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The Photochemistry of Matrix-Isolated Di-*tert*-butyldiazidosilane. Observation of Di-*tert*-butylsilylene and *N*,*N'*-Di-*tert*-butylsilanediimine[†]

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Abstract: The major product from 254-nm irradiation of matrix-isolated di-*tert*-butyldiazidosilane (**3**) is di-*tert*-butylsilylene (**4**), a highly reactive ground-state singlet species with λ_{max} 480 nm, which undergoes a subsequent photochemical C–H insertion to give the stable 1-*tert*-butyl-2,2-dimethyl-1-silacyclopropane (**5**). The photochemical formation of **4** proceeds in at least two steps. A small amount (<5%) of a photochemical precursor to **4** is observed, with λ_{max} 300 nm and an IR band at 2150 cm^{-1}, tentatively assigned as di-*tert*-butyldiazosilane (**7**). The irradiation of **3** also yields *N*,*N'*-di-*tert*-butylsilanediimine (**6**) as a minor (11%) product, with λ_{max} 240 and 385 nm. This process also involves at least two steps, and a very small yield of an intermediate (λ_{max} 725 nm) of an unknown structure was detected.

In recent years considerable research has been done on the photochemistry and thermal chemistry of main group element azides,[2] especially those of silicon. Monoazidosilanes have long been employed in the photochemical generation of silanimines,[3-5] compounds containing a silicon–nitrogen double bond. These products arise from the thermal or photochemical loss of molecular nitrogen accompanied by a 1,2-shift of a substituent from silicon to nitrogen. The facility with which dimethylsilylene is generated by the photodegradation of dimethyldiazidosilane has recently been reported.[6,7] Even more dramatically it has been shown that photolysis of matrix-isolated 2,2-diazidohexamethyltrisilane (**1**) leads to the formation of bis(trimethylsilyl)silanediimine (**2**),[9] the first silicon analogue of a carbodiimide (eq 1). This species is

$$\underset{\mathbf{1}}{(Me_3Si)_2Si(N_3)_2} \xrightarrow{h\nu} \underset{\mathbf{2}}{Me_3Si{-}N{=}Si{=}N{-}SiMe_3} \qquad (1)$$

of particular interest as it is one of only a few known examples of observed compounds that contain a digonal, "sp-hybridized" silicon atom.[10-12] The thermolysis of phenyltriazidosilane results in the formation of phenylsilaisonitrile,[13,14] whereas its irradiation yields a mixture of both benzosilanitrile and phenylsilaisonitrile.[14] These have been observed spectroscopically and trapped with *tert*-butyl alcohol.[14]

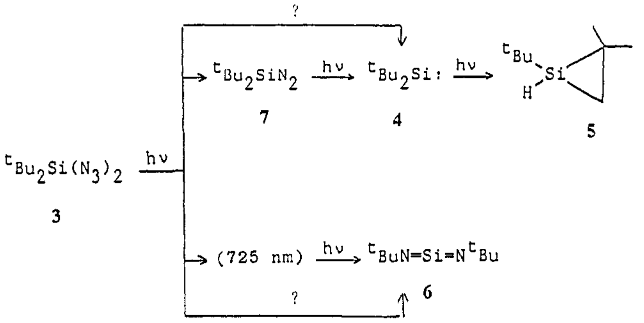
Di-*tert*-butyldiazidosilane (**3**) seemed a possible precursor for the photogeneration of di-*tert*-butylsilylene (**4**), a species of considerable interest because of its two bulky alkyl substituents.[15] In this paper we report the photochemistry of matrix-isolated **3**, leading to **4** and its photorearrangement product **5**, as well as smaller amounts of silanediimine **6**, diazosilane **7**, and an additional product of unknown structure (Scheme I).

Results and Discussion

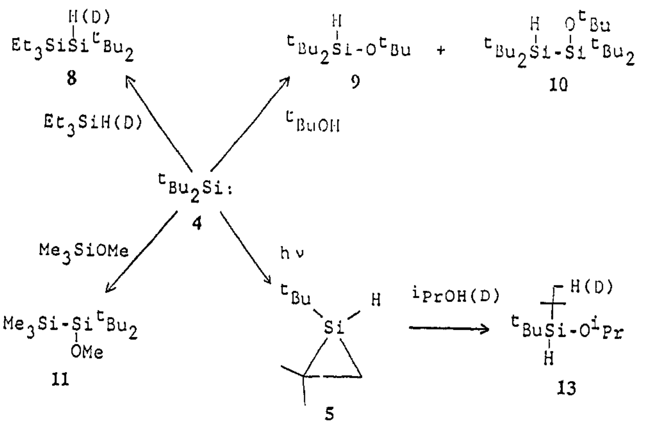
The photolysis of **3** in 3-methylpentane (3-MP) glass at 77 K or in an argon matrix at 10 K yielded several products, most readily referred to by their UV–visible absorption maxima as the 480-nm product, the 300-nm product, the 240- and 385-nm product, and the 725-nm product (Figure 1).

A. Di-*tert*-butylsilylene (4). As noted above, one of the products from the irradiation of **3** was an orange species with λ_{max} 480 nm (Figure 2). It had prominent IR peaks at 1471, 1459, 1386, 1357, 1014, 778, and 586 cm^{-1} (Figure 3). The species was destroyed by 500-nm light, with simultaneous decrease of its UV and IR bands and of the yields of its trapping products from 20 to 25% to less than 5%. The product of the 500-nm irradiation was the stable and isolable silacyclopropane **5**. The orange species was identified unequivocally as di-*tert*-butylsilylene (**4**) by its spectra, the nature of its trapping products, and the structure of **5** (Scheme II).

Scheme I. Photolysis of **3** in an Argon Matrix at 10 K or a 3-Methylpentane Glass at 77 K



Scheme II. Reactions of Di-*tert*-butylsilylene (**4**)



[†] This project was initiated at the University of Utah.

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(7) The assignment of dimethylsilylene to the absorption maximum at 453 nm was initially questioned,[8] but it has now been conclusively demonstrated that it was correct; see ref 6b and Nazran, N. S.; Hawari, J. A.; Griller, D.; Alnaimi, I. S.; Weber, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5041.

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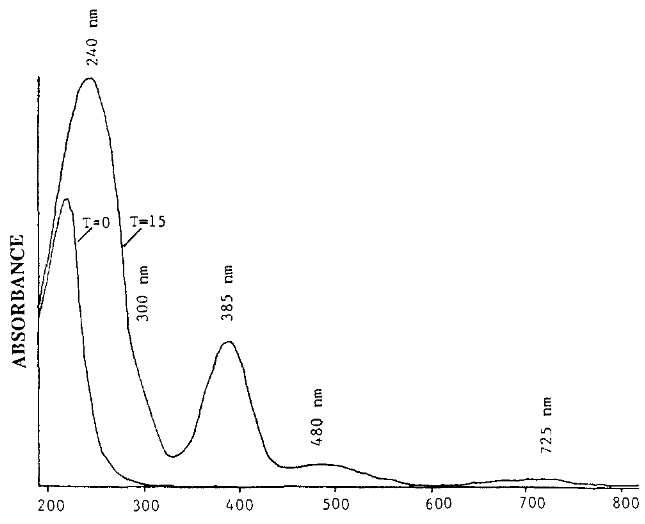

Figure 1. UV-visible spectrum of **3** in a 3-methylpentane glass at 77 K before irradiation ($T = 0$) and after exposure to 254-nm light for 15 min ($T = 15$).

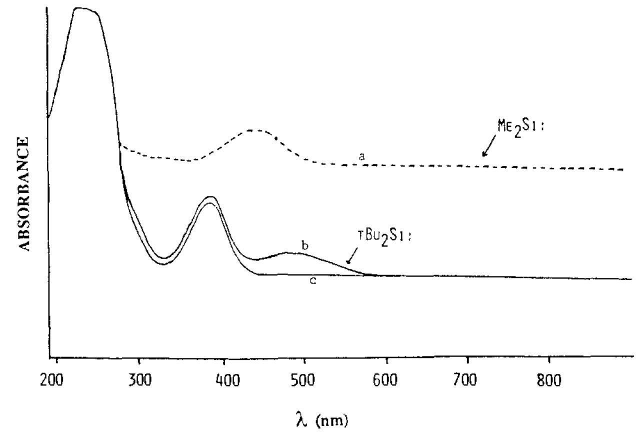

Figure 2. (a) UV-visible absorption spectrum of dimethylsilylene[16] at 77 K. (b) Spectrum of **3** (3-MP, 77 K) after irradiation at 254 nm and photobleaching at wavelengths greater than 700 nm. (c) Spectrum b following photolysis at 500 nm. The absorption maximum at 480 nm has been assigned to di-*tert*-butylsilylene (**2**).

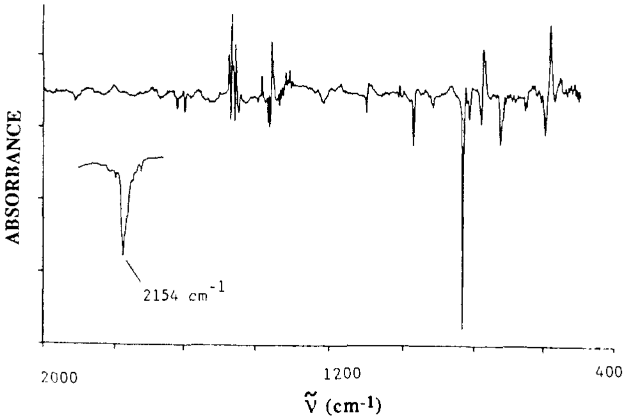

Figure 3. FT-IR difference spectrum of **4** (positive bands) and **5** (negative bands) in an argon matrix at 10 K. Inset: the Si-H stretching frequency of **5** at 2154 cm^{-1}. Compound **4** was generated by the irradiation (254 nm) of matrix-isolated **3**. Subsequent bleaching by 500 nm light gave **5**.

Table I. Calculated and Observed UV-vis Absorption Spectra[a]

compd	transition energy (10^3 cm^{-1}) calcd	transition energy (10^3 cm^{-1}) exptl	osc. strength calcd[b]	osc. strength exptl
4	15.0	20.8	0.10	
	40.4		0	
	46.1		0.11	
6	17.5		0	
	20.5		0	
	21.1		0	
	31.9		0.02	
	33.6	26.0	0.04	w
	42.2		0.03	
	44.4		0	
	44.5		0.02	
	56.3		0.25	
	58.0	41.7	0.32	s
	58.8		0.75	
7	9.6		0	
	30.0	33.3	0.15	
	32.7		0.05	
	47.8		0	
18	9.7		0	
	16.4		0	
	21.5		0	
	36.0		0	
	41.4		0.12	
	43.9		0.03	
	45.3		0.14	
	45.4		0.02	
	58.4		0.80	
19	17.7		0.03	
	25.8		0.01	
	30.4		0.01	
	36.9		0.05	
	46.3		0.02	
	49.9		0.08	
21	14.7		0.003	
	20.6		0.14	
	29.2		0.03	
	41.6		0.09	
	52.7		0.04	
22	7.3	12.75	0	w
	44.5		0.14	
	45.2		0	

[a] INDO/S[17b] calculation at MNDO[17a]-optimized geometry, *tert*-butyl groups replaced by methyl groups. [b] Using the dipole length-dipole velocity combination formula.

Chemical Trapping upon Warmup of a 3-MP Glass. Reaction of **4** with triethylsilane, an efficient silylene trap, led to the isolation of 1,1,1-triethyl-2,2-di-*tert*-butyldisilane (**8**) in 22% yield. The trapping of **4** with Et$_3$SiD gave **8**-d_1 with the deuterium on Si-2. Photolysis of **3** in glassy 3-MP containing 1% *tert*-butyl alcohol gave di-*tert*-butyl-*tert*-butoxysilane (**9**) and 1,1,2,2-tetra-*tert*-butyl-1-*tert*-butoxydisilane (**10**). Monosilane **9** clearly arises from the insertion of **4** into the O-H bond of the alcohol, while disilane **10** could be the product of alcohol addition to the tetra-*tert*-butyldisilene (from dimerization of **4** before trapping) or insertion of **4** into the Si-O bond of previously generated **9**. The latter was shown to be the likely pathway by employing authentic **9** as a silylene trap; **10** was obtained in 20% yield. The reaction of **4** in 3-MP with methoxytrimethylsilane gave 1,1,1-trimethyl-2,2-

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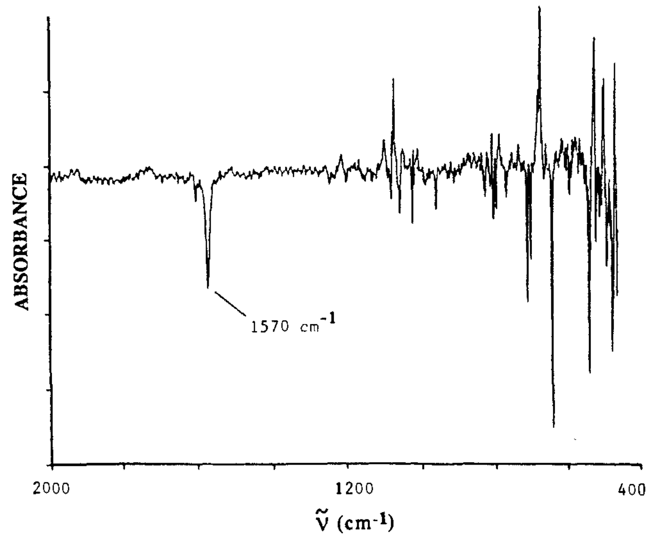

Figure 4. FT-IR difference spectrum of **4**-d_{18} (positive) and **5**-d_{18} (negative) at 10 K. Note the Si–D stretch at 1570 cm^{-1}.

di-*tert*-butyl-2-methoxydisilane (**11**) in 20% yield.

Chemical Trapping upon Warmup of an Argon Matrix. Photolysis of **3** in an argon matrix sandwiched between layers of a methanol/argon mixture gave, upon warmup, di-*tert*-butylmethoxysilane (**12**), showing that **4** was generated in argon matrix as well as in hydrocarbon glass.

UV-vis Spectrum. The broad visible absorption band at 480 nm (Figure 2) is consistent with those observed for other dialkylsilylenes[16] and is attributed to an n–p transition as usual, in agreement with an INDO/S[17a] calculation at an MNDO[17b]-optimized geometry, which underestimates the transition energy for silylenes,[17c] but predicts no further transitions up to quite high energies (Table I). As discussed below, the discrepancy between the experimental and computed transition energies represents a composite of the errors of the MNDO and INDO/S methods. Dimethylsilylene[6,7] exhibits λ_{max} at 453 nm. As bulkier substituents are placed on the silicon, the absorption maximum shifts bathochromically; **4** has the longest wavelength absorption yet observed for a dialkylsilylene. The trend can be rationalized by a gradual increase of the CSiC angle with increasing steric bulk, destabilizing the filled n orbital of the silylene and decreasing the n–p transition energy.[18]

IR Spectrum. The observed infrared spectrum (Figure 3) is compatible with the assignment to **4**. No Si–H stretch was present and the symmetric and antisymmetric C–Si stretches were observed at 586 and 778 cm^{-1}, respectively. In the IR spectrum of perdeuterated **4** (Figure 4), these bands were shifted to 528 and 676 cm^{-1}. When ^{15}N-labeled **3** was used in the experiment, none of the observed bands were shifted, indicating that no nitrogen was present in **4**. The IR spectrum of dimethylsilylene has been analyzed in detail[6,7] and the spectrum assigned to **4** was consistent with this analysis. It also agreed fairly well with MNDO calculations, which predict the symmetric and antisymmetric C–Si stretches to lie closer together: at 657 and 723 cm^{-1}, respectively, in **4**, and at 579 and 659 cm^{-1}, respectively, in **4**-d_{18}.

Spin Multiplicity. The reactions of **4** with trapping reagents resemble similar reactions observed for other singlet silylenes.[19] Based on these results and the absorption maximum at 480 nm, there is little doubt that **4** has a singlet ground state. This assignment is supported by ESR measurements performed on matrices containing the silylene, either at 77 K in 3-MP or in argon at both 10 and 4 K. In repeated measurements no signal that could be assigned to a triplet silylene was ever observed.

Molecular Geometry. Our MNDO calculations performed on **4** yield an optimized C–Si bond length of 185 pm and CSiC bond angle of 120°. Ab initio MCSCF calculations with second-order CI, using a 6-31G** basis set, predict that at HSiH angles of 129° or greater the triplet state of the parent silylene becomes more stable than the singlet state.[20] Neglecting electronic effects due to alkyl substitution, one would then expect **4** to be a ground-state singlet, as observed. Recent 3-21G* SCF calculations have predicted a singlet ground state for **4**, with the triplet at least 4 kcal/mol higher in energy[15b]. The singlet silylene was predicted to possess a CSiC bond angle of 111.7° and a C–Si bond length of 194.5 pm.

We believe that the MNDO value of the CSiC valence angle in **4** is too large and that the ab initio value of 112°, with relatively long C–Si bonds, is more nearly correct. This belief is based on the results of INDO/S calculations of the excitation energies of a series of dialkylsilylenes.[17c] Using MNDO-optimized geometries, these reproduce nicely the differences in the excitation energies[16] of dimethylsilylene, methylethylsilylene, diethylsilylene, *tert*-butylmethylsilylene, tetramethylenesilylene, and pentamethylenesilylene, although all of the computed transition energies are about 3000 cm^{-1} too low. However, the excitation energy computed for **4** is far out of line, about 6000 cm^{-1} too low. This is most easily understood if the MNDO geometry optimization overestimates the steric interaction of the two *tert*-butyl groups in **4** and the resulting increase in the CSiC valence angle relative to, say, dimethylsilylene.

Photoisomerization. Although the trapping experiments described above confirm the presence of **4**, the yields of trapping products are low because **4** undergoes further photolysis to an isomeric product, **5**. This photoisomerization was followed by infrared spectroscopy. When an argon matrix containing photolyzed **3** was irradiated at 500 nm, the bands assigned to **4** gradually disappeared and those for **5** increased simultaneously. The new product shows strong IR bands at 2140 and 836 cm^{-1}, which shift to 1680 and 630 cm^{-1} when **4**-d_{18} is used instead of **4**. These are assigned respectively as the Si–H (D) stretching and bending modes. The IR of **5** is the same irrespective of whether **3** or **3**-^{15}N is used as the starting material.[21]

Confirmation of the structure assigned for **5** was obtained by reaction with 2-propanol. Irradiation of **3** in 3-MP at 77 K, followed by photobleaching, warming to room temperature, and quenching with excess 2-propanol gave **13** in 85% yield based on the amount of **3** consumed.[22] Use of *i*-PrOD led to the isolation of **13**-d_1 with the deuterium incorporated into a *tert*-butyl group. Compound **5** could be isolated by bulb-to-bulb distillation at low temperatures. In the ^{1}H NMR the Si–H could be observed at 3.72 ppm as the X portion of an ABX pattern. In the mass spectrum the parent ion was not observed; however, a strong peak corresponding to m/e 85 ($M^+ - C_4H_9$) was present.

There are many known instances of intramolecular C–H insertion in thermal reactions of silylenes,[19] but, to our knowledge, this is the first reported case of a photochemical C–H insertion by a silylene. Compound **5** is apparently the first stable silacyclopropane containing an Si–H bond.[23]

B. Di-*tert*-butyldiazosilane (7). The mechanism by which silylenes are formed in the photolysis of diazidosilanes is not known, but most likely involves several steps. We have noted that one

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(21) The ^{15}N labeled diazide was prepared by treating di-*tert*-butyldichlorosilane with singly labeled sodium azide. This gave **1** containing one ^{15}N per azide with the label evenly distributed between the end nitrogen and the nitrogen adjacent to the silicon.

(22) The alcohol added exclusively across the less hindered Si–C bond in **8**; isobutyl-*tert*-butylisopropoxysilane was not observed as a trapping product.

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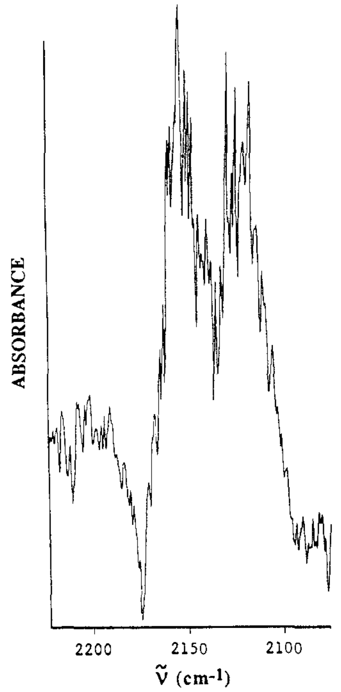


Figure 5. FT-IR difference spectrum of matrix-isolated **7** (positive) and **5** (negative), which have been generated from **3**-$^{15}N_2$.

of the products from the 254-nm irradiation of **3**, characterized by a weak UV absorption at 300 nm and an IR absorption band at 2150 cm^{-1}, is photolabile. Irradiation with 300-nm light caused a complete disappearance of its spectral features and a concurrent increase in the IR and UV-vis bands of **4**. Thus, this new product is a direct photochemical precursor to di-*tert*-butylsilylene, but it is possible that other paths from **3** to **4** are in operation as well.

When **3** ^{15}N-labeled once in each azido group (equally at N_1 and N_3) was used in the experiment, the strong IR band of this species at 2150 cm^{-1} was replaced by a doublet at 2150 and 2110 cm^{-1} (Figure 5), proving that this species still contains nitrogen. A tempting assignment is di-*tert*-butyldiazosilane (**7**). An otherwise obvious alternative, 1,1-di-*tert*-butyl-1-siladiazirine, would not be expected to have an intense band at such a high frequency.

If our assignment is correct and this product indeed is di-*tert*-butyldiazosilane (**7**), this is the first example of the observation of this type of structure.[24] MNDO calculations were carried out for dimethyldiazosilane as a model for **7** and for comparison with previous ab initio 3-21G SCF and MNDO calculations for the parent compound, H_2SiN_2.[25] The carbon–silicon–nitrogen framework is calculated to be essentially planar, with a CSiC bond angle of 128°. The Si-N bond length was calculated to be 164 pm, which is slightly longer than the experimental value of approximately 157 pm for a Si=N double bond.[26] The calculated geometry is thus similar to those of diazoalkanes, in contrast to the 3-21G SCF result for the parent H_2SiN_2, best described as the donor–acceptor complex between H_2Si and an N_2 molecule.[25]

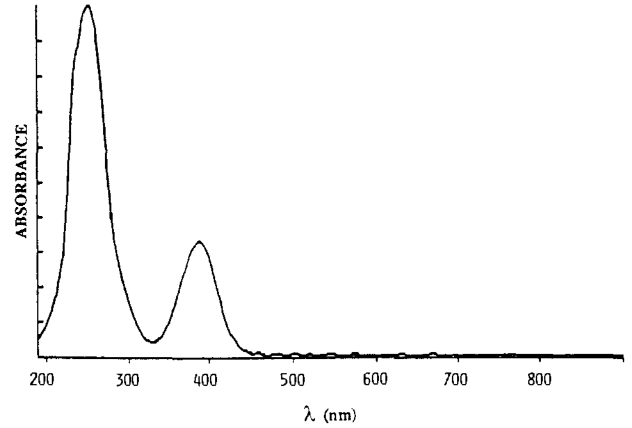
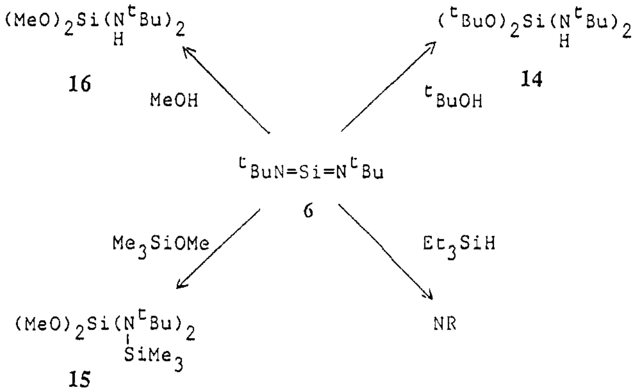


Figure 6. UV–visible absorption spectrum of **6** in a 3-methylpentane glass at 77 K.

Scheme III. Trapping Reactions of *N,N'*-Di-*tert*-butylsilanediimine (**6**)



The calculated IR and UV-vis spectra for dimethyldiazosilane agree well with the spectra observed for **7**. INDO/S calculations at MNDO-optimized geometry predicted a UV transition of intermediate strength at 333 nm and a weaker band at 306 nm in addition to a forbidden transition at 1042 nm (Table I). These values are in reasonable agreement with the observed absorption at 300 nm; very weak absorption in the visible or near-IR region would not be observable under our conditions. The observed IR band at 2150 cm^{-1} is consistent with the value of 2360 cm^{-1} obtained by MNDO, which is known to overestimate vibrational frequencies by approximately 10%. The calculation yields 2322 cm^{-1} for $Me_2SiN^{15}N$, 2320 cm^{-1} for $Me_2Si^{15}NN$, and 2280 cm^{-1} for $Me_2Si^{15}N^{15}N$. This agrees well with our observation of a doublet at 2150 and 2110 cm^{-1} if both nitrogen atoms of **7** originate in the same azido group, so that doubly labeled **7** is absent. The photochemical mechanism of formation of **7** deserves further study.

C. *N,N'*-Di-*tert*-butylsilanediimine (**6**). Another product from the irradiation of matrix-isolated **3** is characterized by UV absorption bands at 240 and 385 nm. UV and IR spectroscopic evidence and results of chemical trapping experiments (Scheme III) demonstrate conclusively that this is a silicon analogue of carbodiimide, *N,N'*-di-*tert*-butylsilanediimine (**6**). Judging by the chemical trapping experiments, it is formed in approximately 10% yield. This result parallels the recent observation that *N,N'*-bis(trimethylsilyl)silanediimine (**2**) is photochemically generated from 2,2-diazidohexamethyltrisilane (**1**).[9]

Chemical Trapping. Irradiation (254 nm) of **3** in a 3-MP glass containing *tert*-butyl alcohol at 77 K followed by warming to room temperature gave, in addition to the silylene trapping products **9** and **10**, bis(*tert*-butylamino)di-*tert*-butoxysilane (**14**) in 11% yield. This product corresponds to the addition of two molecules of the alcohol to **6**. A similar experiment with Me_3SiOMe gave bis(*tert*-butyltrimethylsilylamino)dimethoxysilane (**15**), and the irradiation of **3** in an argon matrix sandwiched between layers of argon doped with methanol gave bis(*tert*-butylamino)dimethoxysilane (**16**). As expected, **6** did not react with triethylsilane.

UV-vis Spectrum. The pale yellow silanediimine exhibited two absorption maxima in its UV-vis spectrum, at 240 and 385 nm, in an approximately 5:1 intensity ratio (Figure 6). This was different from the UV–vis spectrum of **2**, where one strong transition at 324 nm was observed.[9] Both absorption bands (at 240 and 385 nm) grew in at the same rate when the matrix was irradiated at 254 nm. They also simultaneously decayed when

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[24] A complex between a silicon atom and molecular nitrogen, SiN_2, has been observed. This species exhibits an IR band at 1731 cm^{-1}, which is shifted to 1676 cm^{-1} upon labeling with ^{15}N. See: Lembke, R. R.; Ferrante, R. F.; Weltner, W., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 416.

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the matrix was gently annealed (38 K for Ar and 100 K for 3-MP), providing evidence that both bands belong to the same species. As was observed for **2**,[9] **6** was photostable, and irradiation at 248 or 400 nm produced no change in its spectrum. The calculated (INDO/S at MNDO-optimized geometry) UV–vis spectrum of dimethylsilanediimine (Table I) contained three weak absorption bands in the 310–240-nm region and three bands stronger by an order of magnitude in the 180–170-nm region. It is not clear whether the excessively high excitation energies reflect a shortcoming of the INDO/S method, an error in the MNDO-optimized geometry, or both.

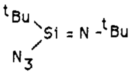
IR Spectrum. As a result of the complexity of the photolysis of **3** and the photostability of the silanediimine, which precluded photobleaching experiments, it was impossible to obtain a definitive IR spectrum of this product. A band was observed at 1654 cm^{-1} which, upon labeling with ^{15}N, was shifted to 1619 cm^{-1}. It is conceivable but unlikely that this band belongs to the Si=N stretching mode. It is at an unexpectedly high frequency and does not exhibit the two expected isotopic shifts corresponding to the incorporation of both one and two ^{15}N labels. This was observed[10,11] for matrix-isolated O=Si=O, whose 1416.5-cm^{-1} antisymmetric stretching frequency is shifted to 1399.2 cm^{-1} by the first ^{18}O substitution and to 1379.8 cm^{-1} by the second, consistent with expectations for a linear molecule. Thus, it seems most likely that the band we observe at 1654 cm^{-1} belongs to an otherwise undetected by-product that contains a C=N moiety.

Molecular Geometry. The geometry of dimethylsilanediimine (as a model for **3**) was optimized using MNDO. The NSiN bond angle is 172° while the CNSi bond angle is 153°. The molecule has an essentially planar W-shaped geometry and a computed carbon-to-carbon dihedral angle of only 3°. The Si=N bond length is predicted to be 151 pm, which is shorter than the length of 157 pm found in a stable silanimine.[26] The small dihedral angle is unusual and calls for a calculation at a better level of approximation. A previous ab initio 3-21G SCF result[25] for the parent HN=Si=NH is similar, however, in that the optimized geometry is planar and trans-bent. The electronic structure computed for the ground state of **6** at the MNDO level contains one perfect allyl-anion-like system of four electrons in three p orbitals, with very high electron density on the nitrogen termini, and one slightly perturbed such system in which the participating orbitals on the N atoms have some s character. It is apparently energetically advantageous to perturb only one of the three-center π systems by a slight in-plane bending of the Si–N–C angle from 180° on both ends than to perturb both π systems by bending each on one end, in two orthogonal planes. In carbodiimide the opposite is true and the dihedral angle is nearly 90°.

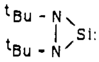
The vibrational modes computed for the molecule at the MNDO level are strange in that there are two nearly uncoupled Si=N vibrations and therefore essentially a single ^{15}N isotopic shift. The MNDO frequencies are 1667 and 1670 cm^{-1} for the $^{14}N_2$, 1632 and 1670 cm^{-1} for the $^{14}N_1{}^{15}N_1$, and 1631 and 1634 cm^{-1} for the $^{15}N_2$ isotopomer of $CH_3N=Si=NCH_3$. Although vibrational coupling through heavier atoms is known to be inefficient, such total uncoupling appears quite unrealistic in view of the results for SiO_2 quoted above. We believe that the agreement with the behavior observed for the 1654-cm^{-1} band is coincidental and that a better level of computation is clearly called for.

D. A Fourth Photoproduct. A small amount of a highly photolabile intermediate with a visible λ_{max} at 725 nm was also observed when **3** was irradiated at 254 nm in inert matrices. This species, when bleached with 700-nm light, was apparently converted to the silanediimine **6**; a slight (3–5%) increase in the UV absorption bands at 240 and 385 nm was observed and the percent yield of the silanediimine trapping product **16** increased from 11 to 14%. It is possible but by no means certain that all of the observed **6** was formed via this intermediate. Because of its extreme photosensitivity and the small quantities present, we were unable to obtain a complete IR spectrum of this species; however, bands were observed at 1606, 1324, and 1181 cm^{-1}.

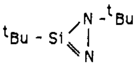
With the data currently available the identity of this species cannot be determined with certainty. Five possible structures will be considered here. These are the di-*tert*-butyl derivatives of azidosilanimine (**17**), 1-siladiaziridine-1,1-diyl (**18**), 1-*H*-2-siladiazirine (**19**), the linear 1,3-dipolar species **20**, and the bent azosilylene **21**.



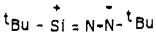
17



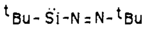
18



19


$^{t}Bu-\overset{+}{Si}=N-\overset{-}{N}-{}^{t}Bu$

20


$^{t}Bu-\ddot{Si}-N=N-{}^{t}Bu$

21

$Me_3Si-N=N-SiMe_3$

22

It has been shown that when **2** is generated from **1**, an azidosilanimine is a spectroscopically observable intermediate that has been trapped and exhibits no absorption in the visible region and a strong UV absorption at 274 nm.[9] Neither these features nor an azido stretching vibration in the IR spectrum were observed for the intermediate with λ_{max} 725 nm and we have therefore ruled out **17** as a possible structure.

Although at present we cannot disinguish in a definitive manner among the remaining four possibilities, we are inclined to favor **18**, based on the following qualitative hints: (i) it is the most straightforward photochemical precursor for **6**, (ii) it is calculated to be relatively stable, (iii) it best fits the expected IR spectrum, and (iv) it best fits the expected UV–vis spectrum.

(*i*) Potential for Photoconversion to 6. The silylene **18** could easily rearrange to **6** by an electrocyclic ring opening. The reaction paths that would have to be followed by the other candidates are more convoluted. The siladiazirine **19** conceivably could be photochemically converted to **6** by shifting the *tert*-butyl from silicon to nitrogen with cleavage of the N–N bond. The conversion of **20** or **21** to **6** could occur via the intermediacy of **19**.

(*ii*) Relative Stability. MNDO structure optimization was performed for the dimethyl analogues of all four structures **18**–**21**. It produced local minima in the ground-state potential surface for **18** (ΔH_f = 48 kcal/mol), **19** (83 kcal/mol), and **21** (46 kcal/mol). The linear structure **20** collapsed to **21** and will not be considered further. The antiaromatic ring structures **18** and **19** were relatively unexceptional, with the substituted ring atoms pyramidalized. A previous ab initio 3-21G SCF optimization for the parent ring system of **18**, with hydrogens replacing methyls, surprisingly reported a far lower triplet than lowest singlet energy.[25] A similar result was reported for MNDO.[25] In our hands, the MNDO optimized triplet energy lies 32 kcal/mol above that of the optimized singlet, and we have excluded the triplet from further consideration. A previous 3-21G SCF optimization[25] for the parent of **19** failed to produce a bound species.

In the MNDO-optimized structure **21** (Figure 7), the lone pair of the nitrogen atom adjacent to silicon was lined up with the empty 3p orbital of the latter, and the π-symmetry 2p orbitals of the azo group were lined up with the lone pair of the latter, permitting delocalization in the sense of formula **20**. This was accomplished by twisting the C–Si bond strongly out of the SiNNC plane. However, the bond between the two nitrogens was clearly double (121 pm) and the Si–N bond not much shorter than single (172 pm), so that the structure **21** is a much better representation of the bonding conditions than **20**. A similar structure was obtained in an ab initio 3-21G SCF optimization[25] of the geometry of the parent molecule, HSiN=NH.

(*iii*) The IR Spectrum. Qualitatively, it would appear that the 1606-cm^{-1} vibration would be best accommodated by structure **21**, where it could be assigned to the N=N stretch. In the other structures, an intense band might not be expected at this frequency at first sight. However, the structures are all unusual and there is not much precedent for an empirical analysis.

A better, though still imperfect, guide is offered by the frequencies calculated by the MNDO method. Considering that they

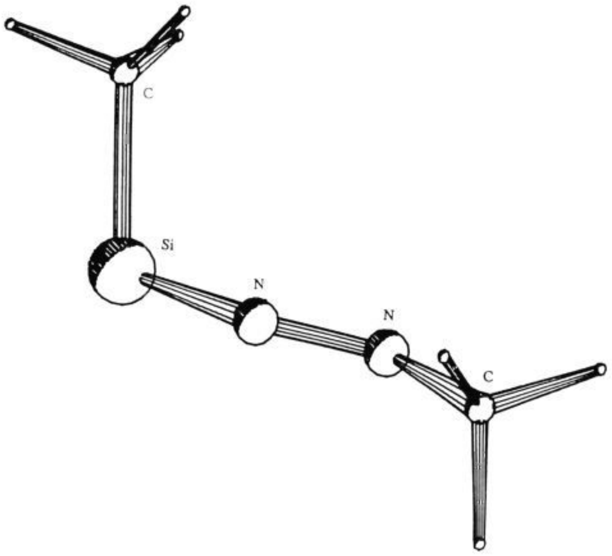


Figure 7. MNDO optimized structure of methylazo(methyl)silylene (cf **21**).

usually are about 10% too high, they are quite compatible with **18** (calculated frequencies: 1600, 1695 cm^{-1}, both fairly intense) and argue against the structure **19** (no calculated vibrations between 1577 and 3212 cm^{-1}). They predict that **21** should have an intense 2181-cm^{-1} vibration of the type characteristic for cumulenes, and otherwise none between 1499 and 3251 cm^{-1}. This is not compatible with our observations for the 725-nm species.

(iv) The UV-vis Spectrum. This might well be more valuable for a structure assignment than the normally far more information-rich IR spectrum. This is due as much to the presence of a highly unusual low-energy transition in the visible spectrum as it is to the very fragmentary nature of the available IR spectrum. Qualitative considerations do not distinguish between the possible candidates. Both **18** and **19** could exhibit an absorption maximum at 725 nm since they are "antiaromatic", with four π electrons in a three-membered ring. When one recalls the 784-nm absorption peak[27] of bis(trimethylsilyl)diimide (**22**), it is clear that **20** or **21** could conceivably also be responsible for the long wavelength absorption.

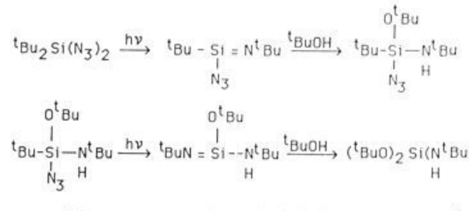
To obtain better guidance, we have performed INDO/S calculations of electronic excitation energies and intensities at the MNDO optimized geometries. In order to calibrate the method, we have first calculated the spectrum of **22**. Its experimental $n\pi^*$ transition energy of 12 750 cm^{-1} is underestimated by 5000 cm^{-1} and no further transitions are predicted up to very high energies, in agreement with experiment (Table I). When we recall the systematic error of 3000 cm^{-1} for most dialkylsilylenes[17c] and the 6000-cm^{-1} error for **4**, it becomes obvious that the MNDO–INDO/S combination of methods represents only a very crude guide to the UV–visible spectra of silicon compounds with unusual structure. It is clear that absolute errors of several thousand cm^{-1} in the transition energy must be expected. In particular, the energies of the $n\pi^*$ states tend to be underestimated severely. Only the general patterns in the spectra rather than the details are likely to be predicted correctly.

The results for **18**, **19**, and **21** are collected in Table I. Relatively low-energy excitations were calculated for all three structures as anticipated on intuitive grounds. Once again, the agreement is best for **18**, where the weak observed band at 13 800 cm^{-1} can be assigned to the first forbidden transition, calculated 4000 cm^{-1} too low. The other forbidden transitions at higher energies could be well covered up by the absorptions due to other species present in our matrices. The assignment to **19** is less likely since it requires that the error in the calculated first excitation energy be 4000 cm^{-1} in the opposite direction, which would be unusual. The assignment to **21** is least likely since the very much stronger transition 6000 cm^{-1} above the first one should be definitely recognizable in the spectrum.

Although all four arguments point to the unusual silylene **18** as the correct structure for the 725-nm product, additional experiments and better quality calculations are clearly needed before an assignment can be made with confidence.

E. Solution Photolysis of Di-*tert*-butyldiazidosilane. As has been shown, photolysis of matrix-isolated **3** proceeds toward the silylene **4** as the predominant pathway, with only small amounts of the products arising from the migration of the alkyl groups being observed. However, in solution at 25 °C the product ratio is reversed, with migration of *tert*-butyl groups predominating.

Photolysis of **3** was carried out in pentane at ambient temperature with a 254-nm light source; both triethylsilane and *tert*-butyl alcohol were employed as trapping reagents. Irradiation of **3** with *t*-BuOH led to the formation of **14** and **9** in 80 and 10% yields, respectively. The alkoxysilane **9** is believed to be the product of insertion of **2** into the O–H bond of *t*-BuOH, and **14** arises from the formal addition of two molecules of alcohol to **6**, although in this case the trapping undoubtedly occurs sequentially via an azidosilanimine intermediate, **17** (eq 2).[9] Irradiation under similar conditions, except using triethylsilane as a trapping reagent, gave **8** as the only volatile product in 8% yield. This is believed to result from the insertion of **4** into the Si–H bond of Et_3SiH.



$$ {}^tBu_2Si(N_3)_2 \xrightarrow{h\nu} {}^tBu-\underset{N_3}{Si}=N^tBu \xrightarrow{^tBuOH} {}^tBu-\overset{O^tBu}{\underset{N_3}{Si}}-\underset{H}{N}{}^tBu \qquad (2)$$

$$ {}^tBu-\overset{O^tBu}{\underset{N_3}{Si}}-\underset{H}{N}{}^tBu \xrightarrow{h\nu} {}^tBuN=\overset{O^tBu}{Si}{-}{-}\underset{H}{N}{}^tBu \xrightarrow{^tBuOH} ({}^tBuO)_2Si(\underset{H}{N}{}^tBu)_2 $$

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry nitrogen or argon. Solvents were dried using standard techniques and glassware was baked at 120 °C for several hours prior to use. Methods for the preparation of dimethoxydichlorosilane,[28] di-*tert*-butoxydichlorosilane,[29] and *tert*-butyltrimethylsilylamine[30] have been previously described. ^1H NMR spectra were recorded on a Bruker WP-270 spectrometer, ^{13}C NMR spectra were obtained on a JEOL FX-200. A Bruker AM-500 spectrometer was employed for ^2H NMR spectroscopy. All spectra were recorded at ambient temperature and chemical shifts are reported relative to an internal standard of tetramethylsilane.

Mass spectrometry and exact mass determinations were performed on a Kratos MS-80 mass spectrometer operating at an ionizing voltage of 30 eV. A Kratos MS-25 equipped with a Carlo Erba gas chromatograph was employed for GC/MS. The gas chromatograph was fitted with a 30 m × 0.36 mm i.d. fused silica capillary column coated with 5% phenylmethylsilicone.

A Hewlett-Packard 5890 gas chromatograph with a flame ionization detector and a 10 m × 0.56 mm i.d. Megabore column coated with 5% phenylmethylsilicone was used for analytical gas chromatography. Hexadecane was used as an internal standard and, where possible, authentic samples of the compounds of interest were used to determine relative response factors; if an insufficient amount of sample was available, structurally similar model compounds were employed. Preparative gas chromatography was performed on a Gow Mac Model 550P gas chromatograph using a thermal conductivity detector and helium as the carrier gas. Normally, a 6 ft × 0.25 in. column packed with 5% SE-30 adsorbed on Chromosorb-W was used. Elemental analyses were performed by Galbraith Laboratories Inc.

Argon Matrix-Isolation Spectroscopy. Argon matrices were prepared on CsI windows attached to the cold tip of an Air Products CS-202 Displex closed-cycle helium cryostat with indium gaskets. The shroud of the cryostat was fitted with a pair of high-quality CsI windows for spectroscopic measurements and one Suprasil window to facilitate photolyses. Standard vapor mixing techniques were used, and in all cases

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the ratio of argon to diazide was approximately 1000:1. Deposition rates were about 0.5 mmol/min. The argon deposition temperature was maintained at 26–28 K. Irradiations were performed with a Lambda Physik excimer laser with a KrF gas mixture. Photobleaching experiments were carried out with an ILC Technologies high-pressure xenon lamp equipped with appropriate cutoff and/or broadband interference filters. All UV–vis spectra were recorded on a Cary 17 spectrophotometer interfaced to a PDP-11/23 computer, and the IR spectra were recorded on a Nicolet 6000 series Fourier-transform spectrometer.

Hydrocarbon Glass Experiments. All spectroscopic and chemical trapping experiments performed in 3-methylpentane glass at 77 K employed a cuvette constructed from Suprasil glass measuring 3 × 1 × 1 cm. Attached to the cuvette was a stem with a high-vacuum stopcock and an O-ring joint. The cuvette was suspended in a liquid nitrogen filled quartz Dewar equipped with Suprasil windows for spectroscopic measurements. UV-visible spectra were obtained on a Perkin-Elmer Model 3840 Lambda Array spectrophotometer connected to a PE Series 7000 computer.

In a typical experiment, **3** (5–15 mg) was dissolved in 3-methylpentane (5 mL) and, unless otherwise noted, hexadecane (1 mg) was added as an internal standard for analytical gas chromatography. In chemical trapping experiments 50 mg of the desired reagent was added to the solution; for spectroscopic measurements no trapping reagents were employed. The cuvette was charged with 4 mL of the solution and the remainder was reserved for comparison following the photolysis. The sample was thoroughly degassed at 5 × 10^{-6} torr prior to irradiation.

A Rayonet Model RPR-100 photoreactor equipped with low-pressure mercury lamps was employed for photolyses at 254 nm. All other photolysis were performed with an Oriel illuminator fitted with a 200-W high-pressure xenon lamp. A variety of Schott glass cutoff filters and Balzer broadband interference filters were employed in the photochemical bleaching experiments.

Solution Photolyses. Photochemical experiments in solution at ambient temperature were conducted using a Rayonet Model RPR-100 photochemical reactor equipped with low-pressure mercury lamps. Normally a sample of **3** (20–30 mg), hexadecane (1 mg), and the desired trapping reagent (50–100 mg) were dissolved in deolefinated pentane (11 mL) and the solution was placed in a quartz tube equipped with a Schlenk-type side arm to permit evacuation. The total volume of this photolysis cell was approximately 10 mL. Prior to irradiation the cell and its contents were freeze–pump–thaw degassed (5 cycles, 5 × 10^{-6} torr).

Preparation of Di-*tert*-butyldiazidosilane (3). Di-*tert*-butyldichlorosilane (Petrarch, 5.00 g, 23.4 mmol) was dissolved in acetonitrile (25 mL). Sodium azide (Fluka, 3.8 g, 58.5 mmol) was added to the solution and the formation of sodium chloride was immediately obvious. Stirring at room temperature was continued for 3 h, diethyl ether (25 mL) was added, and the sodium chloride and excess sodium azide were removed by filtration. Removal of the solvent and distillation at reduced pressure [64 °C (0.1 torr)] afforded di-*tert*-butyldiazidosilane (**3**) as a colorless, mobile liquid, yield 4.93 g (93%): ^{1}H NMR (C_6D_6) δ 0.95 (s); mass spectrum *m/e* (%) 226 (11), 169 (44), 127 (100). Exact mass determination: Calcd for $C_8H_{18}N_6Si$: 226.1362, measured 226.1362. Anal. Calcd for $C_8H_{18}N_6Si$: C, 42.45; H, 8.01; N, 37.13. Found: C, 42.77; H, 8.27; N, 36.19.

Synthesis of Perdeuteriated Di-*tert*-butyldiazidosilane (3-d_{18}). *tert*-Butyllithium-d_9 was prepared using a modification of a literature procedure.[31] A 100-mL flask, the inner surface of which had been thoroughly scratched by a stirred suspension of silicon carbide in water, was charged with pentane (50 mL) and lithium dispersion containing 2% sodium (Aldrich, 2.5 g, 362 mmol). 2-Chloro-2-methylpropane-d_9 (Aldrich, 5.00 g, 49.5 mmol) was dissolved in pentane (15 mL) and added to the refluxing lithium slurry in a very slow dropwise manner. The addition required 22 h and after completion the mixture was stirred at reflux for an additional 8 h. The reaction mixture was then cooled and the lithium chloride and excess lithium metal were removed by filtration under an inert atmosphere. The solution was analyzed by the Gilman double titration method[32] indicating a 45% yield of the desired lithium reagent.

Dichlorosilane (Petrarch, 1.2 g, 11.9 mmol) was condensed at −76 °C and dissolved in pentane (100 mL) cooled to −76 °C. The deuterated *tert*-butyllithium was slowly added to the silane. The formation of lithium salts was immediately evident. The addition required 3 h, after which the temperature of the milky white reaction mixture was raised to room temperature and stirring was continued an additional hour. The salts were removed by filtration under nitrogen and the pentane was distilled. GC analysis of the residue revealed a >9:1 ratio of the desired di-*tert*-butylsilane-d_{18} to *tert*-butylchlorosilane-d_9. The silane proved to be sensitive to moisture and bulb-to-bulb distillation gave 1.70 g (88%) of product, which was used without further purification.

Di-*tert*-butylsilane-d_{18} was converted to the corresponding dichloride in CCl_4.[33] The silane (1.65 g, 10.2 mmol) was dissolved in carbon tetrachloride (25 mL) and $PdCl_2$ (10 mol %) was added. The mixture was stirred at reflux for 3 days, after which the $PdCl_2$ and a fine black powder were removed by filtration. Di-*tert*-butyldichlorosilane-d_{18} was purified by bulb-to-bulb distillation and was obtained in near-quantitative yield: 2.28 g (98%).

In a manner similar to that described above for the preparation of **3**, di-*tert*-butyldichlorosilane-d_{18} (0.5 g, 2 mmol) was treated with sodium azide (0.3 g, 5 mmol) in acetonitrile. Removal of the salts and solvent left **3**-d_{18} (0.5 g), which was purified by preparative GC prior to use. ^{2}H NMR (C_6H_{12}) δ 1.19 (s).

Photolysis of 3 in 3-MP Glass with Triethylsilane. Irradiation of a sample of **3** in 3-MP glass at 77 K with triethylsilane as a trapping reagent for 2 h resulted in consumption of 65% of the starting material. One new product, 1,1,1-triethyl-2,2-di-*tert*-butyldisilane (**8**), was formed in 22% yield. The sample was concentrated in vacuo and **8** was isolated by preparative GC: ^{1}H NMR (C_6D_6) δ 3.68 (s, 1 H), 1.15 (s, 18 H), 1.05 (t, 9 H), 0.78 (q, 6 H); mass spectrum *m/e* (%) 258 (8), 202 (43), 201 (32), 115 (100). When Et_3SiD was employed as the trapping reagent, the adduct **8**-d_1 was obtained in 19% yield: mass spectrum *m/e* (%), 259 (12), 203 (20), 202 (18), 115 (93).

Photolysis of 1 in 3-MP Glass with *tert*-Butyl Alcohol. The sample was cooled to 77 K, irradiated for 30 min and allowed to warm to room temperature. This cycle was repeated five times; analysis showed that 86% of **3** had been depleted. A product with capillary GC retention times and mass spectral characteristics identical with those of bis(*tert*-butylamino)di-*tert*-butoxysilane (**14**) was found in 11% yield. Also observed were di-*tert*-butyl-*tert*-butoxysilane (**9**, 6%) and 1,1,2,2-tetra-*tert*-butyl-1-*tert*-butoxydisilane (**10**, 5%). The structure of the disilane **10** was assigned on the basis of its mass spectrum: *m/e* (%) 358 (5), 343 (8), 301 (28), 273 (15), 258 (38). The spectroscopic properties and GC retention times of **9** were identical with those of an authentic sample.

Photolysis of 3 in 3-MP Glass with Me_3SiOMe. A sample of **3** in 3-MP was prepared as described above with trimethylmethoxysilane added as a trapping reagent. Following irradiation the solution was concentrated and analyzed by GC/MS. The two major products observed were **11** and **15** formed in 21 and 9% yields, respectively. Compound **11**: mass spectrum *m/e* (%) 246 (1), 231 (10), 189 (92), 89 (100). Compound **15**: mass spectrum *m/e* (%), 363 ($M^+ - CH_3$, 14), 307 (8), 259 (70).

Reaction of 5 with 2-Propanol. A sample of **3** in 3-MP was prepared in a manner analogous to that described above. The solution was cooled to 77 K, irradiated at 254 nm for 30 min, photobleached with the output of an unfiltered high-pressure xenon lamp and warmed to room temperature. This cycle was repeated until all of the diazide was consumed. 2-Propanol (0.5 mL) was transferred under vacuum to the cell containing the photolysate and the mixture was vigorously shaken and warmed to reflux for several hours. Di-*tert*-butylisopropoxysilane (**13**) was formed in 85% yield. It exhibited capillary GC retention times and a mass spectral fragmentation pattern that were identical with those observed for an authentic sample: mass spectrum *m/e* (%) 202 (3), 145 (40). This experiment was repeated with 2-propanol-*O*-*d*: mass spectrum *m/e* (%) 203 (5), 146 (21), 145 (18).

Isolation of 1-*tert*-Butyl-2,2-dimethyl-1-silacyclopropane (5). A sample of **3** was prepared and irradiated as above. Once the starting material had been exhausted the 3-MP was removed at low temperature in vacuo [−45 °C (5 × 10^{-5} torr)]. For the NMR experiment the silirane was vacuum transferred at room temperature to an NMR tube: ^{1}H NMR (C_6D_6) δ 3.72 (m, 1 H), 1.20 (s, 3 H), 1.15 (s, 3 H), 1.03 (s, 9 H), 0.54 (m, 2 H). For mass spectrometric measurements **5** was vacuum transferred to a specially drawn glass capillary attached directly to the high-vacuum line: mass spectrum *m/e* (%) 85 ($M^+ - C_4H_9$, 100).

Synthesis of Di-*tert*-butyl-*tert*-butoxysilane (9). Di-*tert*-butylchlorosilane (Aldrich, 5.0 g, 28 mmol) was dissolved in THF (200 mL) and to this solution potassium *tert*-butoxide (3.2 g, 28 mmol) in THF (25 mL) was added. After refluxing overnight the salts and solvent were removed leaving **9** as a colorless oil: yield 4.66 g (93%) in greater than 95% purity; ^{1}H NMR (C_6D_6) δ 4.35 (s, 1 H), 1.22 (s, 9 H), 1.07 (s, 18 H); mass spectrum *m/e* (%) 216 (4), 201 (8), 159 (20), 103 (68), 75 (100). Exact mass determination: calcd for $C_{12}H_{28}OSi$, 216.1909; measured, 216.1902.

Synthesis of Di-*tert*-butylmethoxysilane (12). Following a modification of a procedure reported by Doyle and West[34] di-*tert*-butylchloro-

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silane (5.0 g, 28 mmol) was dissolved in ether (200 mL). Triethylamine (5.7 g, 56 mmol) and methanol (1.8 g, 56 mmol) in ether (25 mL) were added in a dropwise manner to the chlorosilane solution. After stirring for 12 h the salts and solvent were removed leaving **12** as a colorless oil: yield 4.7 g (97%); ^{1}H NMR (C_6D_6) δ 4.16 (s, 1 H), 3.45 (s, 3 H), 1.04 (s, 18 H); mass spectrum *m/e* (%) 174 (13), 117 (46), 89 (100). Exact mass determination: calcd for $C_9H_{22}OSi$, 174.1440, measured, 174.1423.

Synthesis of Bis(*tert*-butylamino)di-*tert*-butoxysilane (14). To a solution of *tert*-butylamine (30.9 g, 422 mmol) and triethylamine (42.7 g, 422 mmol) in diethyl ether (300 mL) was added di-*tert*-butoxydichlorosilane (15.0 g, 70.3 mmol). After addition was complete, the mixture was warmed to reflux and stirred overnight. Removal of the salts by filtration and stripping of the solvent and excess amines by rotary evaporation afforded di-*tert*-butoxy-*tert*-butylaminochlorosilane, which was further purified by distillation at reduced pressure [56 °C (0.1 torr)]: yield 18.2 g (92%) as a colorless liquid; ^{1}H NMR (C_6D_6) δ 1.38 (s, 18 H), 1.20 (s, 9 H); mass spectrum *m/e* (%) 266 (21, $M^+ - CH_3$), 210 (12), 154 (47). Exact mass determination (for $M^+ - CH_3$): calcd for $C_{11}H_{25}ClNO_2Si$, 266.1343; measured, 266.1338.

Further treatment of the chlorosilane with *tert*-butylamine failed to give the desired product. It was necessary to use the corresponding lithium amide. *tert*-Butylamine (0.52 g, 7.09 mmol) in ethyl ether (25 mL) was treated with *n*-BuLi (2.5 M in hexane, 2.8 mL) to give lithium *tert*-butylamide. The amide solution was added to the chlorosilane prepared above (2.00 g, 7.09 mmol) in ether (25 mL); after approximately 1 h a precipitate began to form. The solution was allowed to stir overnight. Removal of the solvent and salts afforded **14** in 95% purity (2.10 g, 93%). Further purification was effected by preparative GC: ^{1}H NMR (C_6D_6) δ 1.39 (s, 18 H), 1.30 (s, 18 H), 0.76 (br s, 2 H); mass spectrum *m/e* (%) 318 (1), 303 (100), 287 (4), 247 (42). Exact mass determination: calcd for $C_{16}H_{38}N_2O_2Si$, 318.2702; measured, 318.2703. Anal. calcd for $C_{16}H_{38}N_2O_2Si$: C, 60.32; N, 12.02; H, 8.79. Found: C, 60.11; N, 11.98; H, 9.48.

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Electronic Structure of Dicyanobarrelenes Studied by Integration of Photoelectron Spectroscopy, Cyclic Voltammetry, Electronic Spectroscopy, Molecular Orbital Theory, and Composite Molecule Theory

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Abstract: The photoelectron spectra, electronic absorption spectra, and reduction potentials of 2,3-dicyanobarrelene (DCB) and its 5,6,7,8-tetramethyl derivative were measured. On the basis of these experimental data, the electronic and orbital structure of these compounds in the ground and electronically excited states was discussed from the standpoints of MO theory and composite molecule (molecules-in-molecule) theory, the group orbital concept being adopted as the common basis throughout the discussion. Special attention was paid to intramolecular 3D orbital interactions. It was established that the first LU-π-MO of each compound is almost completely localized on the maleonitrile (MN) type moiety from the reduction potential data. The first singlet–singlet electronic transition of each compound is an almost pure LUMO ← HOMO transition with the character of an intramolecular charge-transfer (CT) transition accompanied by the electron migration from the cyclohexadiene (CHD) type moiety b_2 HO-π-O to the MN type group a_2 LU-π-O and provides a typical example of an unusual type of CT transition, a CT transition between the orbitals CT interaction forbidden. From the photoelectron and electronic absorption spectral standpoints independently the mixing coefficients for the component basis HO-π-Os of the CHD-like moiety and the MN-like one were evaluated for each compound consistently with each other. The mutual consistency of the results of the mixing coefficients estimated from the two standpoints independently substantiates strongly the validity of the intensity-borrowing model that the first electronic transition of each compound owes its intensity to the allowed LU-π-O ← HO-π-O type electronic transition of the MN-like moiety. This is also supported by a kind of composite molecule type approach. This is the first experimental substantiation of intensity borrowing by intramolecular CT transitions from local excitations.

The concept of orbital interaction is now recognized to be fundamentally important in various fields of chemistry, for example, physical organic, physical inorganic, and theoretical chemistry, and even for materials science. Among orbital interactions three-dimensional (3D) intramolecular orbital interactions between equivalent or inequivalent orbitals are particularly attractive. In order to study these types of interactions, 2,3-dicyanobarrelene (bicyclo[2.2.2]octa-2,5,7-triene-2,3-dicarbonitrile, DCB) and its 5,6,7,8-tetramethyl derivative (TMDCB) have been adopted as model systems in this paper (Figure 1). The reasons why these systems are chosen are as follows: First, as these compounds are simple-structured and of rather high symmetry, that is, are of C_{2v} symmetry, a straightforward clear-cut discussion is expected to be possible in the analysis of 3D orbital interactions. Second, each compound is regarded to contain two electron-donor (D) type groups and one electron-acceptor (A) type one in the same molecular framework in a unique configuration, which is almost inaccessible in intermolecular cases. In addition, generally

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