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Multiply Bonded Silicon: Matrix Isolation and Chemical Trapping of Products of Pyrolysis and Photolysis of Triazidophenylsilane

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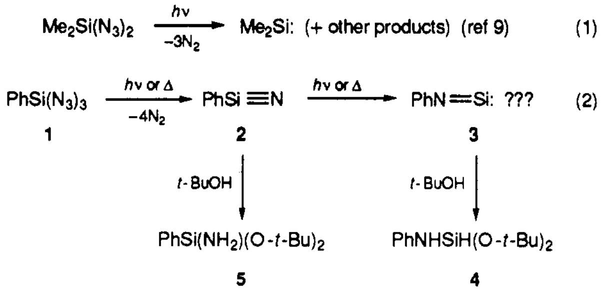
Triazidophenylsilane (**1**) yields phenyl isosilacyanide (**3**) upon irradiation in matrix isolation and by pyrolysis followed by trapping in noble gas matrix. Annealing from 12 to 15 K causes significant changes in the IR spectrum of photochemically produced **3**, attributed to the release of hydrostatic pressure in the matrix. The matrix reaction of pyrolytically produced **3** with *t*-BuOH to yield an independently synthesized trapping adduct **4** has been followed spectrally. An aligned sample of **3** was produced by photoselection and polarized IR spectra were recorded. The UV and IR absorption spectra of **3** have been interpreted and agree well with *ab initio* and semiempirical calculations. In contrast, the intermediacy of benzenesilonitrile (**2**), a representative of a so far unknown class of species with a –Si≡N triple bond, in the photofragmentation of matrix-isolated **1**, is merely strongly suggested but not proven by trapping of the photoproducts from matrix-isolated **1** with *t*-BuOH to yield the adduct **5** in addition to **4**. The silonitrile **2** did not accumulate in the matrix in amounts sufficient for spectral characterization.

Introduction

Ever since the isolation of stable compounds containing Si=C[2] and Si=Si[3] double bonds there has been an explosion of interest in the preparation and characterization of compounds of multiply bonded silicon (for reviews, see refs 4 and 5). Compounds of triply bonded silicon appear to represent the next frontier, in spite of the fact that the first spectroscopic observation of a silicon compound that can be formulated as triply bonded in one of its formal valence-bond structures, the diatomic $^\bullet$Si≡N: ↔ :Si=N$^\bullet$, now is three-quarters of a century old.[6] A second such compound, the triatomic $^-$Si≡N$^+$H ↔ :Si=NH, was first observed in matrix isolation a quarter of a century ago.[7] Still, to this date no compounds of triply bonded silicon appear to have been isolated.[8]

Since the irradiation of a matrix-isolated geminal diazidosilane, diazidodimethylsilane, produced dimethylsilylene and molecular nitrogen[9] (eq 1), it was of interest to irradiate a matrix-isolated geminal triazide or to subject it to vacuum pyrolysis followed by trapping in a cold inert matrix in the hope that a silicon analogue of a nitrile or an isocyanide would result and could be observed directly and perhaps also trapped chemically with *t*-BuOH (eq 2).



$$Me_2Si(N_3)_2 \xrightarrow[-3N_2]{h\nu} Me_2Si\text{: (+ other products) (ref 9)} \quad (1)$$

$$\begin{tikzcd} \underset{\mathbf{1}}{PhSi(N_3)_3} \arrow[r, "h\nu \text{ or } \Delta", "-4N_2"'] & \underset{\mathbf{2}}{PhSi\equiv N} \arrow[r, "h\nu \text{ or } \Delta"] \arrow[d, "t\text{-BuOH}"'] & \underset{\mathbf{3}}{PhN{=}Si\text{: ???}} \arrow[d, "t\text{-BuOH}"'] \\ & \underset{\mathbf{5}}{PhSi(NH_2)(O\text{-}t\text{-Bu})_2} & \underset{\mathbf{4}}{PhNHSiH(O\text{-}t\text{-Bu})_2} \end{tikzcd} \quad (2)$$

Both of these products, **2** and **3**, would represent structures about which little is known from direct observation. According to *ab initio* calculations,[7e,10] the parent hydrogen isosilacyanide, HN=Si:, contains a divalent silicon atom and an :Si=N double bond and is far more stable than the so far hypothetical isomeric hydrogen silacyanide, HSi≡N:, computed to contain an Si≡N: triple bond with a similar force constant. To our knowledge, no compound with this latter type of bond has ever been observed. Similar *ab initio* results have been obtained

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more recently[11] for the relative stabilities of R—N=Si: and R—Si≡N:, R = CH_3 and C_6H_5.

At the time of our preliminary report[12] of evidence for matrix-isolated benzenesilonitrile (**2**, named by analogy to arenecarbonitriles) and phenyl isosilacyanide (**3**, named by analogy to aryl isocyanides), Bock and Dammel[13] reported the photoelectron spectrum of the pyrolyzate of **1** and assigned the structure as **3** by comparison with orbital energies computed by the MNDO method for **2** and **3**.

We now present a full report of the results obtained in our laboratory for the photolysis and pyrolysis of **1**. We have obtained quite complete and unequivocal spectroscopic and chemical trapping evidence for the isosilacyanide **3**, confirming Bock and Dammel's original structure assignment[13] for the pyrolysis product. In contrast, in spite of years of intermittent intensive effort, in which we succeeded in obtaining reasonably but not completely convincing chemical trapping evidence for the intermediate formation of the silonitrile **2** in the matrix photolysis, we have never been able to accumulate enough **2** in a matrix to obtain an unequivocal spectroscopic characterization.

Experimental Part

Synthesis. Triazidophenylsilane (1) was prepared by a published procedure.[14] ^{15}N-labeled material was prepared in a similar fashion from $Na^{15}NNN$. Freshly distilled $PhSiCl_3$ (0.1 g, 1.5 mmol) was slowly added to a stirred suspension of sodium azide (0.1 g, 0.48 mmol) in dry acetonitrile at 0 °C. The reaction was monitored using GC until completion. The azide was purified by preparative GC.

***N*-(Di-*tert*-butoxysilyl)aniline, $C_6H_5NHSiH(O\text{-}t\text{-}Bu)_2$ (4).** This was prepared by adding $SiHCl_3$ (27 g, 0.2 mol) in benzene (50 mL) to aniline (75 g, 0.81 mol) in benzene (150 mL) at 0 °C under argon and heating the product with *t*-BuOH (30 g, 0.4 mol) in benzene (60 mL). Distillation (114–120 °C/0.5 Torr) yielded **4** of 90% purity (41.7 g, 78%, moisture sensitive and easily decomposing). IR (neat): 995 (w), 1023 (m), 1052/1063 (Si–O–C, vs), 1198 (Si–NH, m), 2180 (Si–H, m), 690 (Ph, m), 750 (Ph, m), 1367/1388 (CMe, s), 3380/3410 (SiN–H, w broad) cm^{-1}. UV, λ_{max} [nm] (ϵ [M^{-1} cm^{-1}]): 280 (681, fine structure), 228 (3640), 192 (12 050) in the gas phase. ^1H NMR ($CDCl_3$): δ 1.41 (s, 18H, *t*-Bu), 3.77 (s, 1H, NH), 4.86 (d, $J = 1.8$ Hz, 1H, SiH), 6.75–6.85 (m, 3H, Ph), 7.15–7.23 (m, 2H, Ph). EIMS: *m/z* 267 (M, 40), 252 (M – Me, 18), 211 (M – C_4H_8, 16), 196 (M – Me – C_4H_8, 22), 155 (M – $2C_4H_8$, 100), 138 (155 – OH, 22), 120 (138 – H_2O, 18), 103 (138 – H_2O – OH, 6), 93 ($PhNH_2^+$, 28), 77 ($C_6H_5^+$, 3), 57 ($C_4H_9^+$, 13). Anal. Calcd for $C_{14}H_{25}NO_2Si$: C, 62.87; H, 9.42. Found: C, 62.71; H, 9.48.

Amino(di-*tert*-butoxy)phenylsilane, $C_6H_5Si(NH_2)(O\text{-}t\text{-}Bu)_2$ (**5**) was prepared from $C_6H_5SiCl_3$ (10.4 g, 50 mmol) in dry THF (50 mL) by adding a slurry of *t*-BuOK (10.5 g, 0.14 mol) in THF (50 mL) and stirring at –70 °C (1 h) and then at 25 °C (2 h) and subsequently treating with $NaNH_2$ (1.88 g, 47 mmol) and stirring at –70 °C (20 min) and at 25 °C (36 h). Distillation (150 °C/0.4 Torr) yielded **5** (7.5 g, 56%). IR (neat): 3485/3409 (NH_2, w, broad), 2976 (*t*-Bu, vs), 2930/2870 (w), 1545 (w), 1430 (s), 1389 (s), 1365 (vs), 1241 (s), 1205 (vs), 1191 (vs), 1121 (s), 1058 (Si–O, vs), 1026 (vs), 999 (vs), 864 (s), 806 (w), 741 (s), 702 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 0.8 (s, broad, 2H, NH_2), 1.33 (s, 18H, *t*-Bu), 7.27 (m, 3H, Ph), 7.92 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 138.3 (ipso-C), 134.8, 129.3, 127.4 (arom C), 73.0 (O–C–), 32.0 (–CH_3). EIMS: *m/z* 267 (M, 14), 252 (M – Me, 16), 196 (M – Me – C_4H_8, 7), 194 (M – Me – C_3H_6O, 11), 138 (M^+ – Me – C_3H_6O – C_4H_8, 100). HRMS (EI): *m/z* (calcd for $C_{14}H_{25}NO_2Si$: 267.16547) 267.16544. This compound remains pure for a few hours at room temperature, but a 3–5% loss is observed in a 24-h period by NMR spectroscopy. We did not attempt to obtain a combustion analysis.

In an alternative synthesis of **5**, $(Me_3Si)_2NLi$ (50 mmol, 1 M solution in THF) was added slowly to a stirred solution of $C_6H_5SiCl_3$ (10.6 g, 50 mmol) in dry THF (40 mL) at 0 °C under argon. The mixture was refluxed for 2 h and the solvent removed and replaced with pentane. The solution was filtered and distilled (99–104 °C/ 1.5 Torr) to yield crude (90% purity) $C_6H_5SiCl_2N(SiMe_3)_2$ (10.8 g, 64%). IR (neat): 3070 (m), 3050 (m), 2980 (sh), 2950 (s), 2897 (m), 1630 (m), 1590 (m), 1407 (m), 1330 (w), 1302 (w), 1252 (s), 1120 (s), 1115 (s), 1025 (w), 995 (sh), 958 (vs), 860 (vs), 845 (sh), 765 (s), 737 (s), 705 (s), 693 (s), 675 (s), 652 (m), 615 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.29 (s, 18H), 7.32–7.85 (m, 5H). EIMS: *m/z* 320 (M – Me, 100), 300 (M – Cl, 4), 284 (M – Me – HCl, 14), 268 (3.1), 231 (5), 218 (8), 212 (7), 192 (15), 181 (8), 169 (95), 146 (50), 130 (14), 119 (7), 69 (17), 58 (10). The crude intermediate (5.2 g, 15 mmol) was stirred at –78 °C in dry THF (30 mL), and a solution of freshly sublimed *t*-BuOK (3.4 g, 30 mmol) in THF (30 mL) was slowly added. The solution was allowed to warm up to 0 °C and then to room temperature with vigorous stirring. The solvent was replaced with pentane and the mixture filtered. Distillation (90–92 °C/1.15 Torr) yielded crude (90% purity) $C_6H_5Si(O\text{-}t\text{-}Bu)_2NHSiMe_3$ (5.8 g, 57%). IR (neat): 3390 (w), 3070 (m), 3050 (m), 2980 (s), 2930 (sh), 2900 (sh), 2870 (sh), 1590 (vw), 1460 (m), 1430 (m), 1389 (m), 1363 (s), 1305 (vw), 1245 (s), 1190–75 (s), 1118 (s), 1055 (vs), 1025 (m), 998 (w), 935 (s), 860 (m), 838 (s), 830 (sh), 820 (sh), 805 (w), 765 (w), 750 (w), 740 (s), 712 (m), 700 (s), 685 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.15 (s, 9H), 1.30 (s, 18H), 7.34–7.81 (m, 5H). EIMS: *m/z* 339 (M, 13), 324 (M – Me, 3), 268 (M – Me – C_4H_8, 5), 252 (2), 212 (268 – C_4H_8, 100), 210 (11), 194 (11), 132 (4), 58 (8), 57 (4). The crude intermediate (3.4 g, 10 mmol) and THF (10 mL) were stirred at room temperature under argon, and dry *t*-BuOH (4.5 g, 50 mmol) was added. The solution was warmed to reflux. When GC analysis indicated that the alcoholysis was two-thirds complete, the product **5** (1.8 g, 60%) was collected in 60% purity by distillation (73–79 °C/1.5 Torr) and purified by preparative GC (15% SF 96, 10′ at 150 °C).

Apparatus. All low-temperature matrix samples were prepared using closed-cycle helium refrigerators: either a 10 K two-stage Displex (Air Products, 202-E) or a 3.7 K three-stage Heliplex (APD Cryogenics). Infrared absorption spectra were measured at 0.5-cm^{-1} resolution using a Nicolet 60-SXR instrument and a IGP-225 polarizer (Cambridge Physical Sciences). All peaks attributed to products and listed in this paper were present reproducibly and even those that appear very weak in the figures at the magnification used were easily distinguishable from noise. UV–visible absorption spectra were recorded on a Varian 2300 spectrometer, and emission spectra were obtained using an SLM Instruments SPF-500C spectrofluorometer.

All photochemical work was performed by irradiation with an excimer laser (Lambda Physik: 308 nm, XeCl; 248 nm, KrF_2; 193 nm, ArF) or a 1000-W Xe-Hg lamp equipped with solution and Corning 7-54 filters, with or without a Glan-Thompson polarizer.

Procedures. In flow pyrolysis experiments the following conditions were used: inert gas flow rate, 0.2–2.0 mL/min, **1** distilled at 26–35 °C, hot zone temperature ~900 °C, and length, 60 mm. Samples used for photolytic work were prepared by slow distillation of the triazide **1** (kept at 24–34 °C, depending on the optical density required) into a stream of noble gas and condensation on an optical window at 4.2 K (Ne), 28 K (Ar, N_2), or 55 K (Xe). The matrix ratio was estimated to always be higher than 1:500.

Samples used in the photolytic trapping experiments were prepared either by passing Ar mixed with *t*-BuOH vapor (2–20%) over a sample of **1** and condensation on a cold window or by successive deposition of sandwiched thin layers of pure Ar, Ar with **1**, pure Ar, Ar with *t*-BuOH, etc., followed by irradiation. For pyrolytic experiments we used separate inlets for simultaneous deposition of pyrolyzed **1** in Ar and of *t*-BuOH, which was

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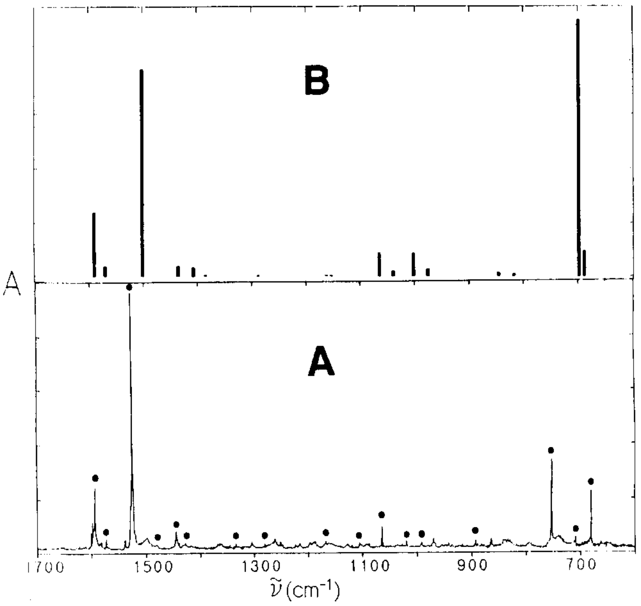

Figure 1. IR spectrum of **3**, the pyrolysis product from **1**, in an argon matrix (12 K). Top: calculated (MP2/6-31G*) IR spectrum of **3** (frequencies scaled by 0.95).

either neat or diluted with Ar, with the same results. The inlets were located at angles of +45 and −45° from the window surface normal in order to minimize any gas-phase reaction of **1** with *t*-BuOH.

Both the irradiated and the pyrolytic samples were examined by IR spectroscopy during gentle annealing, and spectral changes were recorded in the relatively sparse regions of transparency that remained free of interference by the excess *t*-BuOH present. Subsequently, the matrix was coated with excess 3-methylpentane by vapor deposition and warmed to room temperature. The solution was separated from an insoluble coating on the window and subjected to GC–MS analysis (DB-5 capillary column).

Calculations. The IR spectra were calculated at the MP2/6-31G* (analytical) level with the CADPAC program system.[15] The UV spectra were calculated by the INDO/S method,[16] using MP2/6-31G* optimized geometries and about 200 configurations.

Results and Discussion

Synthesis of the Trapping Products. Our choice of the chemical trapping reagent for the anticipated products **2** and **3** was dictated by several considerations. The agent had to be transparent at the wavelengths of irradiation, sufficiently inert to the triazide **1** and yet highly reactive toward **2** and **3** even below 50 K. It had to yield different isolable products from **2** and **3**. After some experimentation, we selected *t*-BuOH. The adducts **4** and **5**, though still somewhat unstable, are much easier to handle than those obtained from lower alcohols. Their synthesis is straightforward. Since the slow decomposition of neat **5** at room temperature made it difficult to obtain a combustion analysis, we secured its structure beyond doubt by synthesizing it in two independent ways.

Pyrolytic Formation of the Isosilacyanide 3. Flow pyrolysis of phenyltriazidosilane (**1**) and [^{15}N]-**1** at around 900 °C followed by trapping on an optical window with excess noble gas produced a new product, characterized by distinct IR (Figure 1) and UV (Figure 2) absorption spectra. The sample showed no detectable emission spectrum in the UV–visible region. The IR spectrum fits the standard pattern for a monosubstituted benzene: intense bands near 690 and 750 cm^{-1}, peaks near 1450, 1500, 1575, and 1600 cm^{-1}, and CH stretching peaks above 3000 cm^{-1}. It corresponds well to expectations for **3** based on an *ab initio* MP2/6-31G* (analytical) calculation (Table I), leaving no unassigned bands of significant intensity. The UV absorption is that expected for a strongly perturbed benzene chromophore and is reasonably compatible with results of an INDO/S calculation for **3** performed at the *ab initio* optimized geometry.

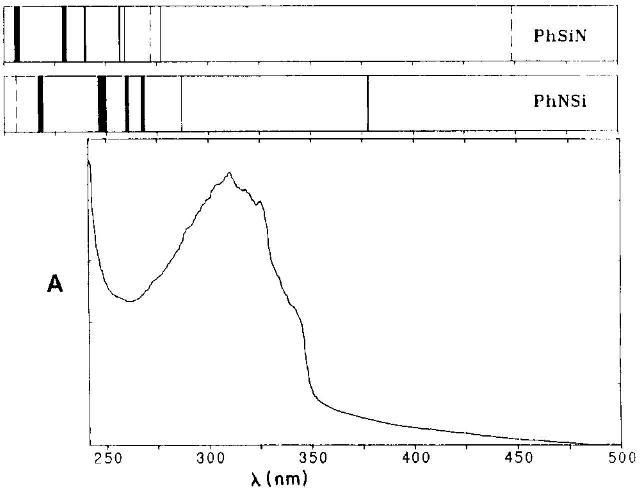

Figure 2. UV absorption of **3**, the pyrolysis product from **1**, in an argon matrix (12 K). Top: INDO/S calculations of the UV spectra of **2** and **3**. The oscillator strength *f* computed from the dipole length formula is shown by the gradation of line thickness. Symmetry-forbidden transitions are not shown (**2**, 552 and 446 nm; **3**, 418, 376, and 215 nm). Key: *f* up to 0.01 (dashed); *f* up to 0.02 (full thin); *f* up to 0.2 (full thicker); *f* up to 0.5 (thick); *f* above 0.5 (very thick).

Conclusive evidence resulted from matrix trapping with *t*-BuOH. Upon gentle annealing of a matrix doped with *t*-BuOH, we observed the disappearance of phenyl isosilacyanide (**3**) absorptions and the concurrent appearance of the peaks of **4** in the IR spectrum. Peaks of the precursor **1** were also present but did not disappear upon annealing. The matrix IR spectrum of **4** was known independently from a measurement on an authentic sample. GC analysis revealed the presence of only one new volatile product, all other GC peaks being at least 1 order of magnitude weaker. The product was identified as **4** by GC–MS comparison with an authentic sample.

The assignment of the structure of the pyrolysis product agrees with the prior attribution by Bock and Dammel[13] and can now be considered confirmed beyond reasonable doubt.

Phenyl isosilacyanide (**3**) spectra obtained from the samples prepared pyrolytically were much weaker than those measured on photolytic samples as described below. A substantial amount of the unreacted precursor **1** was always present in the matrices, regardless of the way in which the samples were prepared. At higher pyrolysis temperatures the amount of unreacted triazide **1** decreased, but so did that of the phenyl isosilacyanide product.

The presence of the remaining triazide **1** was detrimental to the quality of the spectra, since computer subtraction always left unwanted artifacts due to the different condensation conditions used in the pyrolytic and the reference experiments. This also made a direct comparison between the pyrolytic and photolytic experiments somewhat unreliable, especially for weak absorption bands.

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Table I. Vibrations of Phenyl Isosilacyanide (3)

obsd				calcd[a]					
$\tilde{\nu}$ (cm^{-1})				$\tilde{\nu}$ (cm^{-1})					
^{14}N	^{15}N	I[b]	d[c]	^{14}N	^{15}N	I (km/mol)	sym[d]	mode[e]	Wilson no[f]
				115	115	2.4	b_1	CNSi opb	
				122	122	2.0	b_2	CNSi ipb	
				305	300	5.4	b_1	CNSi opb + op ring def	16b
				400	400	0	a_2	op ring def	16a
				407	406	0.6	a_1	ip ring def + s CNSi stretch	6a(1)
472	460	m	–	480	469	12.4	b_2	CNSi ipb + CCN ipb	18b
				480	480	0.6	b_1	op ring def (ring puckering)	4
				533	531	0.03	b_1	CCN opb + CNSi opb	17b
				635	634	0.1	b_2	ip ring def	6b
687		s	+	725	725	8.9	a_1	s CNSi stretch + ip ring def	1(6a)
717		w							
758		s	+	736	736	89.5	b_1	CH opb	11
				821	821	0	a_2	CH opb	10a
				861	861	0.6	b_1	CH opb	10b
841 ?[g]		w	–						
				888	888	0	a_2	CH opb	17a
899		w	+	892	892	1.1	b_1	CH opb	5
997		w		1028	1028	2.2	a_1	ip ring def	12
1023		w		1056	1055	8.0	a_1	ip ring def	20a
1041	1035	w		1095	1089	1.6	a_1	s CNSi stretch + CH ipb	18a
1069		w		1122	1122	8.2	b_2	CH ipb	15
1109		w		1216	1216	0.01	b_2	CH ipb	9b
1175		w	+	1225	1225	0.17	a_1	CH ipb	9a
1285		vw	–	1356	1356	0.07	b_2	CH ipb	3
1335		vw							
1432		w		1457	1457	0.3	b_2	ip ring stretch (Kekulé)	14
1448	1430	m	+	1480	1459	2.9	a_1	as CNSi stretch + CH ipb + ip ring stretch	
1492		w	–	1509	1509	3.4	b_2	ip ring stretch	19b
1530	1514	vs	+	1579	1568	72.2	a_1	as CNSi stretch + ip ring stretch	19a
1575	1574	w	–	1652	1652	3.4	b_2	ip ring stretch	8b
1598		m	+	1673	1673	22.4	a_1	ip ring stretch	8a
3055		vw		3224	3224	2.6	a_1	CH stretch	13
				3232	3232	3.5	b_2	CH stretch	7b
				3241	3241	8.9	a_1	CH stretch	7a
3075		w		3245	3245	14.7	b_2	CH stretch	20b
3079		vw		3252	3252	11.3	a1	CH stretch	2

[a] MP 2/6-31G* (analytical). No scaling. [b] Relative intensity. [c] Sign of linear dichroism (+, $A_Z > A_Y$; –, $A_Z < A_Y$). [d] z, 2-fold symmetry axis, y, in-plane short axis; x, out-of-plane short axis. [e] op = out-of-plane, ip = in-plane, b = bend, s = symmetric, as = asymmetric, def = deformation. [f] Mode number in Wilson notation for monosubstituted benzenes: Wilson, E. B. *Phys. Rev.* 1934, *45*, 706. [g] This band most likely does not belong to 2.

As expected, 3 appears to be extremely reactive and matrix warmup in the absence of trapping agents yields polymeric materials. On the other hand, 3 was completely inert to UV light (193–400 nm), even when high intensity light sources and long exposure times were used.

Photochemical Formation of the Isosilacyanide 3. Irradiation of matrices containing 1 or [^{15}N]-1 with 193- or 248-nm light, or with a high-pressure Xe–Hg lamp, produced samples which gave IR and UV–visible absorption spectra nearly identical to those obtained after pyrolysis, especially in Ne and Xe matrices, in which the IR bands were relatively broad and structureless. Figure 3 shows the IR spectra obtained by irradiation of the natural abundance and ^{15}N-labeled samples. Isotopic splittings were observed for five bands and are reproduced very well by the *ab initio* calculations, in further confirmation of the structural assignment. The spectra of the irradiated matrices showed richer site structure and broader peaks, and it appeared that the matrices were generally less well annealed and showed more aggregation.

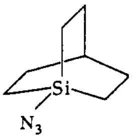
Since the *ab initio* calculations that account very nicely for the IR spectra of 3 also predict rather comparable IR intensities for the CH out-of-plane bends in 2 and 3, it is quite obvious that the latter is not present in the irradiated matrix in significant amounts. However, very weak bands attributed to trace amounts of at least one intermediate containing an azido group were observed by IR. Their presence is not surprising, considering that the loss of four N_2 molecules in eq 1 could hardly be expected to occur in a single photochemical step, but the weakness of their IR bands precluded a thorough characterization. We estimate that these additional products were present in amounts at least 2 orders of magnitude smaller than those of 3. One of the anticipated intermediates of the production of 3 would be 2. We have therefore employed more sensitive spectroscopic tools in the hope of identifying its spectroscopic signature.

Spectral Search for the Silonitrile 2. In contrast to the matrices prepared by pyrolysis, the photolyzed samples exhibited strong red photoluminescence. This emission was easily detectable in all the photolytic samples and none of the pyrolytic samples. It consisted of a weaker broad emission band peaking at 550 nm and a stronger red emission, most likely phosphorescence, with a maximum at 630 nm. The ratio of their intensities varied somewhat from experiment to experiment, and they appear to belong to two different species. The excitation spectra of the two emissions were similar but not identical, with maxima near 280 and 440 nm. The composite origin of the emissions was also clear from bleaching experiments. Long irradiation with intense UV or visible light caused a gradual disappearance of the species responsible for the 550-nm emission band, while the red emission at 630 nm persisted. The triplet nature of one of the excited states was proven by the observation of a very weak EPR triplet signal at $\Delta m = 2$ during irradiation, but not in the dark.

Signals that may have been present in the $\Delta m = 1$ region were too weak to observe.

The UV–visible absorption spectrum of the photolyzed samples also provided evidence for the same minor species. When thick matrices, exhibiting a very high optical density due to 1, were exposed to prolonged irradiation with intense UV light (260–290 nm), we detected a weak new absorption band with a maximum near 440 nm, coincident with the longer-wavelength peak in the excitation spectrum of the red emission. Like the red emission itself, this absorption was never observed in pyrolytically prepared samples. However, it was also observed in irradiated 3-methylpentane glasses containing 1. Our suspicion that the same species is responsible for this absorption and for the red emission is further supported by the observation that even upon very intense irradiation (broad visible output from an argon-ion laser) and long irradiation times, the intensity of this weak absorption did not decrease at all. The amazing photostability of this molecule, and even the lesser photostability of the species responsible for the 550-nm band, argue against the assignment of either one as 2, which could be expected to be rather photolabile.

Clearly, the photochemical preparation of matrix-isolated 3 is less clean than the pyrolytic route, but even in this case, 3 dominates by far in the observed matrix-isolated mixture. Our initial enthusiasm for attempting to unravel the structure of the minor products and to find out whether one of them is 2 was dampened by the accidental observation that an essentially identical double photoluminescence is observed when matrix-isolated 1-azido-1-silabicyclo[2.2.2]octane (6) is irradiated at 248 nm. Neither of the species responsible for the emissions is therefore 2. They may result from deep-seated fragmentations of 1 and 6 or perhaps from similar but crucial minor impurities in our samples of 1 and 6.



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Trapping Search for the Silonitrile 2. All of the spectral results agree that 3 is the dominant species in the irradiated matrices and fail to provide any evidence for the presence of 2 or any other significant photoproduct. However, we were able to obtain evidence for the intermediacy of a species still containing the C–Si–N moiety in the photochemical formation of 3 by chemical trapping with *t*-BuOH: in the presence of *t*-BuOH in the argon matrix, either admixed or sandwiched, exhaustive irradiation and subsequent warming yielded not one but two major volatile products, as revealed by a GC–MS analysis. All other GC peaks were far less intense. The photoproducts responsible for the two strong peaks were identified by comparison of retention times and mass spectra with those of authentic samples. One (~30%) was the already familiar adduct 4, but the major product (~70%) was $C_6H_5Si(NH_2)(O\text{-}t\text{-}Bu)_2$ (5). The irradiation window was coated with a nonvolatile insoluble yellowish residue, presumably of polymeric nature. In the IR measurements on irradiated *t*-BuOH-doped matrices during warmup, only the formation of the peaks of 4 was observed. The peaks of 5 lie in regions obscured by *t*-BuOH.

The ~2:1 preponderance of 5 in the trapping product mixture is most readily rationalized by postulating that the silonitrile 2 is an intermediate in the photoconversion of 1 to 3 in the matrix and that an adjacent molecule of *t*-BuOH is capable of reacting with it even at the very low temperature. The structure of 5 is exactly that expected from the addition of two molecules of the alcohol to the –Si≡N bond.

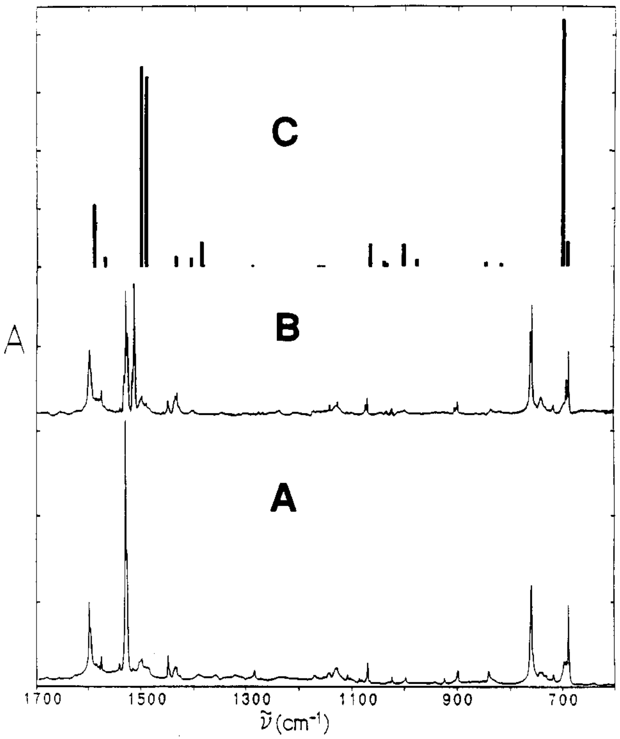

Figure 3. IR spectra. (A) [^{14}N]-3; (B) a mixture of 3 and [^{15}N]-3 obtained by irradiation of [^{15}N]-1 in an argon matrix (12 K); (C) calculated (MP2/6-31G*) for a 1:1 mixture of 3 and [^{15}N]-3 (frequencies scaled by 0.95).

In the absence of such an adjacent molecule of the trapping agent, 2 presumably proceeds on to form 3, either thermally before it loses its initial excess vibrational energy or perhaps photochemically, by absorbing another photon. If the latter is the case, the quantum yield for the photodestruction of 2 and its extinction coefficient would have to be quite high relative to those of 1, at all wavelengths examined, but this could easily be the case. Under such circumstances, 2 would never accumulate in the matrix to a significant extent.

The trapping experiments were repeated dozens of times under a variety of conditions (various rare gases, various concentrations of *t*-BuOH, slow or fast warmup, various layer thickness in a sandwich arrangement in which matrix layers alternately contained 1 in argon, pure argon, *t*-BuOH in argon, pure argon, etc.). An example of specific trapping conditions follows: 3% *t*-BuOH in Ar was deposited from one inlet and 1 in Ar (~1:500) from the other inlet at the same time. The window temperature was 28 K, the flow rate was about 0.1 mmol Ar/min through each inlet, and the deposition time was 30 min. The sample was irradiated at 10 K for 12 h with a low-pressure Hg lamp and the conversion to product was 65% as judged by the IR spectrum, which contained peaks of 1 and 3 in the spectral windows provided by *t*-BuOH. Upon warming to 32 K, the peaks of 3 were gradually replaced by peaks of 4. The matrix was coated with 3-methylpentane and warmed to room temperature. GC–MS analysis (DB-5 capillary column, 2 min at 130 °C, then warmed up at 2 °C/min) showed only two strong peaks with retention times of 6.34 and 8.15 min, identical with those of authentic samples of

5 and **4**, respectively. The mass spectra of the two GC peaks agreed with those of the authentic samples.

The results of all the experiments were the same, except that **4** and **5** were not formed when rather thick sandwiched layers were used, in which the *t*-BuOH trapping agent was spatially well separated from the photolysis products. The reactivity of **3** apparently is so extreme that the dimerization or polymerization then occurred before the trapping agent could penetrate into the matrix layers in which **3** was present. In thinner sandwiched layers, there was apparently enough diffusion during deposition that at least some molecules of **1** were adjacent to molecules of *t*-BuOH.

Unfortunately, but not unusually, the trapping evidence for **2** is indirect and somewhat equivocal. While it is possible and most economical to postulate that an adjacent molecule of *t*-BuOH reacts with **2**, it is probable that it reacts with the very first photoproduct from **1** that contains a Si=N bond, and this need not be **2**. Little is known about the mechanism of the photochemical loss of four N_2 molecules. The 1:1 ^{14}N:^{15}N ratio in the product from [^{15}N]-**1** is most readily understood by postulating the loss of the central nitrogen atoms of all three azido groups. Successive loss of terminal pairs of N atoms in the azido groups is a possibility, suggesting intermediate structures such as an azidosiladiazirine and an isomeric diazo compound [$(C_6H_5Si(N_3)=N_2)$]. Even though these may look unlikely, we cannot exclude the possibility that they might be the species that actually react with *t*-BuOH to yield **5** in some complicated sequence of photochemical and/or thermal steps. However, in order to account for the formation of **5**, rather contorted mechanisms need to be written and we consider **2** to be the most likely candidate for the structure that is being trapped.

The feasibility of trapping of an early intermediate was demonstrated in an experiment in which the matrix was doped with CO. Under these conditions, irradiation of **1** produced a small amount of an isocyanate, detected by its most intense IR absorption at 2252 and 2285 cm^{-1}. This presumably resulted from CO addition to an intermediate nitrene, perhaps after a loss of a single N_2 molecule. When cold CO was added to the effluent from the hot oven in the pyrolysis of **1** and co-condensed on the cold window, no isocyanate bands were observed.

Hydrostatic Pressure Effects in the Matrix. For all vibrational bands of the photolysis products in Ar and N_2 matrices we have observed fine structure (with a largest splitting of 6.5 cm^{-1} on the 1530-cm^{-1} band), very sensitive to temperature changes. Already at 14 K we have observed dramatic relative intensity changes for some of these fine structure features (Figure 4). Similar changes were induced by brief low intensity irradiation at 308 nm. We attribute them to a release of the high hydrostatic pressure exerted on the phenyl isosilacyanide molecule by the four photochemically created nitrogen molecules, which relaxes upon purely thermal or light-induced annealing. This explanation is supported by similar concurrent changes in the $^{15}N^{14}N$ absorption region when a 50% ^{15}N-labeled precursor was used. Such relaxation was not observed either in solid Ne, which is quite soft even at 4.2 K, or in solid Xe, which perhaps is too "roomy". As Figure 4 shows, the difference IR spectrum before and after the brief annealing pinpoints the location of the bands of the photoproduct and separates them cleanly from the bands of impurities and starting material. We have found this useful in other matrix isolation IR measurements as well.

Vibrations of Phenyl Isosilacyanide (3). Attempts to achieve selective orientation of either **2** or **3** by photoselection in order to resolve the spectra of the two compounds did not lead to the desired goal, but they provided additional characterization of the vibrations of **3**. When a matrix containing **1** was illuminated with broad polarized output (260–285 nm) from the Xe–Hg lamp or the 248-nm laser line, photoorientation occurred for both the starting triazide **1** and for the phenyl isosilacyanide product **3**. The degree of orientation of **3** was always very low. Still, we were able to use the results to assign relative symmetries for twelve of its vibrational transitions.

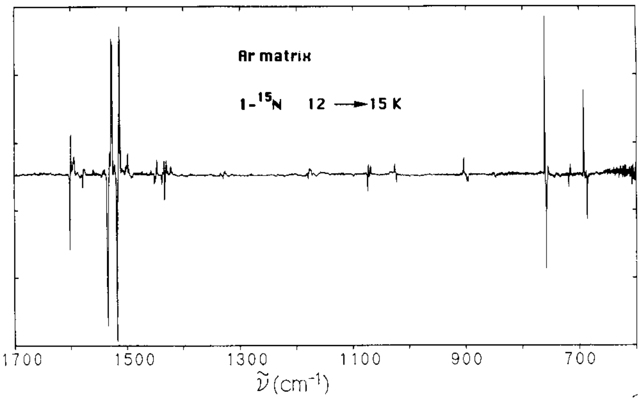

Figure 4. Difference IR spectrum of an irradiated argon matrix isolated sample of [^{15}N]-**1**, before (down) and after (up) a warmup from 12 to 15 K.

The frequencies and their isotopic shifts, as well as the observed relative polarizations, were compared with the results of MP 2/6-31G* calculations in order to arrive at vibrational assignments. Limited attention was paid to the calculated intensities, which are not reliable at this level of approximation.

The results of the comparison are shown in Table I. Qualitative mode descriptions and Wilson mode numbers are based on the inspection of normal mode displacements. Vibrations at frequencies lower than 400 cm^{-1} would not have been observable on our instrument. At and above 400 cm^{-1}, only ten of the calculated 33 fundamental vibrations do not have obvious experimental counterparts. Three of the ten are of the symmetry-forbidden a_2 species, two are C–H stretching vibrations that would be expected to overlap with those that are observed, and the remaining five are calculated to be very weak relative to most of the transitions observed. It is quite plausible to assume that the ten missing fundamentals are indeed present but too weak to have been observed.

Three of the observed weak vibrational peaks have no calculated counterparts (717, 841, and 1335 cm^{-1}). They may belong to combination bands, but the first two may possibly also be a_2 transitions with intensity induced by matrix perturbation; the 841-cm^{-1} peak is likely to belong to an impurity.

The assignment of the observed to calculated vibrations is easiest for the vibrations that exhibit significant ^{15}N isotopic shifts. Four such vibrations are observed, and four are calculated in the observed region. The observed values for ^{14}N (^{15}N) compounds are 472 (460), 1041 (1035), 1448 (1430), and 1530 (1514) cm^{-1}. The (unscaled) calculated ones are b_2, 480 (469); a_1, 1095 (1089); a_1, 1480 (1459); and a_1, 1579 (1568) cm^{-1}. According to the calculations, the 472-cm^{-1} vibration is a mixture of CNSi and CCN in-plane bends, the 1041-cm^{-1} vibration is a symmetric CNSi stretch mixed with a CH in-plane bend, and the 1448- and 1530-cm^{-1} vibrations are an antisymmetric CNSi stretch strongly mixed with in-plane ring CC stretching motions.

In addition to fundamentals characterized by antisymmetric (1448, 1530 cm^{-1}) or symmetric (1041 cm^{-1}) CNSi stretching and in-plane CNSi bending (472 cm^{-1}) character, we would expect one or more b_1 modes containing CNSi out-of-plane bending displacements. There indeed is one additional calculated fundamental with a significant ^{15}N shift. It is located at 305 cm^{-1} (300 for ^{15}N), is of b_1 symmetry, and is best described as a CNSi out-of-plane bend mixed with an out-of-plane ring deformation. The computed frequency lies outside the observed region.

Of the four observed vibrations identified fairly safely on the basis of their ^{15}N shifts, the b_2 mode at 472 cm^{-1} exhibits a negative dichroism, and the a_1 modes at 1448 and 1530 cm^{-1} exhibit a positive dichroism. We were unable to measure the dichroism of the 1041-cm^{-1} peak. These results mean that the short in-plane molecular axis (y) of the photoselected assembly is preferentially tilted away from the laboratory direction Z of the electric field of the light used in the irradiation of 1, and the long (symmetry) molecular axis (z) is tilted toward it. The positive dichroism observed for the 687-, 1175-, and 1598-cm^{-1} vibrations and the negative dichroism observed for the 1285-, 1492-, and 1575-cm^{-1} vibrations support the assignments of the former as a_1 and of the latter as b_2, as proposed in Table I. This agrees with the assignments reached by a consideration of frequencies alone. In order to describe the nature of the orientation distribution even qualitatively, we need to know the preferential tilt direction of the out-of-plane axis (x).

According to the assignments proposed in Table I, only two x-polarized b_1 vibrations have been observed. These are the strong peak at 758 cm^{-1} and the weak one at 899 cm^{-1}. Both exhibit positive dichroism. We consider the assignment of the strong out-of-plane bend at 758 cm^{-1} as b_1 to be quite safe in view of the analogy to all other monosubstituted benzene derivatives, and conclude that the x axis is tilted toward Z. The positive dichroism of the 899-cm^{-1} peak is then compatible with the assignment in Table I.

In principle, the orientation distribution deduced from the dichroic data is compatible with two possible photoselection mechanisms. In the first of these, the absorption region of 1 excited by the light used is of mixed polarization (x, z) and the molecules of 1 that happen to lie with their x, z plane oriented at a small angle to Z are preferentially converted to 3. This appears highly unlikely since the bulk of the absorption of 1 selected by the exciting light at the wavelengths used is surely of $\pi\pi^*$ character and cannot be polarized along x. Indeed, one would expect it to be due to the benzene L_b transition and thus polarized along y. The second possibility is that the photoselection does not occur on the reactant 1 but on the product 3. This appears unlikely at first sight since the product is photostable. However, if the UV-induced relaxation associated with the release of hydrostatic pressure permits at least some molecular rotation, it is possible that the small observed degree of alignment results. In order to observe a tilt of the y axis away from Z, the absorption would have to be predominantly polarized along y, and this is plausible. The very small magnitude of the orientation effects has thwarted attempts to measure the dichroism accurately and to perform a more quantitative analysis.

Table II. MP2/6-31G* Optimized Geometries of 2 and 3[a]

	2	3
	Bond Lengths (Å)	
SiN	1.626	1.589
C_iSi	1.869	
C_iN		1.381
C_iC_o	1.404	1.403
C_oC_m	1.394	1.392
C_mC_p	1.395	1.396
C_oH	1.088	1.087
C_mH	1.087	1.087
C_pH	1.087	1.087
	Bond Angles (deg)	
$C_oC_iC_o$	119.8	119.7
$C_iC_oC_m$	119.8	119.9
$C_oC_mC_p$	120.3	120.4
$C_mC_pC_m$	120.0	119.8
C_iC_oH	120.6	118.9
C_oC_mH	119.6	119.5

[a] Both molecules are of C_{2v} symmetry. i = ipso, o = ortho, m = meta, p = para.

The vibrations of phenyl isosilacyanide (3) and the calculated form of the normal modes appear to be quite unexceptional. They correspond closely to the Wilson normal modes for a C_6H_5X structure (Table I) and almost all of them have frequencies that lie within the expected regions. The only exceptions are (i) Wilson mode 4, which is unobserved but which is calculated to lie about 200 cm^{-1} lower than usual, and (ii) Wilson modes 5 and 14, calculated and observed about 100 cm^{-1} lower than usual. These three anomalies may be due to interference with the NSi stretching motion.

The presence of the additional atom in the C_6H_5NSi structure relative to the C_6H_5X model is responsible for the occurrence of three additional vibrations that have no Wilson numbers. Two of these are due to bending displacements of the added Si atom and are computed to lie in the far infrared region, at 115 (b_1) and 122 (b_2) cm^{-1}. The third is due to a stretching displacement of the Si atom and corresponds most closely to the 1448-cm^{-1} a_1 vibration. It is mixed quite strongly with the a_1 CH in-plane bend (Wilson no. 18a) and the a_1 in-plane ring CC stretch (Wilson no. 19a). Still, if any one vibration in the molecule had to be identified as most closely associated with the SiN stretch, this would be the one. However, because of the low intrinsic frequency of the stretch of an isolated –NSi group relative to an isolated –NC group, aryl isosilacyanides do not have a truly characteristic group frequency of the kind that is well established for ordinary aryl isocyanides.

Structure of Phenyl Isosilacyanide (3). We have no experimental information on the structure of 3. The fully optimized MP2/6-31G* structure is of C_{2v} symmetry. It is likely to be imperfect but represents an improvement in reliability over previous optimization at the AM1 level and a partial optimization at the RHF 3-21G* level.[11] The MP2/6-31G* structural data are collected in Table II. Noteworthy are the nearly ideal hexagon ring structure, nearly unperturbed by the substituent, and the linearity of the CNSi group, already predicted by prior AM1 and RHF/3-21G* calculations,[11] as well as the short Si=N: distance, 1.587 Å. Not surprisingly, this is significantly longer than computed at the RHF/3-21G* level (1.534 Å).[11] It coincides nearly exactly with the length of the SiN bond in the diatomic, SiN (1.571 Å),[6] and in hindered silanimines (1.568 Å).[17] All of these compounds thus appear to contain a silicon–nitrogen double bond.

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[17] Wiberg, N.; Schurz, K.; Reber, G.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1986**, 591.

Table III. Calculated Vibrations of Benzenesilonitrile (2)[a]

$\tilde{\nu}$ (cm^{-1})		I			Wilson
^{14}N	^{15}N	(km/mol)	sym[b]	mode[c]	no.[d]
73	71	4.5	b_1	CSiN opb	
102	100	8.1	b_2	CSiN ipb	
184	184	2.0	b_1	CSiN opb + op ring ref	16b
302	339	8.8	b_2	CSiN ipb + CCSi ibp	18b
342	339	13.3	a_1	ip ring def + s CSiN stretch	6a (1)
389	389	0	a_2	op ring def	16a
429	429	1.5	b_1	CCN opb + CSiN opb	17b
536	536	0.6	b_1	op ring def (ring puckering)	4
629	629	0.1	b_2	ip ring def	6b
685	684	3.1	a_1	s CSiN stretch + ip ring def	1 (6a)
729	729	81.0	b_1	CH opb	11
851	851	0	a_2	CH opb	10a
885	885	0.3	b_1	CH opb	10b
914	914	0	a_2	CH opb	17a
915	915	0.05	b_1	CH opb	5
1011	1008	0.3	a_1	ip ring def	12
1032	1022	35.9	a_1	as CSiN stretch + ip ring def	20a
1078	1075	22.3	a_1	as CSiN stretch + CH ipb	18a
1124	1124	0.8	b_2	CH ipb	15
1163	1158	0.2	a_1	as CSiN stretch + CH ipb	
1224	1224	0.0003	a_1	CH ipb	9b
1248	1248	0.6	a_1	CH ipb	9a
1367	1367	1.9	b_2	CH ipb	3
1449	1449	1.1	b_2	ip ring stretch (Kekulé)	14
1496	1496	14.1	b_2	ip ring stretch	19b
1540	1540	3.0	a_1	ip ring stretch	19a
1646	1646	1.4	b_2	ip ring stretch	8b
1662	1662	0.2	a_1	ip ring stretch	8a
3222	3222	0.07	a_1	CH stretch	13
3225	3225	0.6	b_2	CH stretch	7b
3234	3234	0.2	a_1	CH stretch	7a
3244	3244	12.8	b_2	CH stretch	20b
3252	3252	12.3	a_1	CH stretch	2

[a] MP2/6-31G* (analytical). No scaling. [b] z, 2-fold symmetry axis, y, in-plane short axis, x, out-of-plane short axis. [c] op = out-of-plane, ip = in-plane, b = bend, s = symmetric, as = asymmetric, def = deformation. [d] Mode number in Wilson notation for monosubstituted benzene: Wilson, E. B. *Phys. Rev.* **1934**, *45*, 706.

Vibrations and Structure of Benzenesilonitrile (2). We have no experimental structural or spectral data for this elusive formally triply bonded species, only fully optimized MP2/6-31G* results. These, too, represent an advance over previous AM1 and RHF/3-21G* calculations.[11] The equilibrium geometry (Table II) is of C_{2v} symmetry. Noteworthy is the nearly ideal hexagonal structure of the phenyl group, once again suggesting little net interaction with the substituent in the ground state, and the linearity of the CSiN group. Both of these are in agreement with the earlier RHF/3-21G* calculations (AM1 predicted a nearly regular hexagon but a strongly bent CSiN group).[11] The computed length of the formal triple bond, Si≡N:, is 1.626 Å. This is about 0.1 Å longer than calculated previously at the RHF/3-21G* level (1.537 Å).[11] Although a still higher level of calculation would be necessary to obtain a truly reliable value, the near equality of the calculated lengths of the "double bond" in Ph—$\ddot{\text{N}}$=Si: and the "triple bond" in Ph—Si≡N: is likely to persist. For the purposes of qualitative discussion, it is probably reasonable to view the silonitrile group as containing a triple bond that is so highly polarized that it is effectively doubly bonded and zwitterionic, Ph—Si$^+$=$\ddot{\text{N}}$:$^-$, and this is reflected in its computed atomic charges and very large dipole moment. At the MP2/6-31G* level, the Mulliken atomic charges are +0.56 (Si), −0.53 (N), and −0.25 (C_i) in **2** [0.45 (Si), −0.78 (N), and +0.36 (C_i) in **3**], and the dipole moment is 8.4 D in **2** (1.0 D in **3**).

The computed vibrational modes and frequencies of **2** are similar to those of **3** (Table III). In view of the excellent agreement with observations on the isomer **3**, we believe that the spectral predictions in Table III are quite reliable, except for the computed intensities. The frequencies of the Wilson modes lie in the same order in the two compounds, with very few exceptions, and these can be mostly traced to the increased mass of the atom attached to the ring (Si in **2**, N in **3**). In **2**, the in-plane (Wilson no. 18b) and out-of-plane (no. 17b) CCSi substituent bending motions occur at much lower frequencies than in **3**. The frequencies of the out-of-plane and in-plane bending motions of the CSiN group (no Wilson number) also are distinctly lower in **2** than in **3**. The SiN stretching motion in **2**, like the analogous motion in **3**, couples strongly to other in-plane motions and contributes to several normal modes of a_1 symmetry: 1, 6a, 20a, 18a, and a mode at 1163 cm^{-1}. Although the ^{15}N isotope shift is the largest for 20a, we prefer to leave the mode at 1163 cm^{-1} without a Wilson number and identify it very approximately as the one stretching mode due to the presence of the additional atom. Its frequency is quite low compared with its 1480-cm^{-1} (calcd), 1448-cm^{-1} (obsd), analogue in **3**. Because of the much lower frequency of the modes with SiN stretching character, the calculated pattern of ^{15}N shifts in **2** is very different from the one computed and observed for **3**. In **2**, no ^{15}N shifts larger than 1 cm^{-1} are predicted above 1200 cm^{-1}, whereas in **3**, two bands with very large ^{15}N shifts are calculated and observed in this region. This represents an additional confirmation of the structural assignment.

Relative Energies of Phenyl Isosilacyanide (3) and Benzenesilonitrile (2). It has been clear ever since the initial matrix work on HNSi[7] that the isosilacyanides, R—N=Si:, are likely to be intrinsically more stable than silonitriles, R—Si≡N:, and this has been confirmed by all calculations performed so far (R = H,[10] CH_3,[11] C_6H_5[11,13]). Our results are no exception: at the fully optimized MP2/6-31G* level, and including zero-point corrections, **3** is 55.0 kcal/mol more stable than **2**. The contrast to the case of isocyanides and carbonitriles, where the latter are more stable, is qualitatively understandable by reference to the inability of silicon to form strong π bonds and the reluctance with which carbon accepts divalency.

Electronic Spectra of Phenyl Isosilacyanide (3) and Benzenesilonitrile (2). The observed absorption spectrum of **3** can be compared with expectations based on an INDO/S calculation at the MP2/6-31G* optimized geometry (Figure 2). The calculated spectrum starts with a few forbidden or very weak transitions at low energies, which may well be unobserved. These are followed by a cluster of stronger transitions in the energy region where strong absorption is observed in the measured spectrum. The excited states of the weak transitions are calculated to be the in-phase and the out-of-phase combination of the $\pi' \rightarrow \pi^*$ and $\pi \rightarrow \pi'^*$ a_2 configurations in the NSi bond (the prime denotes the in-plane "π-system"), the $\pi' \rightarrow \pi'^*$ configuration of the NSi bond strongly mixed with benzene L_a state, and at significantly higher energy, the benzene L_b state. The excited states of the strong transitions include the benzene B_a and B_b states and excitations of $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ types. Since the validity of the theoretical method for an unusual structure such as **3** is uncertain, particularly for transitions other than $\pi \rightarrow \pi^*$, the results are not discussed in greater detail, but they appear compatible with the experimental observations.

The INDO/S results for **2** are shown in Figure 2 as well. The nature of the excited states and the relative transition intensities are similar as in 3, but all transitions are shifted to lower energies.

Conclusions

We have gathered convincing spectroscopic and chemical evidence for the pyrolytic and photochemical generation of phenyl isosilacyanide (3) and circumstantial indications for the intermediacy of benzenesilonitrile (2) in the photochemical generation of 3. The IR spectrum of 3, including polarization data and isotopic shifts, has been assigned and is readily understandable in qualitative terms. Its UV spectrum has been accounted for at a lower level of theory. The IR and UV spectra of 2 are predicted.

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