as would be expected [10] for an isolated –C⁝C– length. The formal C–C single bonds are 1·38 and 1·33 Å, which may be compared to the expected value of 1·40 Å for a single bond between two *sp*-hybridised carbon atoms. A simple Hückel theory approach to the π bonding in the octatetrayne system would indicate two degenerate sets of π orbitals extending over the length of the carbon chain, related by a rotation of 90°, and it might be expected that the bond lengths of the formal single and triple bonds would become more equal. However, just as has been observed in the butadi- and hexatri-yne systems the octatetrayne system in both bis(trimethylsilyl)- and bis(phenyl)-octatetrayne shows little evidence of this. For the formal triple bonds the situation is analogous to that observed in metal carbonyls [11] where the length of the carbon–oxygen triple bond is very little affected by strong metal–ligand back donation, even though i.r. stretching frequency shows a significant reduction in the C⁝O bond strength. This has been interpreted in terms of a very non-linear bond-length–bond-order correlation, due to high interatom repulsion forces in triple bonds. However, in polyacetylenes the force constants for the –C⁝C– stretch are reportedly

TABLE 4

Intermolecular contacts (Å): for C · · · C $<4{\cdot}0$, C · · · H $<3{\cdot}3$, and H · · · H $<3{\cdot}0$ Å

C(9) · · · C(10^{I})	3·88	C(2) · · · H(18^{II})	3·12
C(3) · · · C(13^{II})	3·96	C(4) · · · H4^{III})	3·08
C(2) · · · C(11^{IV})	3·85	C(2) · · · H(6^{IV})	3·07
C(3) · · · C(11^{IV})	3·96	C(3) · · · H(6^{IV})	3·14
C(9) · · · C(2^{I})	3·19	H(17) · · · H(17^{V})	2·90
C(3) · · · H(9^{II})	3·16	H(1) · · · H(14^{VI})	2·87
C(3) · · · H(13^{II})	3·25	H(1) · · · H(8^{VII})	2·97
C(5) · · · H(12^{II})	3·27		

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at *x*, *y*, *z*:

I $-0{\cdot}5 - x, 0{\cdot}5 - y, 0{\cdot}5 + z$
II $-0{\cdot}5 + x, 0{\cdot}5 + y, 0{\cdot}5 - z$
III $0{\cdot}5 + x, 1{\cdot}5 - y, -z$
IV $-0{\cdot}5 - x, -0{\cdot}5 + y, z$
V $-1{\cdot}0 - x, 1{\cdot}0 - y, -z$
VI $-0{\cdot}5 - x, 0{\cdot}5 - y, -0{\cdot}5 + z$
VII $-1{\cdot}0 + x, 1{\cdot}0 - y, -0{\cdot}5 + z$

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[9] R. Eastmond, T. R. Johnson, and D. R. M. Walton, *Tetrahedron*, 1972, **28**, 4601.

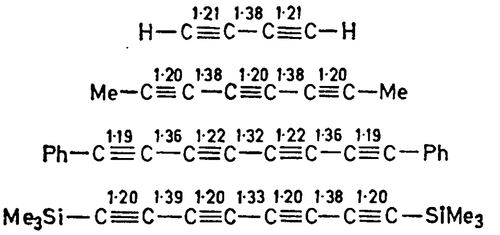
[10] J. Dale in 'Chemistry of Acetylenes,' ed. H. G. Viehe, Dekker, New York, 1969, ch. 1, p. 5.

[11] R. M. Wing, *Inorg. Chem.*, 1965, **4**, 314.

very little affected by the number of conjugated triple bonds.[12] Also it seems surprising that the single bonds, which would be more likely to show the effects of bond equalisation, do not shorten more. In this case only the central single bond shows a significant reduction from the expected value. A comparison of bond lengths observed in molecules containing di-, tri-, and tetra-yne systems is given in Table 5.

TABLE 5

Comparison of bond lengths (Å) in some di-, tri-, and tetra-yne systems



$$\mathrm{H{-}C\overset{1{\cdot}21}{\equiv}C\overset{1{\cdot}38}{-}C\overset{1{\cdot}21}{\equiv}C{-}H}$$

$$\mathrm{Me{-}C\overset{1{\cdot}20}{\equiv}C\overset{1{\cdot}38}{-}C\overset{1{\cdot}20}{\equiv}C\overset{1{\cdot}38}{-}C\overset{1{\cdot}20}{\equiv}C{-}Me}$$

$$\mathrm{Ph{-}C\overset{1{\cdot}19}{\equiv}C\overset{1{\cdot}36}{-}C\overset{1{\cdot}22}{\equiv}C\overset{1{\cdot}32}{-}C\overset{1{\cdot}22}{\equiv}C\overset{1{\cdot}36}{-}C\overset{1{\cdot}19}{\equiv}C{-}Ph}$$

$$\mathrm{Me_3Si{-}C\overset{1{\cdot}20}{\equiv}C\overset{1{\cdot}39}{-}C\overset{1{\cdot}20}{\equiv}C\overset{1{\cdot}33}{-}C\overset{1{\cdot}20}{\equiv}C\overset{1{\cdot}38}{-}C\overset{1{\cdot}20}{\equiv}C{-}SiMe_3}$$

In contrast to the evidence from diffraction techniques and vibrational spectra, the electronic spectra [3] of polyacetylenes have been reported to show good agreement with a model involving delocalised π-bonding. It has been shown [9,13] that the addition of a trialkylsilyl group at the end of a polyacetylene chain causes characteristic red shifts in the wavelength of electronic transitions, and this has been convincingly suggested as evidence of π-bonding between the polyacetylene π-orbitals and the suitable *d*-orbitals on the silicon, with a net flow of electron density from the carbon chain to the silicon atoms.

The mean silicon–carbon distances Si(1)–C(1) and Si(2)–C(8) are 1·820 Å, which is similar to the spectroscopically derived value (1·826 Å) [14] in ethynylsilane. The comparable theoretical value for a silicon to *sp*-hybridised-carbon bond, with no π bonding, is difficult to assess. An Si–C(Me) distance usually lies in the range 1·85—1·89 Å,[15] and Si–C(Ph) is much the same,[16] *viz.* 1·87 Å. Making the usual corrections for the hybridisation state of carbon, we might predict a value for a silicon to *sp*-hybridised carbon of 1·80 Å by comparison with Si–C(Me), and 1·83 Å by comparison with Si–C(Ph). The values found in the present case lie between these two, indicating that there is no observable shortening of the silicon to acetylene distances due to π-bonding.

Our observed values for the Si–C(Me) distances are all rather lower than expected. This is almost certainly due to the very large thermal vibrations of the methyl groups. As can be seen from Figure 1, the thermal vibration ellipsoids are consistent with their motion being largely vibration of the methyl groups about the silicon positions. This would cause an apparent shortening [17] of the Si–C distances, especially for C(13) and C(14), which have the largest vibrational amplitudes. In addition the positional σ values for these carbon atoms are very large giving low accuracy to the bond lengths.

The orientation of the two trimethylsilyl end groups relative to each other is shown in Figure 3. It can be seen that a rotation of 90° would bring the two groups to the eclipsed position. Whilst this is consistent with preferential orientation due to overlap of the silicon *d*-orbitals with the two mutually perpendicular sets of π-orbitals along the tetra-acetylene chain, it may well be a purely coincidental result of crystal-packing forces.

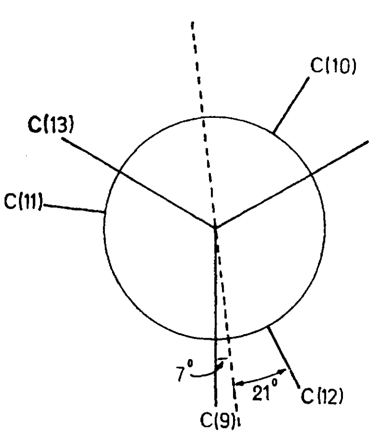


FIGURE 3 Projection along the Si(1) · · · Si(2) direction showing the mean plane of the atoms Si(1), Si(2), and C(1)—(8) relative to the methyl groups

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[14] J. S. Meuntner and V. W. Laurie, *J. Chem. Phys.*, 1963, **39**, 1181.

[15] F. P. Boer and F. P. van Remoorte, *J. Amer. Chem. Soc.*, 1970, **92**, 801; L. S. Bartell, F. B. Clippard, jun., and T. L. Boates, *Inorg. Chem.*, 1970, **9**, 2436.

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[17] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 757.