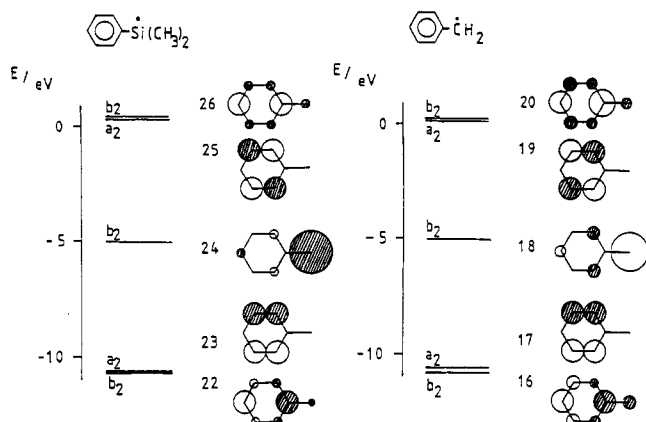


CHART I: SCF-MO Diagrams for the Phenyltrimethylsilyl Radical and the Benzyl Radical^a

^aThe two highest occupied and two lowest unoccupied and singly occupied orbitals are shown (numbers of MO's are 22-26 for the phenyltrimethylsilyl radical and 16-20 for the benzyl radical). These five orbitals are all π -orbitals, and the sign and absolute value of the coefficients of each π -atomic orbitals are expressed schematically by the circles.

band determined by monitoring the 0-0 emission peak (467 nm). A great and positive polarization degree is observed at the 324 nm peak, and a negative one is at the peak of the intense band (272 nm), indicating that directions of the transition moments of these bands are polarized parallel and perpendicular to the 0-0 emission band, respectively. As a result, the intense band at 272 nm is assigned to the 3^2B_2 state, which is calculated to be at $33.60 \times 10^3 \text{ cm}^{-1}$ (298 nm).

As described above, a remarkable similarity is observed between the phenyltrimethylsilyl radical and the benzyl radical fluorescence spectra. This similarity can be explained by the results of MO calculations on these radicals. Values of I_p and E_a of the carbon 2p atomic orbital and the silicon 3p atomic orbital are 11.27 and 0.34 eV and 9.19 and 2.82 eV, respectively.¹⁹ The values of electronegativities $-(I_p + E_a)/2$ for these atomic orbitals, however, are close to each other: -5.805 eV for carbon and -6.005 eV for silicon atom. This accidental coincidence of the valence state electronegativity may be responsible for the similarity in electronic spectrum. As shown in Chart I, the two highest occupied and lowest unoccupied molecular orbitals and the singly occupied orbital of the phenyltrimethylsilyl radical (planar structure with a Si-C(phenyl) bond length of 1.74 Å) are comparable with those of the benzyl radical in the SCF level. These five orbitals are all π orbitals and are closely related to the corresponding molecular orbitals of the benzyl radical in energy and in charge distribution. As a result, the first several electronic transitions of the phenyltrimethylsilyl radical correspond to those of the benzyl radical.

It should be noted that the excitation spectrum of the phenyltrimethylsilyl radical shown in Figure 2 does not correspond to the absorption spectrum of the photolyzed PTMSI shown in Figure 9. The observed absorption spectrum is rather close to the excitation spectrum monitored at the broad emission band. Therefore the phenyltrimethylsilyl radical is a minor product in UV photolysis. Unidentified species responsible for the broad emission band may be major products. We studied GCMS spectra of the photolyzed samples, but no information was obtained to identify the intermediates responsible for the broad emission. Liquid chromatographic analysis of the photolyzed solution shows that the main products are polymeric species, though they are still unknown at the present stage.

The fluorescence quantum yield of the phenyltrimethylsilyl radical could not be determined since its absorption band is weak and is hidden in the broad absorption band. Sakurai et al. tried to study the ESR spectrum of the 3,5-di-*tert*-butylphenyltrimethylsilyl radical produced by hydrogen abstraction from the parent silane molecule using the *tert*-butoxyl radical.⁹ The generated silyl radical was, however, reactive enough to form an ipso-substituted radical even at -10 °C. Since reactivity similar to that of the silyl radical was expected for the phenyltrimethylsilyl radical, we tried to record an ESR spectrum at 77 K for the photolyzed phenyltrimethylsilane but failed to obtain any essential information on the molecular structure of reaction intermediate.

Summary

Sharp fluorescence spectra of the phenyltrimethylsilyl radical have been observed for the first time by the photolyses of phenyltrimethylsilane, phenyltrimethylsilane, and phenylpentamethylsilane at 77 K. The excitation spectrum observed for the sharp emission shows spectral characteristics similar to those of benzyl radicals and is well interpreted by the results of CNDO/S-CI calculations on the phenyltrimethylsilyl radical. Fluorescence lifetimes of these emission bands have been determined to be ca. 1 μs and are comparable with those of benzyl radicals.

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Infrared Spectrum of Dinitrogen Sulfide

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NNS is produced by flash vacuum pyrolysis of 5-aryl-1,2,3,4-thiazotriazoles **1**, **3**, **5**, and **7** and 5-phenoxy-1,2,3,4-thiazotriazole (**9**). The Ar matrix infrared spectrum shows ν_{NN} at 2039 cm^{-1} and ν_{NS} at 752 cm^{-1} . The experimental data are compared with high-level ab initio as well as semiempirical (MNDO) calculated structural and vibrational data. NNS is destroyed photochemically or on heating to 160 K.

N_2S was first observed in 1986 as the product, together with benzonitrile, of flash vacuum pyrolysis (FVP) of 5-phenyl-

1,2,3,4-thiazotriazole (**1**).² N_2S was detected by IR spectroscopy (2030 cm^{-1}) and mass spectrometry (m/z 59.9779)² and shortly

thereafter also by photoelectron spectroscopy.³ N₂S is a sensitive molecule which can only be observed when using very short contact times and hence a vacuum and a pumping speed as high as possible (typically 10⁻³–10⁻⁵ Torr), and indeed previous attempts to detect the molecule in the decomposition of **1** had failed.⁴ In the gas phase, the decomposition leads to S₂ molecules, not S atoms.^{2,3,5}

In 1990 Brown et al.⁶ used the same method (FVP of **1**) to obtain the high-resolution gas-phase IR spectrum of the $\nu_{\text{N=N}}$ fundamental (2047.59 cm⁻¹). Analysis of the fine structure due to the N₂³⁴S and N₂³²S isotopomers afforded the rotational and centrifugal distortion constants and the bond lengths $R_{\text{NN}} = 1.1388$ and $R_{\text{NS}} = 1.5775$ Å. From the equilibrium *B* value, the N–S bending frequency δ_{NS} was estimated as 343 cm⁻¹.

Three problems remain: (i) Neither δ_{NS} nor the N–S stretching vibration ν_{NS} has been observed. (ii) Brown noted that the N₂S gas-phase spectrum was observable only at the maximum pumping capacity of the system, allowing the pyrolysis product from **1** to flow through the 16-m-path length multiple-reflection cell. With less efficient pumping, and hence longer contact time, only a broad, featureless absorption due to a stable compound was observed. The carrier of this absorption (also at 2047 cm⁻¹) was not identified. (iii) Ab initio calculations on N₂S at the HF/6-31G* level had indicated that ν_{NS} should occur at ca. 583 cm⁻¹ and δ_{NS} at ca. 471 cm⁻¹.⁶ Scaling by the usual factor⁷ of ca. 0.9 would still predict these two bands in the 400–525-cm⁻¹ range. Very recently, Davy and Schaefer⁸ carried out higher-level ab initio calculations using double- ζ (DZ) and triple- ζ (TZ) basis sets with polarization functions added (DZP and TZ2P). Vibrational frequencies were obtained using self-consistent-field (SCF) and configuration interaction methods, viz. single and double excitations (CISD), coupled cluster including all singles and doubles (CCSD), and complete active space self-consistent field (CASSCF). They concluded that an accurate theoretical picture of N₂S can only be obtained using correlated methods and were particularly skeptical about the low value of 343 cm⁻¹ estimated by Brown⁶ for δ_{NS} on the basis of the experimental spectrum. Even the most reliable levels of theory in this work⁸ predicted δ_{NS} above 400 cm⁻¹ and ν_{NS} around 700 cm⁻¹.

We have reinvestigated the matrix-isolation IR spectrum of N₂S using several different precursors and located two vibrations, 2039 (ν_{NN}) and 752 cm⁻¹. On the basis of high-level ab initio calculations, the 752-cm⁻¹ band is now assigned to ν_{NS} . The calculated intensity of δ_{NS} is, however, so low that there is little chance of observing it in our spectra.

Experimental Section

The apparatus for flash vacuum pyrolysis (FVP) was as previously described.⁹ FVP was carried out in unpacked quartz tubes (100-mm length, 8-mm i.d.) at 200–700 °C (ca. 10⁻⁴ mbar), and the products were isolated in Ar or Xe matrices at 12–20 K or neat at 77 K.

Infrared spectra were recorded on Mattson Sirius 100 or Perkin-Elmer 1700X FTIR instruments at a resolution of 0.5 or 1 cm⁻¹.

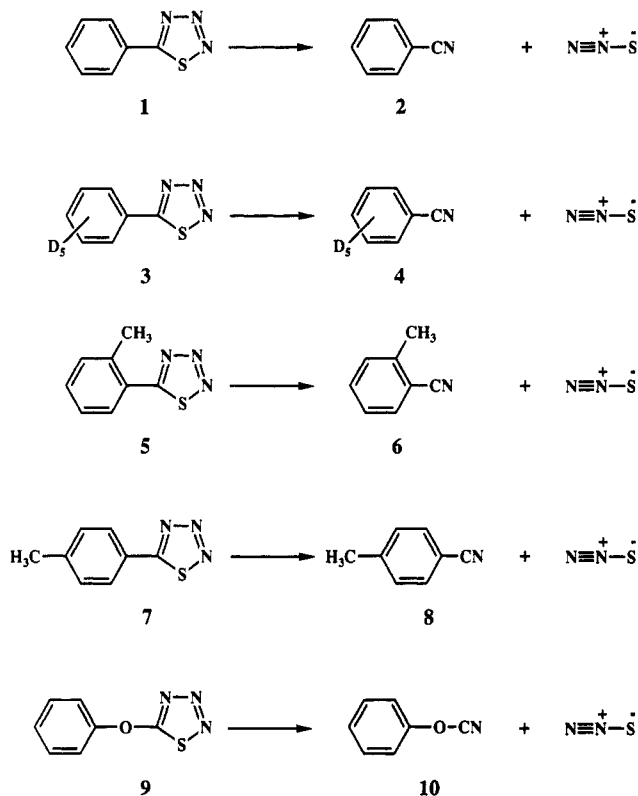
Photolyses were carried out with low-pressure Hg lamps (75 W, 254-nm maximum output) or a high-pressure Xe–Hg lamp (1000 W, Hanovia).

Materials. Benzonitrile and the *o*- and *p*-tolunitriles were obtained from Aldrich Chemical Co. and benzonitrile-*d*₅ (mini-

um 99 atom % D) was from Merck AG. 5-Phenyl-1,2,3,4-thiatriazole (**1**) was prepared by the method of Kirmse.¹⁰ 5-Phenoxy-1,2,3,4-thiatriazole (**9**) and phenyl cyanate (**10**) were prepared according to Reich and Martin.¹¹ [(2-Methylphenyl)thiocarbonyl]thioacetic acid was prepared according to Werbel et al.¹² and converted to 5-(2-methylphenyl)-1,2,3,4-thiatriazole (**5**) as reported by Jensen and Pedersen:¹³ mp 45–46 °C (lit.¹³ 45–46 °C); IR (KBr) 1454 (s), 1394 (s), 1224 (m), 1187 (m), 769 (s), 690 (s) cm⁻¹; ¹H NMR (CDCl₃) δ 2.63 (s, 3 H), 8.25–7.31 (m, 4 H); ¹³C NMR (CDCl₃) δ 21.9, 125.8, 126.8, 131.2, 131.9, 132.2, 137.9, 177.5. The 4-methyl analogue **7** was likewise prepared according to Jensen and Pedersen:¹³ mp 97–98 °C (lit.¹³ mp 97–98 °C).

Benzonitrile-*d*₅ (Aldrich Chemical Co., 99.5 atom % D) was converted into (phenylthiocarbonyl)thioacetic-*d*₅ acid using the procedure of Kjaer¹⁴ for the unlabeled compound: mp 126–127 °C; IR (KBr) 1700 (s), 1218 (m), 1060 (s) cm⁻¹; ¹H NMR (CDCl₃) δ 4.29 (CH₂), 9.09 (COOH); ¹³C NMR (CDCl₃) δ 38.6 (CH₂), 126.3 (t, *J* = 23.0 Hz), 127.9 (t, *J* = 23.8 Hz), 132.4 (t, *J* = 23.8 Hz), 143.8 (s), 172.9 (COOH), 225.5 (C=S); MS *m/z* 219, 218, 217. HRMS *m/z* 217.0278; calcd for C₉¹H₃²H₅O₂S₂: 217.02792.

5-Phenyl-1,2,3,4-thiatriazole-*d*₅ (**3**) was obtained from the foregoing compound using Kirmse's procedure¹⁰ for the unlabeled material: mp 91–93 °C; ¹³C NMR (CDCl₃) δ 126.1 (s), 129.2 (t, *J* = 25.5 Hz), 129.3 (t, *J* = 23.5 Hz), 132.8 (t, *J* = 24.2 Hz), 179.1 (s); MS *m/z* 169, 168; HRMS: *m/z* 168.0520; calcd for C₇²H₅N₃S: 168.05178.



Results and Discussion

The thiatriazoles **1**, **3**, **5**, **7**, and **9** were prepared and subjected to FVP with isolation of the products in Ar matrix at ca. 12 K. In each case, ν_{NN} of N₂S was observed at 2039 cm⁻¹. (The lower

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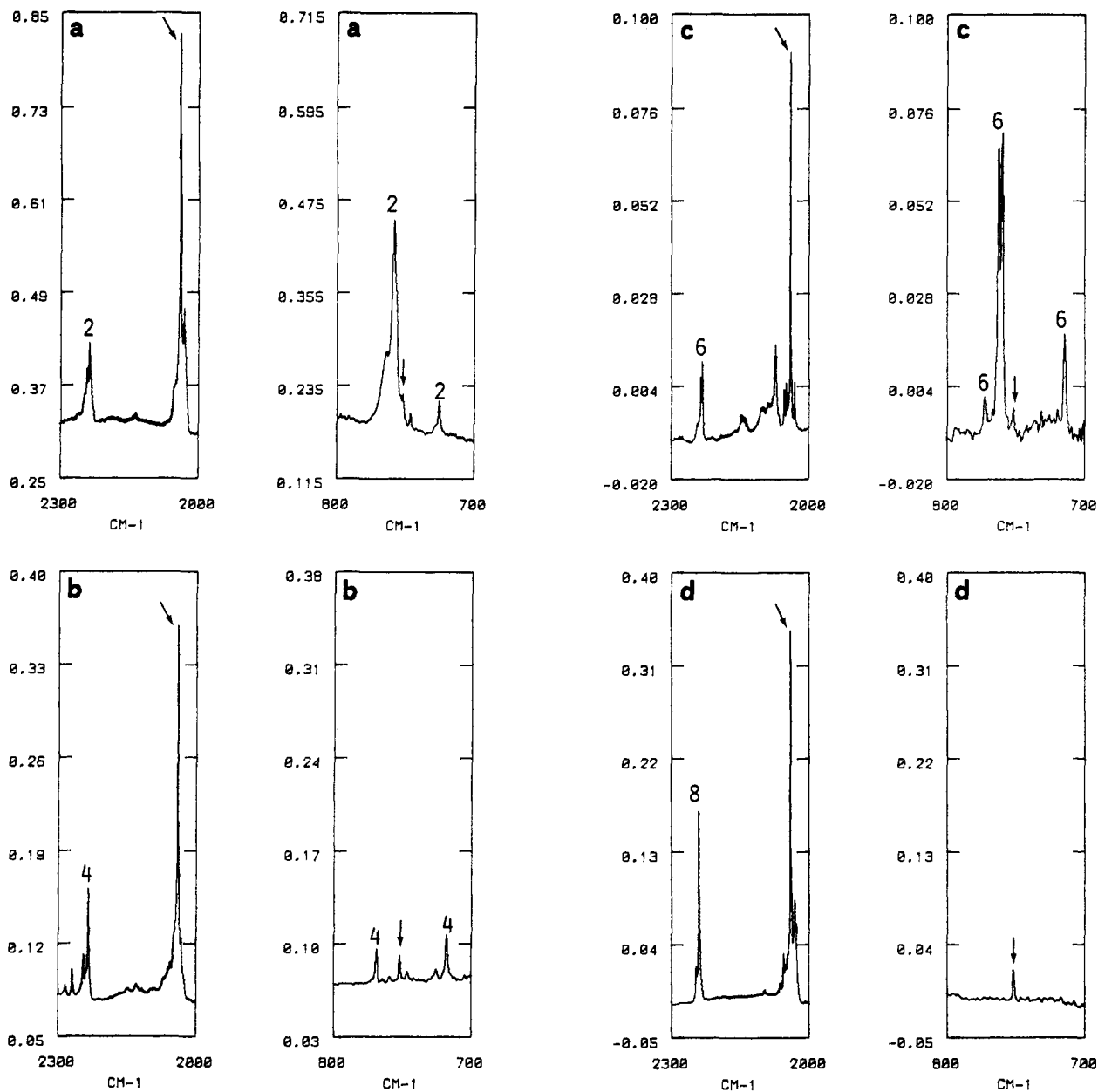


Figure 1. Partial Ar matrix IR spectra of the pyrolyzates of (a) 1, (b) 3, (c) 5, and (d) 7 showing N_2S bands at 2039 and 752 cm^{-1} (arrows) in the presence of nitriles 2, 4, 6, and 8, respectively.

value of 2030 cm^{-1} quoted previously² was obtained on a less precise instrument.) The corresponding nitriles 2, 4, 6, 8, and 10 were identified by comparison of the spectra with those of the matrix-isolated authentic materials. The optimal temperature for N_2S production was 650–700 °C (10^{-4} mbar) for 1, 3, and 5 and 300 °C for 7 and 9. Less N_2S was produced at higher temperatures, but it was still detectable in a pyrolysis of 1 at 1000 °C. The highest ratio of the absorbances of N_2S (2039 cm^{-1}) and benzonitrile (2228 cm^{-1}) was 15:1. The thiazoles were completely converted to products at temperatures below 700 °C. In the case of the 5-phenoxy compound 9, N_2S and phenyl cyanate (10) were observed at a pyrolysis temperature as low as 200 °C. The decomposition of 9 in solution at room temperature is known to give 10, nitrogen, and sulfur.¹¹

Naturally, the temperatures required for decomposition of the thiazoles and for observation of N_2S depend on the experimental conditions, in particular pressure and contact time. If less efficient pumping (longer contact time) is used, N_2S disappears, and only benzonitrile together with a small amount of phenyl isothiocyanate is formed from 1. The formation of 4–10% phenyl isothiocyanate has been established previously.^{2–5,10} Phenyl isothiocyanate absorbs in Ar matrix at 2047 cm^{-1} and in the gas phase gives rise to a strong and broad peak with little fine structure

around 2050 cm^{-1} . The unassigned, stable species observed by Brown et al.⁶ near the N_2S value (2047 cm^{-1}) was therefore very likely due to phenyl isothiocyanate.

In all the reactions of 1, 3, 5, and 7 producing N_2S , a second, much weaker band was observed at 752 cm^{-1} (Figure 1). This band could not be ascribed to the precursors, the nitrile products, or the aryl isothiocyanates which are formed as minor reaction products of 1, 3, 5, and 7.^{2,4,10} The 752- cm^{-1} signal is seen particularly well in the products from 3 and 7, where there is no interference from bands due to the nitriles 4 and 8 (Figure 1b,d). In the case of 9, the 752- cm^{-1} signal was not observable due to the presence of a strong band due to phenyl cyanate (10) at 751 cm^{-1} . For all the other precursors, the ratio of intensities of the 2039- and 752- cm^{-1} bands was always constant. Both bands disappeared in concert on broad-band irradiation with the high-pressure Xe–Hg lamp (15 min) or much more slowly at 254 nm (10 h). N_2S produced from 1 was observable in Xe matrix up to 80 K, when the Xe evaporates, leaving a broad peak at 2038 cm^{-1} which disappeared on further warming to 160 K. Isolation of the products of pyrolysis of 1 at 77 K gave readily observable N_2S (2038 cm^{-1}) together with benzonitrile. Warming to 160 K caused the disappearance of the N_2S band. The 752- cm^{-1} signal was masked, in these cases, by the adjacent broad benzonitrile

TABLE I: Geometries (Å), Vibrational Frequencies (cm⁻¹), and Total Energies (hartree) Calculated at Various Levels of Theory^a

	R_{N-N}	R_{N-S}	NN stretch	NS stretch	NNS bend	energy
HF/6-31G*	1.0857	1.6514	2600 (296.7)	584 (44.8)	469 (1.65)	-506.372 86
HF/DZP	1.0885	1.656	2568 (297.7)	595 (42.5)	484 (1.58)	-506.388 00
HF/6-311++G*	1.0792	1.6518	2574 (294.6)	570 (45.4)	437 (0.80)	-506.424 23
MP2/6-31G*	1.173	1.564	1818 (1468.1)	849 (27.5)	464 (0.01)	-506.848 62
MP2/6-31G* (2d for S)	1.172	1.565	1831 (412)	844 (24.6)	478 (0.002)	-506.874 60
MP2/6-311G*	1.167	1.559	1872 (570)	848 (36.5)	389 (0.07)	-507.061 24
MP2/N(8s,6p,2d), S(9s,6p,3d,1f)	1.156	1.562	1803 (472.3)	834 (31.3)	446 (0.06)	-507.258 69
MP2/N(8s,6p,1d,1f), S(9s,6p,2d,1f)	1.154	1.567	1804 (450)	853 (25.3)	452 (0.17)	-507.264 07
MNDO	1.126	1.539	2030	749 ^b	310 ^b	
experiment	1.139 ^c	1.578 ^c	2039 ^d	752 ^d	~343 ^c	

^aCalculations are for ground-state $^1\Sigma^+$ NNS. The NNS angle is 180° for all calculations. Values in parentheses are vibrational intensities (km/mol). ^bMNDO vibrational frequencies corrected by a factor of 0.8. ^cReference 6 (gas-phase values) (the gas-phase value of ν_{NN} is 2047.59 cm⁻¹). ^dThis work (Ar matrix values).

signal.

The above experiments clearly demonstrate that the carrier of the 2039- and 752-cm⁻¹ signals is the same species, i.e. N₂S. A careful search of the IR spectrum revealed no further band that could be due to N₂S down to 400 cm⁻¹. A further search in the far-IR region down to 200 cm⁻¹ also revealed no new peak, but the weak δ_{NS} would not be detectable on our instrument. Since no other band was found, we can exclude the possibility that the 752-cm⁻¹ signal is due to an overtone,⁵ and it must therefore be due to the N-S stretching fundamental, ν_{NS} .

Since this conclusion is in stark contrast to the early ab initio prediction^{3,6} of ca. 525 cm⁻¹ for ν_{NS} , we performed both semi-empirical MNDO (AMPAC program) and higher-level ab initio calculations¹⁵ of the structure and harmonic vibrational frequencies of the ground state ($^1\Sigma^+$) of linear NNS. The results are summarized in Table I.

The basis sets considered in the ab initio calculations are the split valence plus polarization function (6-31G*, DZP, 6-311++G* (including diffuse functions)) and the large basis set (N-(8s,6p,2d)/S(9s,6p,3d,1f)) which is beyond the TZP basis. The lowering of the calculated total energy as one descends through the table indicates increasing accuracy. The calculated N-N bond length is initially too short (HF/6-31G*) and at the highest level 0.015 Å too long compared with the experimental values. The N-S bond length is initially too long and at the highest level 0.01 Å too short.

Consequently, the calculated NN stretching frequency is initially too high (2600 cm⁻¹) and at the final level too low (1804 cm⁻¹). The NS stretching frequency is initially too low (584 cm⁻¹) but moves to higher values (844–853 cm⁻¹) with the larger basis sets, surpassing the experimental value of 752 cm⁻¹ as the N-S bond length becomes too short. The NNS bending frequency, initially at 469 cm⁻¹, does not vary a great deal, but it does decrease somewhat with the larger basis sets. This NS bending frequency will depend on both the NN and the NS bond lengths, and the

fact that these vary in opposite directions may account in part for the near constancy of the calculated frequency. An actual frequency below 400 cm⁻¹ does not appear to be excluded; however, the extremely low calculated intensity makes it unlikely that δ_{NS} will easily be located experimentally.

The MNDO calculated NN bond length is 0.01 Å too short, and the N-S bond length is 0.04 Å too short. Nevertheless, the MNDO vibrational frequencies are in remarkably good agreement with experiment: after correction of the calculated values by the usual factor of 0.8, the frequencies are 2030, 749, and 310 cm⁻¹.

Conclusion

Linear NNS is produced by FVP of 5-aryl- and 5-phenoxy-1,2,3,4-thiazoles. It is destroyed photochemically and thermally but is observable in the solid state up to 160 K and survives the gas-phase generation at temperatures up to 1000 °C provided the pressure is low (10⁻⁴ mbar) and the contact time consequently short. The thermal decomposition gives, as previously described,^{2,3,5} N₂ and S₂.

The Ar matrix IR spectrum of NNS is characterized by two bands at 2039 (ν_{NN} (s)) and 752 cm⁻¹ (ν_{NS} (w)). These values are in agreement with the ab initio calculations reported here and with those of Davy and Schaefer,⁸ whereby it must be noted that ab initio theory is still unable to calculate either the structure or the spectrum accurately.

The MNDO calculated IR spectrum is, after correction, in very good agreement with the experimental data, but the bond lengths are inaccurate.

The NS bending vibration is predicted to be very weak. It does not seem impossible that the estimate of Brown et al.⁶ of ca. 343 cm⁻¹ for this vibration could be correct.

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Registry No. 1, 34733-85-2; 2, 100-47-0; 3, 138435-36-6; 4, 2102-15-0; 5, 91982-92-2; 6, 529-19-1; 7, 52098-71-2; 8, 104-85-8; 9, 3549-20-0; 10, 1122-85-6; N₂S, 56400-02-3.

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