derived from adding authentic diethyl methylenemalonate into pH 7 phosphate buffer.

The spontaneous aerobic decomposition of **5** was studied by dissolving 300 mg of the cobalamin in 25 mL of pH 7 phosphate buffer. The resulting solution sat for 42 h at room temperature in the dark, and products were analyzed as above. The major product did not migrate on TLC and had an ^{1}H NMR spectrum similar to that of the methylenemalonate polymer obtained in the experiments described above.

Vitamin B_{12s} Trapping Experiments. Cobalamin **5** (37 mg) in a deaerated serum vial was dissolved in 20 mL of a deaerated 3:2 methanol/0.1 M/pH 7 phosphate buffer solution containing 0.4 mL of ethyl bromide. After 42 h, the optical absorption spectrum of an aliquot before and after photolysis revealed 90% ethylcobalamin. The identity of this cobalamin was verified after isolating it by phenol extraction and precipitation with ether. Photolysis of a sample produced ethylene. It also exhibited the same R_f as authentic ethylcobalamin on TLC on cellulose, with 1-butanol:ethanol:water (10:3:7, v/v/v) as the eluent.

Reactions of Cob(I)alamin with Bromosuccinate and Fumarate Esters. In typical experiments, a solution of 311 mg of vitamin B_{12a} (82.9%, 184 μmol) in 10 mL of 5% (w/v) NH_4Br in methanol in a 15-mL centrifuge tube was deaerated with argon. After 300 mg of Zn dust was added, the tube was sealed with a rubber septum stopper. Flushing with Ar continued for 5 min, during which vitamin B_{12s} formation was complete. After centrifugation to pellet the zinc, the supernatant was transferred via catheter under Ar pressure into a deaerated serum vial containing 53 mg (210 μmol) of diethyl bromosuccinate in 6 mL of 5% NH_4Br in methanol. The solution immediately became brown and spectral analysis of an aliquot indicated that vitamin B_{12r} had been formed.

After 5 min, the vial was opened and the solvent removed by rotary evaporation. The residue was separated between water and ether. The ether was dried with $MgSO_4$ and removed by rotary evaporation. A ^{1}H NMR spectrum of the residue in CCl_4 was taken, revealing a 1:1 mixture of diethyl succinate and diethyl bromosuccinate. A control with no vitamin B_{12} left diethyl bromosuccinate unchanged.

In other experiments, diethyl fumarate and *S,S*-diethyl dithiofumarate were reacted with hydridocobalamin in 1:1 $C_2H_5OH:CH_3COOH$, and separately, *S,S*-diethyl dithiofumarate was reacted with vitamin B_{12s} generated in 5% methanolic NH_4Br. The zinc used to reduce the cobalt must always be removed to prevent its reaction with the alkylating agent. Product mixtures were analyzed by NMR as above. In addition, products from *S,S*-diethyl dithiofumarate were analyzed for *S,S*-diethyl methyldithiomalonate by TLC on silica gel (0.25 mm), using benzene: hexanes (2:1) as the solvent and running the solvent 2-3 times. No rearranged product was detected.

Acknowledgment. This work was supported by Grant CHE 79-50003 from the National Science Foundation. We thank Masao Hashimoto for valuable experimental assistance.

Registry No. 1, 71721-47-6; cobalamin **2**, 80662-49-3; cobalamin **3**, 80679-15-8; cobalamin **4**, 62430-52-8; cobalamin **5**, 80662-50-6; neopentylcobinamide, 80679-16-9; cobinamide **3**, 80662-51-7; cobinamide **4**, 80662-52-8; vitamin B_{125}, 18534-66-2; vitamin B_{129}, 13422-51-0; diaquocobinamide, 80662-53-9; methylmalonyl-CoA mutase, 9023-90-9; diethyl methylmalonate, 609-08-5; *O,S*-diethyl methylthiomalonate, 80658-34-0; *O,S*-diethyl dimethylthiomalonate, 62442-85-7; *O,S*-diethyl 2-methyl-4-thiosuccinate, 62442-84-6; diethyl methylsuccinate, 4676-51-1; *O,S*-diethyl (bromomethyl)methylthiomalonate, 62442-83-5; diethyl bromosuccinate, 763-51-9; diethyl fumarate, 623-91-6; *S,S*-diethyl dithiofumarate, 62674-35-5.

Twisted Carbon–Carbon Double Bonds. Crystal and Molecular Structure of 4,5-Di-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclohexa-3,5-diene

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Abstract: 4,5-Di-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclohexa-3,5-diene, $C_{12}H_{20}Si_2F_4$, crystallizes in a monoclinic system with space group $P2_1/c$, $a = 12.584$ (5) Å, $b = 16.843$ (7) Å, $c = 15.293$ (4) Å, and $\beta = 69.70$ (3)°. The density calculated is 1.295 g cm^{-3} with $Z = 8$. Intensity data were obtained on a single-crystal diffractometer with Cu Kα radiation. The crystal structure was solved by direct methods and refined by full-matrix least squares to $R = 0.083$ on F for 1923 independent reflections. The two crystallographic independent molecules are related approximately by a pseudotwofold rotation symmetry. Both molecules have similar dimensions and adopt a twisted-boat conformation which deviates somewhat from C_2 symmetry. The bonds connecting the two *tert*-butyl groups are long, averaging 1.54 (2) Å, as compared to the normal C(sp^2)–C(sp^2) single bond length of 1.48 Å. The averaged Si–Si bond length and Si–Si–C bond angles are 2.331 (7) Å and 95.5 (5)°, respectively. The carbon–carbon double bonds are all twisted and can be understood on the basis of the polarized zwitterionic transition state with the ring strain acting as the steric source and *tert*-butyl and SiF_2 parts as the donor and acceptor groups. The averaged C=C bond lengths and twisted angles are 1.345 Å for a twist of 24° and 1.388 Å for a 27° twist. Both ^{13}C NMR and UV spectra are consistent with this picture.

The twisted carbon–carbon double bond has been a subject of continuous theoretical interest for many years.[1] One recent interest particularly lies on the proposed "sudden polarization" effect of the twisted excited state of olefins and its possible role in vision.[2] At ground state, efforts have been taken in the studies of ethylenes with strong donor groups on one carbon atom and strong acceptors on the other ("push–pull" effect).[3,4] When sufficient steric interactions between these groups exist, these ethylenes are permanently twisted around the carbon–carbon double bonds.[3-5]

One of the most prominent steric interactions in the 1,3-diene system is the case of 2,3-di-*tert*-butyl-1,3-butadiene.[6,7] The

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* T.-H.H., Institute of Molecular Biology. Y.C. and C.-S.L., Department of Chemistry.

(1) For example: (a) Kaldor, U.; Shavitt, I. *J. Chem. Phys.* **1968**, *48*, 191–203. (b) Moskowitz, J. W.; Harrison, M. C. *Ibid.* **1965**, *42*, 1726–1731.

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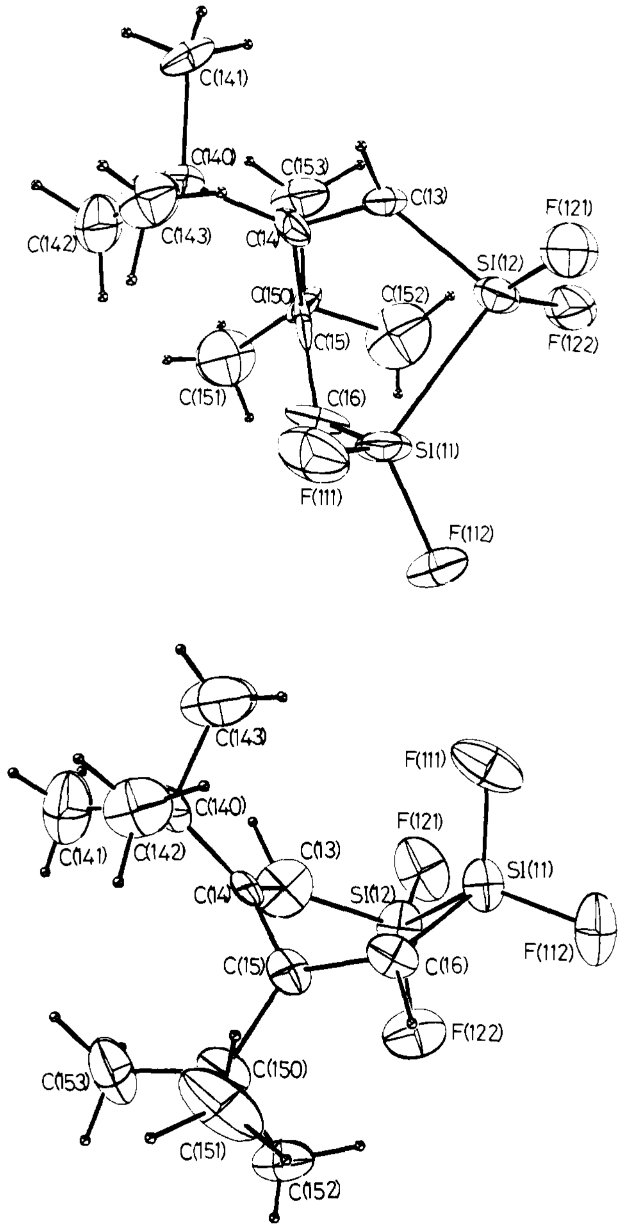
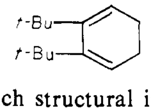
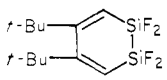


Figure 1. Two perspective views of the structure of molecule I with atom numbering.

conformation of this molecule has been shown to be neither s-trans nor s-cis but nonplanar. However, because of the flexibility of an open-chain structure of the molecule, the two vinyl planes remain planar separately. It would be interesting to know the structure of the vinyl moieties in molecules in which such flexibility is inherently restricted, for example, 2,3-di-*tert*-butylcyclohexa-1,3-diene:



Unfortunately, no such structural information is available. In the cocondensation reaction between *tert*-butylacetylene and difluorosilylene, one of the volatile products is a crystalline compound of the molecular formula $C_{12}H_{20}Si_2F_4$.[8] Mainly based on the ^{1}H and ^{19}F NMR spectra and the reaction pattern in general, the compound was characterized as 4,5-di-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclohexa-3,5-diene.[8]



We now report the results of our structural studies on this novel compound.

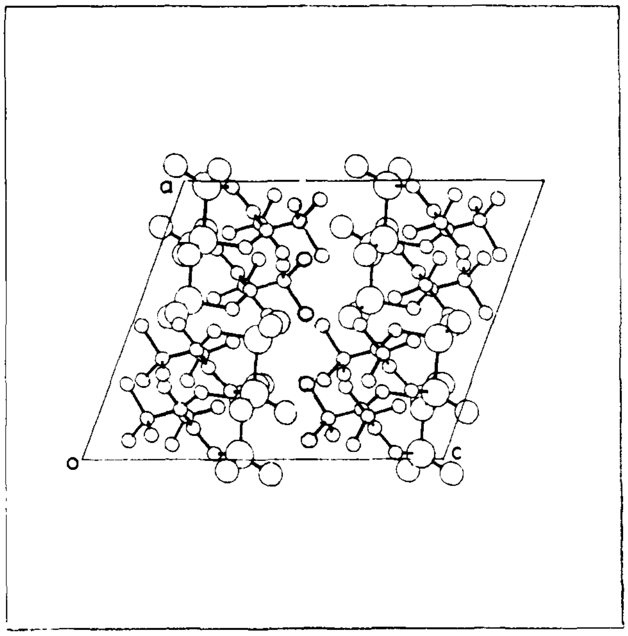


Figure 2. Crystal packing diagram (viewed along the *b* axis).

Experimental Section

Preparation and Physical Measurements. 4,5-Di-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclohexa-3,5-diene was prepared by a cocondensation reaction between *tert*-butylacetylene and difluorosilylene and purified by exhaustive vacuum-line fractionation as previously described.[8] ^{13}C NMR spectra in $CDCl_3$ were obtained on a JEOL FX 100 spectrometer operating at 25.05 MHz. UV spectra were measured using a Cary 17 spectrophotometer.

Crystallographic Measurements. Crystals were obtained by vacuum sublimation. They were extremely air sensitive. A transparent platty single crystal with dimensions 0.5 × 0.3 × 0.08 mm was selected under dry argon atmosphere and sealed into a Lindemann glass capillary. Monoclinic unit cell parameters were obtained by a least-squares fit to the setting angles of 25 reflections measured on a CAD-4F automatic diffractometer with Ni-filtered Cu Kα radiation: a = 12.584 (5) Å, b = 16.843 (7) Å, c = 15.293 (4) Å, and β = 69.70 (3)°. The systematic absence ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) unambiguously fixed the space group as $P2_1/c$. Density calculation indicated that there were two molecules per asymmetric unit (ρ_c = 1.295 g cm^{-3} for Z = 8).

Three-dimensional intensity data were collected at room temperature with θ–2θ scan techniques. At the end of data collection, intensities of three standard reflections were dropped by about 18%. Intensity data were accordingly rescaled by use of a linear interpolation procedure. Of the total 2987 independent reflections collected with Ni-filtered Cu Kα radiation (λ = 1.54178 Å, $2\theta \leq 100°$), 1923 had intensities greater than 3 standard deviations above background and were used in the subsequent analysis. Intensity data were then converted to structure factors after applying Lorentz and polarization corrections in the usual manner. No correction for absorption was made ($\mu_{\mathrm{Cu}\,K\alpha}$ = 23.73 cm^{-1}).

Structure Determination and Refinement. The structure was solved by direct methods and refined by standard least-squares techniques. All nonhydrogen atoms were located from an E map. Full-matrix least-squares refinement with isotropic thermal parameters for these atoms led to an R of 0.170 with $R = \sum||F_o| - |F_c||/\sum|F_o|$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weighting scheme given by Stout and Jensen.[9] The positions of the hydrogen atoms were then located from a difference Fourier map and for part of those in methyl groups calculated with a C–H distance of 0.9 Å and a tetrahedral angle of 109.5°.

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Table I. Fractional Coordinates (10^4)[a]

atom	*x/a*	*y/b*	*z/c*
Si(11)	9814 (4)	8861 (4)	686 (4)
Si(12)	7853 (4)	9003 (4)	1124 (4)
F(111)	10397 (8)	9637 (6)	865 (7)
F(112)	10526 (7)	8609 (6)	−377 (6)
F(121)	7337 (8)	9800 (6)	919 (6)
F(122)	7306 (7)	8304 (6)	749 (6)
C(13)	7610 (11)	8968 (10)	2382 (10)
C(14)	8260 (12)	8574 (9)	2786 (11)
C(15)	8901 (14)	7868 (10)	2204 (12)
C(16)	9775 (12)	8020 (10)	1367 (11)
C(140)	8534 (13)	8847 (10)	3621 (11)
C(141)	7398 (14)	8997 (12)	4464 (11)
C(142)	9298 (15)	8327 (11)	3924 (11)
C(143)	9126 (14)	9655 (10)	3374 (12)
C(150)	8522 (14)	7048 (11)	2523 (11)
C(151)	9456 (15)	6505 (11)	2679 (13)
C(152)	8130 (17)	6626 (11)	1798 (15)
C(153)	7424 (14)	6981 (11)	3426 (11)
Si(21)	2359 (4)	8770 (3)	4104 (4)
Si(22)	4305 (4)	8973 (4)	3658 (4)
F(211)	1758 (7)	9523 (6)	3886 (6)
F(212)	1669 (7)	8545 (6)	5163 (6)
F(221)	4785 (8)	9764 (6)	3871 (6)
F(222)	4878 (8)	8309 (6)	4041 (6)
C(23)	4553 (12)	8973 (10)	2392 (11)
C(24)	3920 (13)	8511 (10)	2061 (11)
C(25)	3304 (13)	7774 (9)	2601 (11)
C(26)	2440 (11)	7917 (10)	3439 (10)
C(240)	3609 (14)	8823 (12)	1215 (12)
C(241)	4755 (12)	8897 (11)	322 (10)
C(242)	2857 (15)	8240 (11)	910 (13)
C(243)	3070 (15)	9615 (11)	1437 (12)
C(250)	3777 (14)	6903 (10)	2281 (12)
C(251)	2837 (15)	6391 (11)	2163 (12)
C(252)	4188 (15)	6572 (11)	2988 (13)
C(253)	4814 (13)	6938 (10)	1351 (10)

[a] Estimated errors are in parentheses.

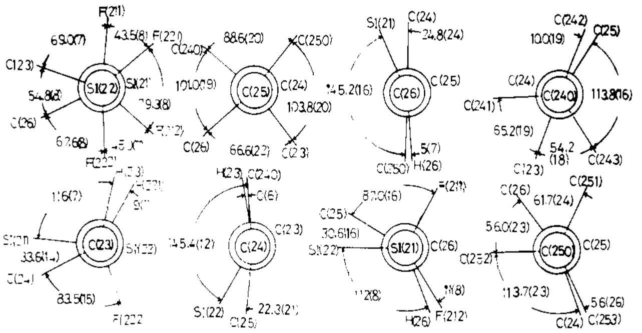

Figure 3. Torsional angles of molecule II. Estimated errors are in parentheses. Angles involving hydrogen atoms of the *tert*-butyl groups are not shown.

The positional and estimated isotropic thermal parameters of the hydrogen atoms were then included in the calculation but not refined. The final refinement with anisotropic thermal parameters for the nonhydrogen atoms led to the values of R and R_w of 0.083 and 0.067, respectively, where $R_w = (\sum w(|F_o| - |F_c|)^2/\sum \omega F_o^2)^{1/2}$. The atomic scattering factors used were all taken from ref 10, with that of Si corrected for anomalous dispersion.

The final atomic coördinates are given in Tables I and II. The errors associated with hydrogen positions are estimated from a least-squares calculation after the final refinement. Two perspective views of the molecule and the atomic numbering scheme are shown in Figure 1. A crystal packing viewed along b axis is presented in Figure 2. Selected bond distances and angles are listed in Table III. The anisotropic thermal parameters and a table of observed and calculated structure factors are available; see paragraph at the end of the paper regarding supplementary materials.

Table II. Fractional Coordinates for H ($\times10^3$)[a]

atom	*x/a*	*y/b*	*z/c*	*B*
H(13)	740 (8)	943 (8)	277 (8)	4.0
H(16)	995 (8)	743 (7)	108 (7)	4.0
H(1411)	681 (9)	868 (7)	437 (7)	6.0
H(1412)	712 (10)	956 (8)	450 (8)	6.0
H(1413)	748 (10)	887 (7)	502 (8)	6.0
H(1421)	936 (10)	860 (8)	445 (8)	6.0
H(1422)	994 (10)	822 (7)	339 (8)	6.0
H(1423)	893 (10)	776 (8)	422 (8)	6.0
H(1431)	874 (10)	993 (7)	299 (8)	6.0
H(1432)	914 (12)	994 (8)	375 (9)	6.0
H(1433)	988 (12)	955 (9)	295 (8)	6.0
H(1511)	905 (10)	609 (8)	309 (8)	7.5
H(1512)	991 (12)	678 (7)	294 (9)	7.5
H(1513)	988 (11)	629 (9)	210 (10)	7.5
H(1521)	747 (12)	693 (9)	176 (10)	8.0
H(1522)	767 (11)	618 (8)	207 (9)	8.0
H(1523)	869 (11)	646 (8)	137 (−9)	8.0
H(1531)	728 (11)	647 (8)	364 (9)	6.5
H(1532)	675 (12)	718 (8)	329 (10)	6.5
H(1533)	747 (11)	733 (8)	392 (9)	6.5
H(23)	482 (12)	948 (9)	213 (10)	4.0
H(26)	221 (8)	731 (7)	369 (7)	4.0
H(2411)	457 (9)	912 (7)	−13 (7)	6.0
H(2412)	539 (10)	921 (7)	39 (8)	6.0
H(2413)	496 (10)	833 (8)	22 (8)	6.0
H(2421)	219 (10)	828 (8)	144 (8)	6.0
H(2422)	302 (11)	774 (8)	80 (9)	6.0
H(2423)	256 (10)	864 (8)	55 (9)	6.0
H(2431)	244 (10)	954 (8)	197 (9)	6.0
H(2432)	280 (10)	975 (7)	110 (9)	6.0
H(2433)	363 (10)	1003 (7)	145 (8)	6.0
H(2511)	313 (10)	613 (7)	159 (8)	8.0
H(2512)	263 (12)	601 (8)	266 (10)	8.0
H(2513)	217 (13)	672 (9)	220 (10)	8.0
H(2521)	478 (12)	691 (8)	319 (9)	7.0
H(2522)	362 (11)	639 (8)	350 (8)	7.0
H(2523)	466 (10)	609 (8)	268 (9)	7.0
H(2531)	539 (11)	732 (9)	134 (10)	6.0
H(2532)	459 (10)	706 (8)	83 (8)	6.0
H(2533)	508 (10)	642 (8)	133 (8)	6.0

[a] Estimated errors are in parentheses.

Results and Discussion

As shown in Table III, the two crystallographically independent molecules, which will be referred to as molecules I and II, have very similar dimensions. They are related in the crystal approximately by a noncrystallographic twofold rotation symmetry (Figure 2). Both molecules adopt a twisted-boat conformation with Cremer–Pople puckering parameters shown in Table IV. However, unlike 1,3-cyclohexadiene,[11] these twisted-boat conformations deviate somewhat from expected C_2 symmetry.

The bond connecting the two *tert*-butyl groups is elongated as compared to that in 1,3-cyclohexadiene (1.468 (14) Å)[11] and approaches the normal C(sp^3)–C(sp^3) single bond length of 1.537 (5) Å.[12] However, the interior bond angle between the *tert*-butyl substituents and the ring edge are close to the value of 120°. Therefore, mutual repulsion of the *tert*-butyl groups leads to substantial bond length elongation without affecting the bond angles. Furthermore, the torsional angles, C(13)–C(14)–C(15)–C(16) = 69.1 (21)° in molecule I and C(23)–C(24)–C(25)–C(26) = 66.2 (22)° in molecule II, suggest conjugation is lost in the butadiene moiety.

The Si–Si bond lengths (2.334 (7) Å in molecule I and 2.328 (7) Å in II) are comparable to those reported for *cis*-4,5-dichloro-1,1,2,2-tetrafluoro-1,2-disilacyclohexane,[13] 2.318 (3) Å, and hexafluorodisilane,[14] 2.324 (6) Å. The endocyclic Si–Si–C bond angles all deviate significantly from the tetrahedral 109.5°, approaching that in *rac*-1,2-diselenane-3,6-dicarboxylic acid, 96

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Table III. Interatomic Distances (Å) and Angles (deg) Excluding Hydrogen Atoms[a]

(a) Distances

Si(11)–Si(12)	2.334 (7)	Si(12)–F(122)	1.569 (12)	Si(21)–Si(22)	2.328 (7)	Si(22)–F(222)	1.551 (13)
Si(12)–C(13)	1.841 (17)	C(14)–C(140)	1.506 (26)	Si(22)–C(23)	1.851 (18)	C(24)–C(240)	1.567 (28)
C(13)–C(14)	1.357 (24)	C(140)–C(141)	1.578 (20)	C(23)–C(24)	1.333 (26)	C(240)–C(241)	1.611 (19)
C(14)–C(15)	1.536 (22)	C(140)–C(142)	1.488 (27)	C(24)–C(25)	1.543 (22)	C(240)–C(242)	1.544 (29)
C(15)–C(16)	1.392 (20)	C(140)–C(143)	1.534 (23)	C(25)–C(26)	1.384 (18)	C(240)–C(243)	1.482 (27)
C(16)–Si(11)	1.749 (18)	C(15)–C(150)	1.487 (24)	C(26)–Si(21)	1.743 (17)	C(25)–C(250)	1.503 (22)
Si(11)–F(111)	1.569 (13)	C(150)–C(151)	1.571 (27)	Si(21)–F(211)	1.570 (12)	C(250)–C(251)	1.584 (27)
Si(11)–F(112)	1.617 (10)	C(150)–C(152)	1.535 (31)	Si(21)–F(212)	1.595 (10)	C(250)–C(252)	1.503 (30)
Si(12)–F(121)	1.570 (12)	C(150)–C(153)	1.583 (20)	Si(22)–F(221)	1.544 (12)	C(250)–C(253)	1.562 (19)

(b) Angles

Si(12)–Si(11)–C(16)	95.9 (5)	C(14)–C(140)–C(143)	106.5 (13)	F(22)–Si(22)–F(222)	106.0 (7)
Si(12)–Si(11)–F(111)	112.1 (5)	C(141)–C(140)–C(142)	109.9 (14)	Si(22)–C(23)–C(24)	119.4 (11)
Si(12)–Si(11)–F(112)	106.1 (7)	C(141)–C(140)–C(143)	106.5 (13)	C(23)–C(24)–C(25)	121.5 (16)
C(16)–Si(11)–F(111)	119.3 (8)	C(142)–C(140)–C(143)	106.7 (15)	C(23)–C(24)–C(240)	118.1 (15)
C(16)–Si(11)–F(112)	106.1 (7)	C(15)–C(150)–C(151)	114.8 (15)	C(25)–C(24)–C(240)	119.3 (15)
F(111)–Si(11)–F(112)	105.3 (6)	C(15)–C(150)–C(152)	109.9 (15)	C(24)–C(25)–C(26)	116.3 (13)
Si(11)–Si(12)–C(13)	94.1 (5)	C(15)–C(150)–C(155)	115.8 (14)	C(26)–C(25)–C(250)	123.7 (14)
Si(11)–Si(12)–F(121)	120.0 (5)	C(151)–C(150)–C(152)	106.5 (15)	C(24)–C(25)–C(250)	119.2 (12)
Si(11)–Si(12)–F(122)	111.9 (5)	C(151)–C(150)–C(153)	107.4 (14)	C(25)–C(26)–C(21)	123.5 (12)
C(13)–Si(12)–F(121)	107.8 (7)	C(152)–C(150)–C(153)	101.3 (14)	C(24)–C(240)–C(241)	108.6 (14)
C(13)–Si(12)–F(122)	115.0 (7)	Si(22)–Si(22)–C(26)	96.2 (5)	C(24)–C(240)–C(242)	113.0 (15)
F(121)–Si(12)–F(122)	107.7 (7)	Si(22)–Si(21)–F(211)	110.7 (4)	C(24)–C(240)–C(243)	109.8 (15)
Si(12)–C(13)–C(14)	125.7 (11)	Si(22)–Si(21)–F(212)	118.6 (5)	C(241)–C(240)–C(242)	104.8 (14)
C(13)–C(14)–C(15)	113.1 (15)	C(26)–Si(21)–F(211)	118.5 (8)	C(241)–C(240)–C(243)	109.2 (14)
C(13)–C(14)–C(140)	126.0 (14)	C(26)–Si(21)–F(212)	107.3 (6)	C(242)–C(240)–C(243)	111.2 (16)
C(15)–C(14)–C(140)	120.0 (15)	F(211)–Si(21)–F(212)	105.9 (5)	C(25)–C(250)–C(251)	111.3 (14)
C(14)–C(15)–C(16)	118.6 (14)	Si(21)–Si(22)–C(23)	94.9 (6)	C(25)–C(250)–C(252)	111.1 (15)
C(16)–C(15)–C(150)	122.3 (14)	Si(21)–Si(22)–F(221)	120.9 (5)	C(25)–C(250)–C(253)	115.6 (13)
C(14)–C(15)–C(150)	119.0 (12)	Si(21)–Si(22)–F(222)	111.3 (5)	C(251)–C(250)–C(252)	105.8 (14)
C(15)–C(16)–Si(11)	123.1 (13)	C(23)–Si(22)–F(221)	106.5 (7)	C(251)–C(250)–C(253)	107.5 (14)
C(14)–C(140)–C(141)	109.4 (14)	C(23)–Si(22)–F(222)	117.6 (7)	C(252)–C(250)–C(253)	104.8 (14)
C(14)–C(140)–C(142)	116.6 (14)				

[a] Estimated errors are in parentheses.

Table IV. Cremer-Pople Puckering Parameters[a]

molecule	q_2	q_3	ϕ_2, deg	Q	θ, deg
I	0.923	−0.191	210.4	0.942	101.7
II	0.912	−0.228	213.0	0.941	104.1

[a] Puckering parameters are calculated according to ref 9. These are to be compared with one twisted-boat conformation of θ = 90° and ϕ = 210°.

(1)°.[15] Interestingly, the two Si–C bond lengths in the molecule are unequal as the two C=C bond lengths are; the longer Si–C bond is associated with the shorter C=C bond, with dimensions of Si(12)–C(13)–C(14) in molecule I and Si(22)–C(23)–C(24) in II approaching those values observed for vinyl silane[16] (Si–C, 1.853 (3) Å; C—C, 1.347 (3) Å; and Si—C=C 122.9 (3)°). Therefore, greater bond length and angle deformation involve grossly only part of the molecule. This part of the molecule has greater twist about the double bond, C(14)–C(15)–C(16)–Si(11) = 28.9 (26)° in molecule I and C(24)–C(25)–C(26)–Si(21) = 24.8 (24)° in II, as compared with C(15)–C(14)–C(13)–Si(12) = 25.6 (20)° and C(25)–C(24)–C(23)–Si(22) = 22.3 (21)°.

In 1,1-bis(methylthio)-2-*p*-bromobenzoyl-2-cyanoethylene,[5] the C=C bond length is 1.369 (7) Å with a twist of 15.2°, and in 1,3-dimethyl-2-[(*p*-bromobenzoyl)cyanomethylene]imidazolidine[5] the corresponding bond length increases to 1.448 (4) Å with a twist of 41.1°. In comparison with these two molecules, the shorter C=C bond length in the present molecule is due to weaker steric interaction between *tert*-butyl and SiF$_2$ groups.

It has been known that "push-pull" ethylenes with sufficient steric interactions between donors and acceptors are permanently twisted around the carbon–carbon double bond. Generally the barrier to rotation around the double bond is lowered as stronger acceptors are attached to the negative end and stronger donors are attached to the positive end of the polarized double bond.[3-5]

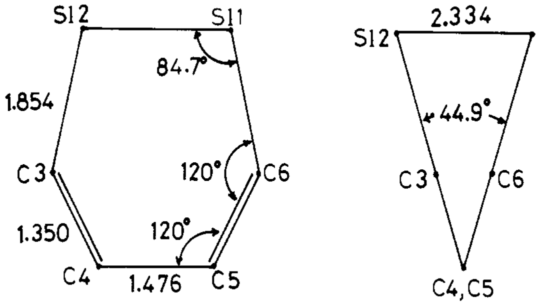

Figure 4. A hypothetical ring structure for 1,2-disilacyclohexa-3,5-diene. The structure is obtained by rotating the C$_4$–C$_5$ bond such that the Si–Si bond has the length of 2.334 Å. The geometry of the sp^2 centers is preserved with bond lengths and angles as indicated. The calculated torsional angle of the Si–Si bond is 73.05°.

Preserving the bond lengths and the geometry of sp^2 centers, a hypothetical structure of 1,2-disilacyclohexa-3,5-diene with twisted-boat conformation of C_2 symmetry is depicted in Figure 4. The substitution of the disilane moiety into the 1,3-cyclohexadiene ring causes severe ring puckering with concomitant reduction in the Si–Si–C bond angle to an exceptionally low value of 84.7°. In comparison with the observed structure, it appears that double bond rotation is the most important ring strain relief mechanism in the present molecule.

The twist of double bonds in the present case, therefore, can be understood on the basis of the picture of the polarized zwitterionic transition state; the ring strain provides the steric effect and the *tert*-butyl and SiF$_2$ groups serve as the "push-pull" donors and acceptors. The *tert*-butyl group as a donor is primarily an inductive effect. Greater stabilization of the twisted double bonds appears to come from the silicon moiety.

Silicon can act either as an electron donor due to its electronegativity or as a π acceptor because of its empty 3d orbitals. Ab initio calculations of vinylsilane have shown that silicon is highly positive and a small π contribution to the Si–C bond involves mainly the silicon d orbitals.[17] Conceivably, the fluorine atoms

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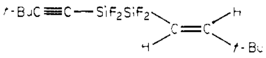
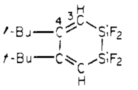
Table V. ^{13}C NMR Chemical Shifts Calculated on the Basis of Additivity and the Deviations from the Experimental Values[a]

	C_3			C_4		
compound	obsd	calcd	Δ_3	obsd	calcd	Δ_4
$ClHC=CH-SiF_2SiF_2-CH_2CH_2Cl$	123.7	122.6	1.1	141.9	143.6	-1.7
$CH_2=CH-SiF_2SiF_3$	130.0	128.3	1.7	142.8	140.3	2.5
$CH_2=CH-SiF_2-CH=CH_2$	128.0	128.0	0	140.0	140.3	-0.3
	113.0	114.1	-1.1	168.1	167.0	1.1
	119.5	114.1	5.4	184.5	167.0	17.5

[a] Chemical shifts measured as δ with internal reference Me_4Si. Numbering of carbons based on the nomenclature of vinyl disilane.

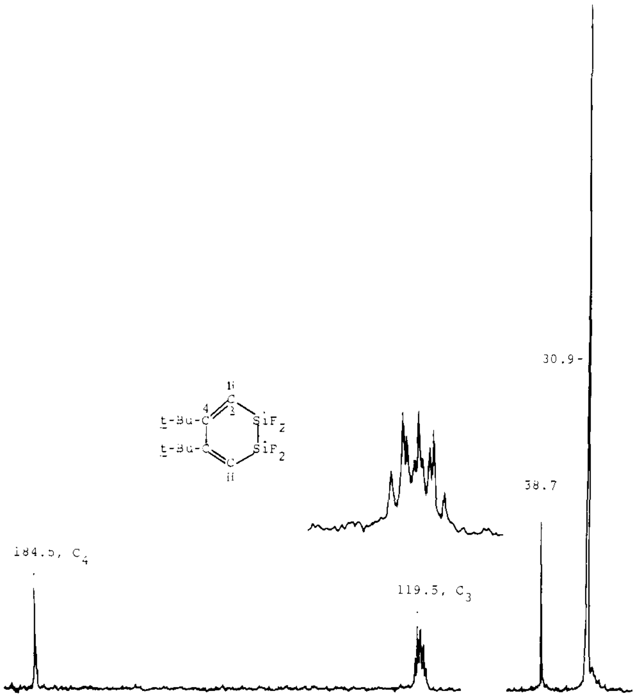


Figure 5. Carbon-13 NMR spectrum of 4,5-di-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclohexa-3,5-diene in $CDCl_3$.

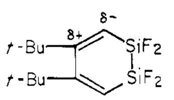
in the SiF_2 groups would further increase the positive character of the Si atoms in the present molecule. The net effect is to enhance the polar character of the Si–C bond. This effect is also evident from the studies of the ^{13}C NMR and UV spectra of this compound.

The ^{13}C NMR spectrum ^{13}C NMR spectrum of this compound is shown in Figure 5. The assignment of the carbons can be made unequivocally with the help of the couplings of the fluorine atoms in the SiF_2 groups. Carbon-13 NMR spectroscopy has been used to study steric effects in a number of cases.[18,19] Empirical rules of additivity which account for different substitution of various systems have been established.[20] An empirical formula accounting for the chemical shifts of C3 and C4 in the vinyl disilane system can be written as follows by using the basic rule for substituted olefins,

$$\delta = 123.3 + 10.6n_\alpha + 7.2n_\beta - 1.5n_\gamma - 7.9n_\alpha' - 1.8n_\beta' + 1.5n_\gamma' + \sigma_{SiF}$$

where α, β, γ and α′, β′, γ′ refer to carbon atoms on the same side and the opposite side of the double bond, respectively. σ_{SiF} is a parameter measuring the substituent effect of the fluorosilicon groups. The calculated and observed chemical shifts for a number of vinyl disilane compounds when σ_{SiF} is taken as 5.0 and 17.0 for C3 and C4, respectively, can be found in Table V. The agreement between calculated and experimental values is generally good for all compounds except the disilacyclohexadiene, where the deviations (Δ) are 5.4 and 17.5 ppm for C3 and C4, respectively. Deviations of ^{13}C NMR chemical shifts from additivity have been used as measures of steric effects.[18] A deviation as large as 17.5 ppm is very unusual. In fact, δ 184.5 for C4 is the lowest field chemical shift that has ever been observed, which almost corresponds to the chemical shift of the carbon in a carbonyl group.

It seems quite certain that besides the effect of steric repulsion, the effect of twisted double bond must also be taken into consideration.



As was mentioned in the previous section, the "push–pull" effects of the *tert*-butyl and SiF_2 groups are expected to stabilize the polarization caused by the twisted double bond. Such polarization would lead to shielding on C3 and deshielding on C4. For C4, all factors exert in the same direction of deshielding which results in the extraordinarily low field chemical shift of 184.5 ppm. For C3, however, the chemical shift must be influenced in a more complex way, for example, the deformation of the bond angles and the twisted double bonds may contribute to the chemical shifts in opposite directions.[18]

The UV spectrum of this compound shows not only the lack of the typical dialkyldiene absorption maximum at 220 nm but an absorption at 208 nm (ϵ_{max} 4200 in *n*-hexane), which is at a shorter wavelength than that of t-Bu—C≡C—SiF_2SiF_2—CH=CH(t-Bu) (λ_{max} 212 nm, ϵ_{max} 3700 in *n*-hexane). It is entirely consistent with the nonplanar 1,3-diene systems such as 2,3-di-*tert*-butyl-1,3-butadiene.[7] The greater energy gap to the excited state would in general cause low-field shifts in the ^{13}C NMR spectra through the contribution of the paramagnetic term. This is also in agreement with the observation.

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Registry No. 4,5-Di-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclohexa-3,5-diene, 36092-03-2; $ClHC=CHSiF_2SiF_2CH_2CH_2Cl$, 80375-29-7; $CH_2=CHSiF_2SiF_3$, 36626-59-2; $CH_2=CHSiF_2CH=CH_2$, 1547-85-9; *trans-t*-BuC≡$CSiF_2SiF_2CH=CHBu$-*t*, 36092-02-1.

Supplementary Material Available: Tables of anisotropic thermal parameters of nonhydrogen atoms and structure factor amplitudes (10 pages). Ordering information is available on any current masthead page.

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