For the saturated ring *C* a slightly deformed chair conformation $^{13}C_9$ ($^4C_1$) may be assigned. The asymmetry parameters are: $\Delta C_s^9 = 4{\cdot}5\,(6)°$ and $\Delta C_2^{11,12} = 6{\cdot}1\,(5)°$. The mean value of torsion angles is 57·4 (5)°. The deviations of C(9) and C(13) from the four-atom least-squares plane through C(8), C(11), C(12) and C(14) are −0·689 (5) and 0·711 (5) Å, respectively. The distortion of the chair conformation in *C* is significantly greater than that in the *A* ring.

The five-membered ring *D* represents a slightly distorted envelope conformation $_{14}E$, as concluded from the asymmetry parameter $\Delta C_s^{14} = 2{\cdot}0\,(6)°$, and from the deviations of ring atoms from the four-atom least-squares plane, being within ±0·012 (5) Å for plane-defining atoms and −0·647 (6) Å for C(14). The O(1) carbonyl atom deviates slightly from that plane [0·099 (2) Å].

The dihedral angles at ring junctions (for convention see Duax & Norton, 1975, p. 22) are: *A*/*A*–*B* 125·3 (3)°, *A*–*B*/*B* 124·2 (2)°, *B*/*B*–*C* 136·6 (2)°, *B*–*C*/*C* 128·0 (2)°, *C*/*C*–*D* 133·8 (2)° and *C*–*D*/*D* 129·4 (2)°.

The dihydropyrazole ring *E* is nearly planar. The values of the endocyclic torsion angles are in the range 0·2–5·5 (6)° [mean value 3·7 (6)°]. The dihedral angle *D*/*E* is 91·8 (2)°.

The configuration at the two new chiral centers C(16) and C(16′) in *E*, formed by cyclization by diazomethane, are of particular interest. If the *S* configuration is assumed for the chiral center at C(13), the *S* configuration must be also assigned to C(16) as well as to C(16′).

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Structure of 2-(1-Adamantyl)-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silaethylene*

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Abstract. $C_{20}H_{42}OSi_4$, $M_r = 410{\cdot}9$, triclinic, $P\bar{1}$, $a = 6{\cdot}541\,(9)$, $b = 10{\cdot}057\,(2)$, $c = 20{\cdot}391\,(3)$ Å, $\alpha = 101{\cdot}69\,(1)$, $\beta = 90{\cdot}86\,(1)$, $\gamma = 105{\cdot}77\,(1)°$, $V = 1261\,(2)$ Å^3, $Z = 2$, D_m not determined, $D_x = 1{\cdot}082$ Mg m^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}70926$ Å, $\mu(\text{Mo}\,K\alpha) = 0{\cdot}240$ mm^{-1}, $F(000) = 452$, $T = 223$ K, $R = 0{\cdot}049$, $wR = 0{\cdot}039$ for 3067 significant reflections with $I > 3\sigma(I)$. The compound is the first crystalline silene to be prepared which is stable at room temperature. The double-bond system is twisted 14·6° and the double bond, 1·764 (3) Å in length, is longer than that, 1·702 (5) Å, subsequently reported for a less sterically hindered silene.

Introduction. Interest in silenes, compounds containing an Si=C double bond, has recently intensified with the discovery of routes for preparing this long-sought but highly reactive species. [Recent reviews are given in Gusel'nikov & Nametkin (1979), Barton (1980), Coleman & Jones (1981) and Schaefer (1982).] An obvious challenge was to attempt the synthesis of a silene sufficiently stable to survive, preferably as a solid, at room temperature.

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* Adamantyl is tricyclo[3.3.1.1^{3,7}]decyl.

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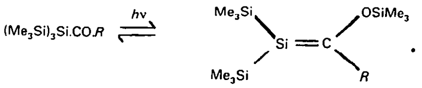
Experiments carried out in this laboratory over several years indicated that silenes are generated by photolysis of acylpolysilanes under mild conditions ($\lambda > 360$ nm, $T < 273$ K; Brook, Harris, Lennon & El Sheikh, 1979):



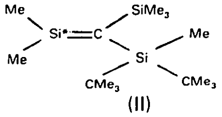
(I)

The stability of the silene increases with the steric bulk of *R*. When it is *tert*-butyl, the silene survives up to two weeks at room temperature in solution where its presence can be monitored by NMR spectroscopy. When *R* is 1-adamantyl, the first reported colourless solid silene, the subject of this report (I), was obtained, m.p. 368 K. This smokes and decomposes spontaneously in air but survives unchanged stored under argon at room temperature for over 4 years. The results of an X-ray crystal structure determination have been briefly reported (Brook, Nyburg, Abdesaken, Gutekunst, Gutekunst, Kallury, Poon, Chang & Wong-Ng, 1982). The detailed results are presented here together with a discussion of the results of two structure analyses of silenes prepared since our original report appeared.

Experimental. Initially, X-ray intensity data were collected at room temperature on a Picker diffractometer. During X-ray exposure, the crystal appeared to acquire an oily coating and slid slowly down the wall of the argon-filled enclosing capillary. Many crystal realignments were therefore required during data collection. Although the resulting intensity data were not of high quality, it was possible to solve the structure using *MULTAN* (Germain, Main & Woolfson, 1971). To obtain more accurate atomic coordinates, the intensity data were recollected from a second, sealed crystal, irregularly shaped, 0·18 × 0·25 × 0·68 mm, on a Syntex $P\bar{1}$ diffractometer at 223 K.* Under these conditions the crystal remained rigidly in place. Lattice parameters were established from fifteen centred reflections in the range $30° < 2\theta < 67°$. Intensity data were collected in the hkl, $\bar{h}kl$, $h\bar{k}l$ and $hk\bar{l}$ octants, $h = \pm 8$, $k = \pm 12$, $l = \pm 26$, to a maximum $(\sin\theta)/\lambda = 1{\cdot}15$ Å^{-1}. No correction for absorption or extinction. Two standard reflections were monitored; there was no perceptible drift in their intensities and no one standard measurement differed by more than 2% from the mean. The raw data were reduced according to Lippart, Lock, Rosaberg & Zvagolis (1977). 5868 unique reflections were measured of which 3067 were taken as of significant intensity on the criterion $I > 3\sigma(I)$ where $\sigma(I) = (\text{scan} + \sum \text{background})^{1/2}$. No equivalent reflections were measured. The structure was refined anisotropically (on *F*) by block-diagonal least squares using program *XFLS*3 (Busing, Martin & Levy, 1971). Weighting was based on $\sigma(F_o) = \{[\sigma(I)\mathrm{Lp}]^2 + 0{\cdot}02F_o^4\}^{1/2}/2F_o$, where Lp is the Lorentz–polarization correction. Scattering factors for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974). H-atom positions were refined isotropically using scattering factors of Stewart, Davidson & Simpson (1965). In the final refinement cycle the largest Δ/σ was 0·1. The final *R* was 0·049 and *wR* 0·039.

Discussion. Atomic coordinates and (equivalent) isotropic temperature factors are given in Table 1.* The molecule is illustrated in Fig. 1. Bond lengths and interbond angles are given in Table 2.

The point of greatest interest in this structure is the geometry of the Si=C double bond. Its length is 1·764 (3) Å (compared with 1·87–1·94 Å for Si—C single bonds) and the double-bond system is not planar, showing a twist of 14·6°. Since our original report appeared, there have been two further crystal structure analyses reported, one for (II) (Wiberg, Wagner & Müller, 1985) and the other, (III), for the tetrahydrofuran adduct of (II), the O atom of the THF molecule being coordinated to the starred Si atom of (II) (Wiberg, Wagner, Müller & Riede (1984).



(II)

The structure of (III), which was determined first, is somewhat abnormal, since although the central C atom has three coplanar bonds and is clearly sp^2 hybridized, the bonding at the central Si atom is neither sp^2 nor regular sp^3 tetrahedral. The O atom of the THF molecule is further from the Si atom, 1·878 (4) Å, than the 1·58–1·67 Å commonly found when Si is bonded to three C atoms and one O atom. (See, for example, Ando, Hamada, Sekiguchi & Ueno, 1982; Glidewell & Liles, 1978; Stensland & Kierkegaard, 1970). However such a long Si-to-O distance is not without precedence, a bond of the same length being present in a dibenzosilepin (Paton, Cody, Corey & Glick, 1976).

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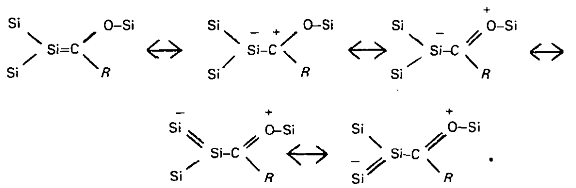
* We are grateful to Professor C. J. L. Lock for arranging, and to R. Faggiani for carrying out data collection at the Department of Materials Science, McMaster University, Hamilton, Canada L8S 4L8.

* Lists of structure factors, anisotropic thermal factors and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42393 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure of (II) itself is more clear-cut. The central skeleton is essentially planar, the torsion angle being only 1·6°. The Si=C bond length is 1·702 (1) Å in spectacular agreement with the best calculated prediction of 1·70 (1) Å for a coplanar system (Apeloig & Karni, 1984).

There are at least two possible explanations for the Si=C bond in the present compound being longer than that in (II). One is that a lengthening would be expected for a non-coplanar double-bond system. However, if the ethylenic C=C system is any guide, lengthening due to non-coplanarity *per se* would be expected to be somewhat less than the 0·06 Å found. Thus, compared to a normal C=C length of 1·33 Å, the following lengths have been found for the torsion angles cited: bifluorenylidene (in several different crystal structures) average 1·366 Å for an average torsional angle of 32·5° (Lee & Nyburg, 1985); perchlorofulvalene, 1·365 Å and 37·0° (Ammon, Wheeler & Agranat, 1973); octabromofulvalene, 1·38 Å and 37·1° (Fallon, Ammon, West & Rao, 1974). As to the twist itself it is not clear what the primary cause is. None of the intramolecular H···H distances is especially short, only four being less than 2·50 Å. Of these, that of 2·35 Å between H(3*A*) of the adamantyl group and H(18*A*) of Si(4)Me$_3$ would not cause twisting but the other three, H(8*A*)···H(17*B*) 2·37, H(8*B*)···H(15*B*) 2·47 and H(12*A*)···H(20*C*) 2·47 Å, could. They are probably also responsible for the marked asymmetry of bond angles at Si(1), namely, C(1)—Si(1)—Si(2) 114·6 (1) and C(1)—Si(1)—Si(3) 126·5 (1)°. It is still possible that the Si=C system shows little resistance to twisting and that this is brought about by crystal packing forces.

The second potential cause of the rather long Si=C bond could be the presence of some single-bond character:



Consistent with this explanation is the remarkably low-field chemical shift found for the sp^2 hybridized C atom and the relatively high-field position found for the ^{29}Si absorption of the sp^2 hybridized Si atom (Brook, Abdesaken, Gutekunst & Plavac, 1982).

The crystal structure is normal in other respects, all bond lengths and angles lying within accepted ranges. There are no short intermolecular contacts.

Thanks are due to the Natural Sciences and Engineering Research Council of Canada for financial support.

Table 1. *Fractional atomic coordinates* (×10^4) *and* B_{eq} *values* (Å^2) *for non-hydrogen atoms, with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Si(1)	−1059 (2)	1748 (1)	−1872 (0·5)	2·3
Si(2)	−2996 (2)	473 (1)	−1134 (0·5)	2·5
Si(3)	1662 (2)	3826 (1)	−1428 (0·5)	2·8
Si(4)	−3030 (2)	−1894 (1)	−3157 (0·5)	2·5
O(1)	−3341 (3)	−303 (2)	−2900 (1)	2·4 (1)
C(1)	−1934 (5)	1062 (3)	−2727 (2)	2·0 (1)
C(2)	−1545 (5)	1761 (3)	−3325 (2)	2·0 (1)
C(3)	−121 (5)	1126 (3)	−3816 (2)	2·3 (1)
C(4)	205 (5)	1823 (4)	−4419 (2)	2·6 (1)
C(5)	−1922 (6)	1621 (4)	−4790 (2)	3·0 (1)
C(6)	−3320 (5)	2295 (4)	−4314 (2)	2·8 (1)
C(7)	−3676 (5)	1589 (3)	−3711 (2)	2·4 (1)
C(8)	−455 (5)	3359 (3)	−3100 (2)	2·4 (1)
C(9)	−93 (6)	4062 (3)	−3706 (2)	2·8 (1)
C(10)	1320 (6)	3407 (4)	−4175 (2)	3·0 (1)
C(11)	−2221 (7)	3864 (4)	−4075 (2)	3·2 (1)
C(12)	−5840 (5)	−230 (4)	−1475 (2)	3·5 (1)
C(13)	−1914 (6)	−951 (4)	−956 (2)	4·1 (1)
C(14)	−2950 (6)	1726 (4)	−313 (2)	4·6 (1)
C(15)	965 (6)	5490 (4)	−1442 (2)	4·2 (1)
C(16)	2173 (7)	3788 (5)	−525 (2)	5·3 (2)
C(17)	4191 (6)	3811 (4)	−1830 (2)	4·3 (1)
C(18)	−4009 (6)	−2575 (4)	−4053 (2)	3·9 (1)
C(19)	−251 (6)	−1869 (4)	−3014 (2)	4·4 (1)
C(20)	−4812 (7)	−3099 (4)	−2689 (2)	4·5 (1)

Table 2. *Bond lengths* (Å) *and interbond angles* (°)

Si(1)—Si(2)	2·341 (1)	C(1)—C(2)	1·518 (4)
Si(1)—Si(3)	2·349 (1)	C(2)—C(3)	1·539 (5)
Si(1)—C(1)	1·764 (3)	C(2)—C(7)	1·540 (5)
Si(2)—C(12)	1·869 (4)	C(2)—C(8)	1·539 (5)
Si(2)—C(13)	1·854 (4)	C(3)—C(4)	1·525 (5)
Si(2)—C(14)	1·874 (4)	C(4)—C(5)	1·517 (5)
Si(3)—C(15)	1·855 (4)	C(4)—C(10)	1·534 (5)
Si(3)—C(16)	1·877 (4)	C(5)—C(6)	1·529 (5)
Si(3)—C(17)	1·860 (4)	C(6)—C(7)	1·531 (5)
Si(4)—O(1)	1·649 (2)	C(6)—C(11)	1·518 (5)
Si(4)—C(18)	1·854 (4)	C(8)—C(9)	1·534 (5)
Si(4)—C(19)	1·829 (4)	C(9)—C(10)	1·518 (5)
Si(4)—C(20)	1·862 (4)	C(9)—C(11)	1·517 (5)
C(1)—O(1)	1·401 (4)		

Si(2)—Si(1)—Si(3)	118·87 (5)	Si(1)—C(1)—C(2)	130·1 (2)
Si(2)—Si(1)—C(1)	114·6 (1)	O(1)—C(1)—C(2)	112·2 (3)
Si(3)—Si(1)—C(1)	126·5 (1)	C(1)—C(2)—C(3)	112·1 (3)
Si(1)—Si(2)—C(12)	108·5 (1)	C(1)—C(2)—C(7)	110·2 (3)
Si(1)—Si(2)—C(13)	114·0 (1)	C(1)—C(2)—C(8)	111·2 (3)
Si(1)—Si(2)—C(14)	108·5 (1)	C(3)—C(2)—C(7)	108·4 (3)
C(12)—Si(2)—C(13)	111·6 (2)	C(3)—C(2)—C(8)	107·6 (3)
C(12)—Si(2)—C(14)	106·7 (2)	C(7)—C(2)—C(8)	107·2 (3)
C(13)—Si(2)—C(14)	107·3 (2)	C(2)—C(3)—C(4)	111·1 (3)
Si(1)—Si(3)—C(15)	114·7 (1)	C(3)—C(4)—C(5)	110·3 (3)
Si(1)—Si(3)—C(16)	105·6 (1)	C(3)—C(4)—C(10)	109·2 (3)
Si(1)—Si(3)—C(17)	111·3 (1)	C(5)—C(4)—C(10)	109·2 (3)
C(15)—Si(3)—C(16)	107·4 (2)	C(4)—C(5)—C(6)	109·1 (3)
C(15)—Si(3)—C(17)	111·0 (2)	C(5)—C(6)—C(7)	109·6 (3)
C(16)—Si(3)—C(17)	106·3 (2)	C(5)—C(6)—C(11)	109·2 (3)
O(1)—Si(4)—C(18)	109·5 (2)	C(7)—C(6)—C(11)	109·8 (3)
O(1)—Si(4)—C(19)	110·9 (2)	C(6)—C(7)—C(2)	111·0 (3)
O(1)—Si(4)—C(20)	107·6 (2)	C(2)—C(8)—C(9)	111·0 (3)
C(18)—Si(4)—C(19)	111·9 (2)	C(8)—C(9)—C(10)	109·9 (3)
C(18)—Si(4)—C(20)	105·7 (2)	C(8)—C(9)—C(11)	109·5 (3)
C(19)—Si(4)—C(20)	111·0 (2)	C(10)—C(9)—C(11)	109·9 (3)
Si(4)—O(1)—C(1)	134·0 (2)	C(9)—C(10)—C(4)	108·5 (3)
Si(1)—C(1)—O(1)	117·4 (2)	C(9)—C(11)—C(6)	109·4 (3)

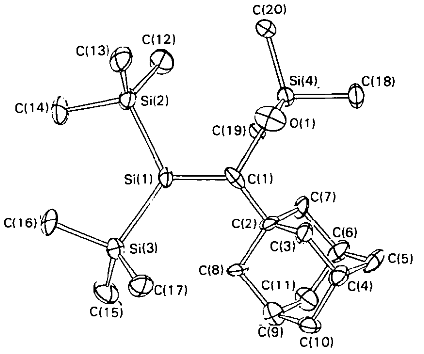


Fig. 1. *ORTEP* plot (Johnson, 1965) of the molecule with 50% probability thermal ellipsoids.

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Structure of the Complex of Dibenzotetrathiafulvalenium Tetrafluoroborate* with Ethanol

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Abstract. $2C_{14}H_8S_4.2C_{14}H_8S_4^{+}.2BF_4^{-}.C_2H_6O$, $M_r = 1437\cdot51$, triclinic, $P\bar{1}$, $a = 10\cdot772\ (5)$, $b = 27\cdot309\ (6)$, $c = 10\cdot623\ (3)$ Å, $\alpha = 85\cdot13\ (2)$, $\beta = 103\cdot87\ (4)$, $\gamma = 100\cdot49\ (4)°$, $V = 2980\cdot3\ (18)$ Å^3, $Z = 2$, $D_m = 1\cdot59$, $D_x = 1\cdot60$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1\cdot5418$ Å, $\mu = 57\cdot64$ cm^{-1}, $F(000) = 1464$, $T = 293$ K, $R = 0\cdot132$ for 7482 observed reflections. The crystal structure consists of two crystallographically independent stacks. Dibenzotetrathiafulvalene molecules, which are planar, are stacked to form columns along the *a* axis [mean interplanar distance 3·6 (1) Å]. The other dibenzotetrathiafulvalene molecule, ethanol and tetrafluoroborate anions stack together to form columns along the same *a* axis.

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* Alternative nomenclature: bis(2,2′-bi-1,3-benzodithiolylidenium) tetrafluoroborate.

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