

enzyme recognition and antibacterial activity.

The lack of antibacterial activity of the demethoxy analogue **18** suggests that the methoxyl group contributes significantly to biological activity. In the crystal state, the methoxy group does not appear to be sterically crowded and it is therefore unlikely that the observed effect is purely of steric origin. However, from the available data, it is not possible to ascertain if the methoxyl group merely serves to increase the strain and hence the reactivity of the  $\beta$ -lactam, or if further fragmentation to a reactive species following enzymatic cleavage of the  $\beta$ -lactam is important in imparting the observed potent antibacterial activity.

**Acknowledgment.** We are grateful to Drs. W. Huffman and H. Rapoport for helpful discussions during the course of this work, S. Fagan and K. Erhard for the preparation of important intermediates, and J. Guarini for the antibacterial results reported in this paper.

## References and Notes

- (1) For part 5 in this series, see J. Finkelstein, K. G. Holden, and C. D. Perchonock, *Tetrahedron Lett.*, 1629 (1978).
- (2) J. L. Strominger, P. M. Blumberg, H. Suginaka, J. Umbreit, and G. G. Wickus, *Proc. R. Soc. London, Ser. B*, **179**, 369 (1971); J. L. Strominger, *Harvey Lect.*, **64**, 1979 (1970).
- (3) D. J. Tipper and J. L. Strominger, *Proc. Natl. Acad. Sci. U.S.A.*, **54**, 1133 (1965).
- (4) W. F. Huffman, K. G. Holden, T. F. Buckley, J. G. Gleason, and L. Wu, *J. Am. Chem. Soc.*, **99**, 2352 (1977).
- (5) R. M. Jacobson, *Tetrahedron Lett.*, 3215 (1974).
- (6) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Interscience, New York, 1967, p 154.
- (7) The observation of an upfield shift in the  $^1\text{H}$  NMR of H-2 in **10a** relative to **11** is consistent with the assigned stereochemistry. See, for example, E. G. Brain, A. J. Eglinton, J. H. C. Nayler, N. F. Osborne, R. Southgate, and P. Tolliday, *J. Chem. Soc., Perkin Trans. 1*, 2479 (1977).
- (8) The observation of a significant proportion of the 1,3-diaxial product points to a remarkably strong anomeric effect in this ring system.
- (9) Satisfactory elemental analyses were obtained for **2**, **3**, **10a**, **10b**, **12**, **13**, and **14**. All other compounds were characterized by spectroscopic methods.
- (10) The antibacterial activities of **14**, **15**, and **18** were compared in a disk assay vs. *B. subtilis* at drug concentration of 100 and 500  $\mu\text{g}/\text{mL}$ .
- (11) J. G. Gleason and P. Siler, unpublished results. The synthesis of this and other 3-hetero-1-dethiacephams will be described elsewhere.
- (12) See, for example, (a) G. Lowe, *Chem. Ind. (London)*, 459 (1975); (b) R. B. Woodward, *Pharm. J.*, **205**, 562 (1970); S. Kukolja, *J. Am. Chem. Soc.*, **94**, 7590 (1972); (c) E. Van Heyningen and L. K. Ahern, *J. Med. Chem.*, **11**, 933 (1968); (d) T. W. Doyle, B. Belleau, B. Y. Luh, C. F. Ferrari, and M. P. Cunningham, *Can. J. Chem.*, **55**, 468 (1977). (e) The sulfur and nitrogen analogues of **18** did not possess useful biological activity (W. F. Huffman and R. Hall, unpublished results).
- (13) (a) G. Lowe, *Chem. Ind. (London)*, 459 (1975); (b) M. Gorman and C. W. Ryan in "Cephalosporins and Penicillins; Chemistry and Biology", E. H. Flynn, Ed., Academic Press, New York, 1972, Chapter 12.
- (14) Compound **10b** was prepared from **8** by thermal addition of benzyl glyoxylate (toluene, 90  $^\circ\text{C}$ ), chromatographic separation of isomers and cyclization (*p*-TsOH, 4- $\text{\AA}$  sieves,  $\text{CH}_2\text{Cl}_2$ , room temperature). Reduction, acylation with phenoxyacetyl chloride and hydrogenolysis afforded exclusively **12**. Single crystals of **10b** were obtained by crystallization from methylene chloride-ether.
- (15) R. M. Sweet and L. F. Dahl, *J. Am. Chem. Soc.*, **92**, 5489 (1970).
- (16) R. M. Sweet in ref 13b, Chapter 7.

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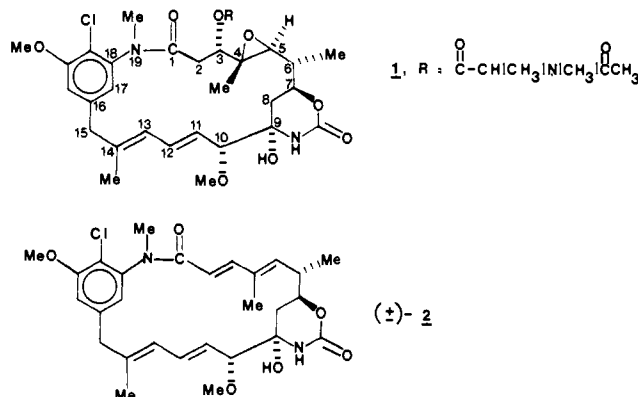
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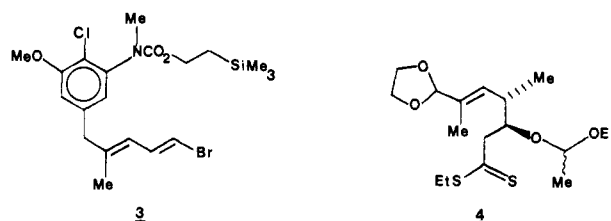
## Progress toward the Total Synthesis of Maytansinoids. Synthesis of ( $\pm$ )-4,5-Deoxymaysine (*N*-Methylmaysenine)

Sir:

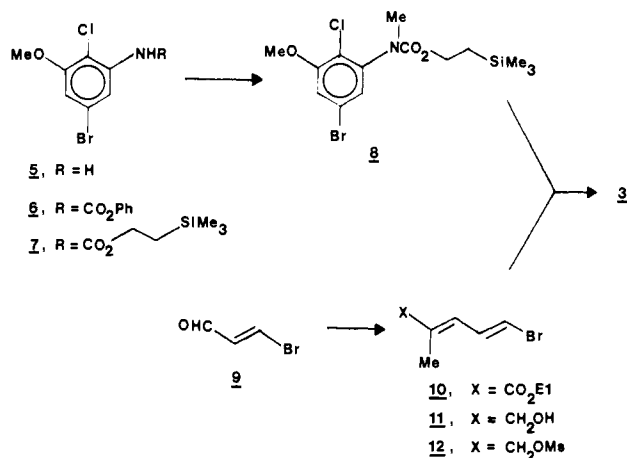
The extensive efforts by a number of laboratories<sup>1</sup> to reach the antitumor macrocycle, maytansine (**1**) have appeared in the past five years. Recently, Corey<sup>2</sup> has reported the first successful synthesis of a maytansinoid, ( $\pm$ )-*N*-methylmay-



senine (4,5-deoxymaysine, **2**). We describe our own total synthesis of **2**, which we anticipate to represent a general route to other maytansinoids. The synthetic strategy leading to **2** was based upon a convergent scheme involving the key intermediates **3** and **4** which were prepared with a high degree of stereoselectivity in multigram quantities. The *E,E* aromatic diene

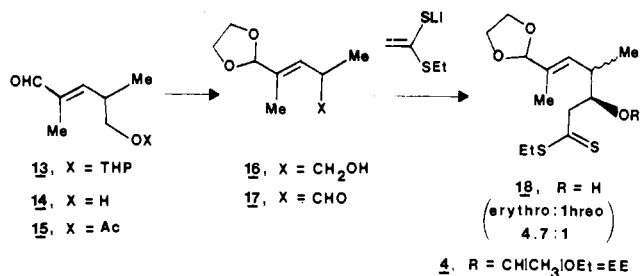


**3** was acquired from the tetrasubstituted benzene **5**<sup>3</sup> which was transformed into the phenylurethane **6** ( $\text{PhOCOCl}$ , pyridine) and then to the silylurethane **7** with  $\beta$ -(trimethylsilyl)ethanol<sup>4</sup> (0–25  $^\circ\text{C}$ , THF, *t*-BuOK). Without purification, the latter was treated with *t*-BuOK–MeI furnishing **8** (80% from **5**).<sup>5</sup> The

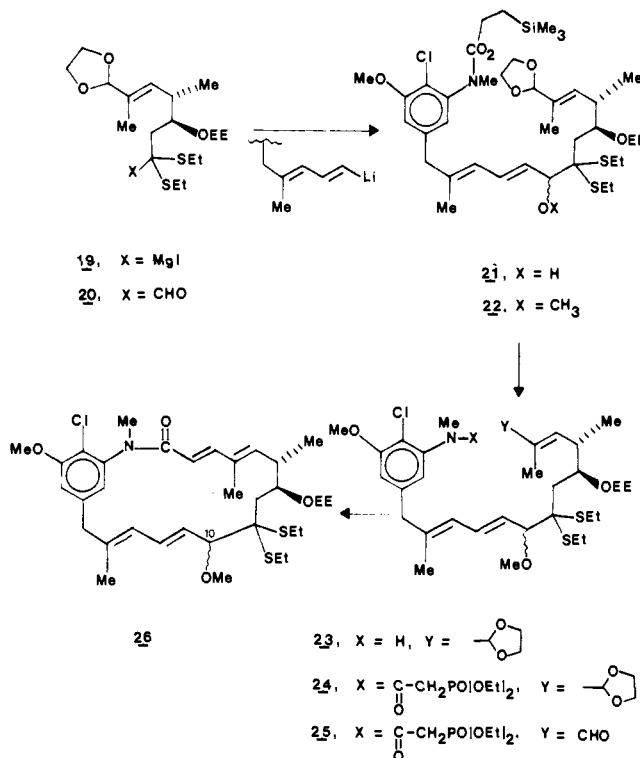


diene moiety in **3** was constructed from  $\beta$ -bromoacrolein **9**<sup>6</sup> which was homologated to the pure *E,E*-diene ester **10** (80%) using ethyl  $\alpha$ -diethoxyphosphonopropionate (*t*-BuOK, –78  $^\circ\text{C}$ , THF). Reduction with diisobutylaluminum hydride (0  $^\circ\text{C}$ , hexane) gave **11** (98%, oil)<sup>7</sup> which was treated with excess methanesulfonyl chloride ( $\text{Et}_3\text{N}$ ,  $\text{CH}_2\text{Cl}_2$ , –25  $^\circ\text{C}$ ) to give the mesylate **12** and used immediately to couple with **8** (*n*-BuLi, –78  $^\circ\text{C}$ ,  $\text{C}_3\text{H}_7\text{C}\equiv\text{CCu}\cdot[(\text{Me}_2\text{N})_3\text{P}]_2$ ,  $\text{Et}_2\text{O}$ , –78  $^\circ\text{C}$ ) providing the bromodiene **3** in 40–45% yield after purification by medium-pressure liquid chromatography (mp 61  $^\circ\text{C}$ ).<sup>9</sup>

The second key intermediate **4** was obtained from the unsaturated aldehyde **13**.<sup>10</sup> Removal of the tetrahydropyranyl ether (5% HCl–THF, (1:1), 100%) to the hydroxy aldehyde **14** was followed by acylation ( $\text{CH}_3\text{COCl}$ , pyridine,  $\text{CH}_2\text{Cl}_2$ , 0  $^\circ\text{C}$ , 95%) to the ester **15**, which was transformed into the ethylene ketal (ethylene glycol, pyridinium tosylate, benzene) and hydrolyzed ( $\text{K}_2\text{CO}_3$ –MeOH) to the hydroxy ketal **16**



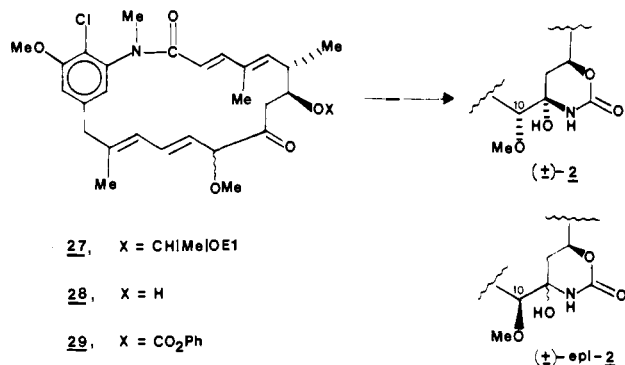
(95%). Oxidation with Collins reagent (0 °C, 30 min) to the aldehyde **17** (80%) was followed by addition of lithio ethyldithioacetate (−78 °C, THF, 6 h). The β-hydroxy dithioester **18** was formed as a 4.7:1 mixture of erythro-threo isomers which were separated (Waters-Prep 500 liquid chromatograph) to give multigram quantities of *erythro*-**18**.<sup>11</sup> The acetal **4** was prepared (ethyl vinyl ether, TsOH, Et<sub>2</sub>O, 25 °C) and, although an additional chiral center was introduced, it presented no problem for the duration of its residence on **4**. Addition of 3.0 equiv of ethylmagnesium iodide to **4** (−23 °C, THF, 2 h) furnished **19** as an acyl anion equivalent<sup>12</sup> which was treated with 2-(*N*-methyl-*N*-formyl)aminopyridine<sup>13</sup> producing **20** (92%) as a 1:1 mixture of diastereomers (due to EE (ethoxyethyl ether) group). The latter was now equipped



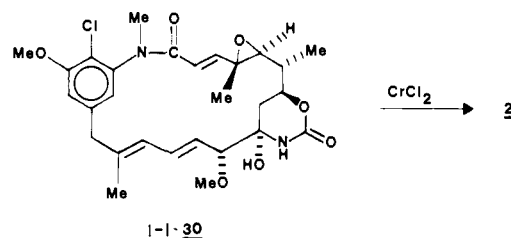
to serve as the electrophile, whereas the bromodiene **3** was prepared to serve as the nucleophile in the key coupling of both major intermediates.<sup>14</sup> Addition of 2.0 equiv of *t*-BuLi to **3** (−120 and −90 °C for 30 min) and introduction of aldehyde **20** (−120 to −60 °C) gave the alcohol **21** (62% after PLC). The methyl ether **22**<sup>15</sup> was formed (85%) using *t*-BuOK-CH<sub>3</sub>I (25 °C, 6 h) and the silyl carbamate removed (Bu<sub>4</sub>N<sup>+</sup>F<sup>−</sup>, CH<sub>3</sub>CN, 45–50 °C, 4 h, 95%) to afford the free amine **23**: IR (film) 3420 (NH) cm<sup>−1</sup>; NMR (CDCl<sub>3</sub>) δ 6.17 (s, 2, ArH), 3.98 (s, 3, ArOCH<sub>3</sub>) 3.26 (s, 3, C<sub>10</sub>OCH<sub>3</sub>), 2.86 (br s, 3, *N*-CH<sub>3</sub>). It is clear that **23** lacks but a two-carbon unit in order to make up the precursor to the 19-membered ring.

This was introduced by transforming **23** into phosphonoamide **24** ((EtO)<sub>2</sub>P(O)CH<sub>2</sub>COCl, pyridine, 0 °C, 91%) and removal of the dioxolane (oxalic acid-THF (1:4), 25 °C) to the aldehyde mixture **25**. Cyclization was performed via the

Wadsworth-Emmons reaction (1.1 equiv of *t*-BuOK, THF, −78 to 25 °C, 18 h) producing **26** in 74% isolated yield: PLC, 30% EtOAc-Et<sub>2</sub>O, *R<sub>f</sub>* 0.5–0.7, includes epimers at C-10 and diastereomers due to ethoxyethyl ether group; NMR (CDCl<sub>3</sub>) δ 7.11 (d, *J* = 15.2 Hz, C-3 H). Removal of the dithioether (HgCl<sub>2</sub>-CaCO<sub>3</sub>-aqueous CH<sub>3</sub>CN) gave the ketone **27** (IR CHCl<sub>3</sub>) 1725, 1650 cm<sup>−1</sup>; 91%) and acidic removal of the ethoxyethyl group (0.1 N HCl-THF (1:4), 0 °C, 30 min) gave the hydroxy ketone **28** (3580, 3420, 1715, 1645 cm<sup>−1</sup>; 81%).



The mixed carbonate **29** was formed using excess phenyl chloroformate and then treated with excess liquid ammonia (−78 °C, THF) producing **2** as a mixture of C-10 epimers in 50% yield.<sup>16</sup> Separation of **2** and *epi*-**2** was accomplished using high-pressure liquid chromatography (Waters 244-System, μ-Porosil, EtOAc-CHCl<sub>3</sub> (1:3), 5 mL/min) and showed both isomers in ~1:1 ratio with retention times of 7.8 min for **2** and 25 min for *epi*-**2**. The configuration of the labile C-9 hydroxyl<sup>16</sup> in *epi*-**2** is unknown at this time. Spectral data for **2**<sup>17</sup> were in total agreement with an authentic sample derived from natural maysine **30**<sup>18</sup> after chromous chloride reduction of the 4,5-epoxy group.<sup>19</sup> This route to (±)-**2** via the *seco* intermediate



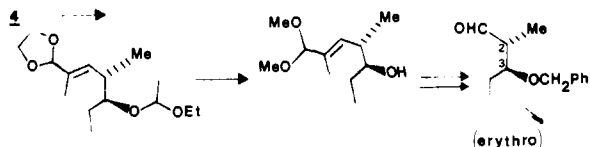
**23** will allow us to pursue the synthesis of other maytansinoids and this effort is currently underway.<sup>20</sup>

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## References and Notes

- Meyers, A. I.; Tomioka, K.; Roland, D. M.; Comins, D. *Tetrahedron Lett.* **1978**, 1375. Foy, J. E.; Ganem, B. *Ibid.*, **1977**, 775. Corey, E. J.; Bock, M. G.; Kozikowski, A. P.; Rama Rao, A. V.; Floyd, D.; Lipshutz, B. *Ibid.* **1978**, 1051. Gotschi, E.; Schneider, F.; Wagner, H.; Bernauer, K. *Helv. Chim. Acta* **1977**, **60**, 1416. Edwards, D. E.; Ho, P. T. *Can. J. Chem.* **1977**, **55**, 371. Elliot, W. J.; Fried, J. *J. Org. Chem.* **1976**, **41**, 2469.
- Corey, E. J.; Weigel, L. O.; Floyd, D.; Bock, M. G. *J. Am. Chem. Soc.* **1978**, **100**, 2916.
- Kane, J. M.; Meyers, A. I. *Tetrahedron Lett.* **1977**, 771.
- Carpino, L. A.; Tsao, J. H.; Ringsdorf, H.; Fell, E.; Heltrich, G. *J. Chem. Soc., Chem. Commun.* **1978**, 358.
- NMR data for **8**: δ (CDCl<sub>3</sub>) −0.10 (br s, 9), 0.90 (br t, 2, *J* = 7 Hz), 3.18 (s, 3), 3.90 (s, 3), 4.19 (br t, 2, *J* = 7 Hz), 7.03 (br s, 2).

- (6) Protopenova, T. V.; Skoldinov, A. P. *Zh. Obsch. Khim.* **1959**, 29, 963; *Chem. Abstr.* **1960**, 54 1288d.
- (7) NMR data for **11**:  $\delta$  (CDCl<sub>3</sub>) 1.77 (s, 3), 2.0 (br s, 1, OH), 4.02 (br s, 2), 5.95 (d of q, 1,  $J = 1$ , 10 Hz), 6.33 (d, 1,  $J = 13$  Hz), 6.93 (d of d, 1,  $J = 10$ , 13 Hz); IR (film) 3340 cm<sup>-1</sup>.
- (8) Corey, E. J., and Beams, D. J. (*J. Am. Chem. Soc.* **1972**, 94, 7210), utilized this mixed cuprate for conjugate additions to enones.
- (9) NMR data for **3**:  $\delta$  (CDCl<sub>3</sub>) -0.08 (s, 9), 0.85 (br t, 2), 1.67 (s, 3), 3.18 (s, 3), 3.28 (s, 2), 3.88 (s, 3), 4.17 (br t, 2), 5.83 (d of q, 1,  $J = 1.2$ , 11.2 Hz), 6.25 (d, 1,  $J = 13.2$  Hz), 6.70 (s, 2), 7.00 (d of d, 1,  $J = 11.2$ , 13.2 Hz); IR (film) 1710 cm<sup>-1</sup>.
- (10) Meyers, A. I.; Shaw, C. C.; Horne, D. A.; Trefonas, L. M.; Majeste, R. J. *Tetrahedron Lett.* **1975**, 1745.
- (11) Structure assignment was made by Raney Ni desulfurization of **4** followed by acetal exchange (MeOH, pyridinium tosylate), benzylation (NaH, PhCH<sub>2</sub>Br), and ozonolysis (O<sub>3</sub>, Me<sub>2</sub>S) as shown. Both isomers of **18** were



transformed as above and their NMR spectra examined. The major erythro isomer showed C-2, C-3 protons with  $J = 2.8$  Hz and the minor threo isomer showed C-2, C-3 protons with  $J = 6.8$  Hz in agreement with authentic samples prepared in this laboratory.

- (12) Meyers, A. I.; Tait, T. A.; Comins, D. L. *Tetrahedron Lett.* **1978**, 4657.
- (13) Meyers, A. I.; Comins, D. L. *Tetrahedron Lett.* **1978**, 5179.
- (14) Use of the mangeseo adduct **19** and the diene aldehyde derived from **3** (see ref 1 and 2) gave poor yields of addition product in our hands.
- (15) Although **22** was a mixture of epimers at C-10, the mixture was carried through until the final separation of ( $\pm$ )-**2** (vide infra).
- (16) Lown, M. J.; Majumdar, K. C.; Meyers, A. I.; Hecht, A. *Bioorg. Chem.* **1977**, 6, 453.
- (17) IR 1700, 1648, 1602, 1575 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>)  $\delta$  7.19 (d, 1,  $J = 15.3$  Hz), 3.99 (s, 3), 3.34 (s, 3), 3.27 (s, 3), 1.67 (s, 3), 1.40 (s, 3), 1.23 (d, 3,  $J = 6.3$  Hz); mass spectrum  $m/e$  532 ( $M^+ + 2$ ), 530 ( $M^+$ ), 512 ( $M^+ - H_2O$ ), 469 (base,  $M^+ - 61$ ), 454, 434. Both synthetic **2** and the reduction product from maysine **30** gave identical retention times in four different solvent systems (HPLC) and essentially identical mass spectra with slight variations in intensities of  $M^+$  and ( $M^+ - H_2O$ ) peaks.
- (18) Kindly supplied by Dr. A. T. Sneden, Virginia Commonwealth University; the material was purified by HPLC prior to use.
- (19) Kupchan, S. M.; Komoda, Y.; Branfman, A. R.; Sneden, A. T.; Court, W. A.; Thomas, G. J.; Hintz, H. P. J.; Smith, R. M.; Karim, A.; Howie, G. A.; Verma, A. K.; Nagao, Y.; Daily, R. G.; Zimmerly, V. A.; Sumner, W. C. *J. Org. Chem.* **1977**, 42, 2349.
- (20) The total synthesis of maysine (**30**) has been accomplished via the epoxy derivative of **23** and will be reported in due course.

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## Molecular Beam Electric Deflection Analysis of (SN)<sub>x</sub> Vapor. Evidence for a Nonpolar Tetramer

Sir:

Polymeric sulfur nitride ((SN)<sub>x</sub>) is a prototype "nonmetallic" metal.<sup>1</sup> One of its unusual properties is sublimation in vacuo to yield a volatile red-purple substance which repolymerizes to form golden, lustrous films that exhibit the same metallic character as the polymer.<sup>2</sup> The predominant species in the vapor has been shown<sup>3</sup> to be a tetramer (SN)<sub>4</sub>, distinct from the known S<sub>4</sub>N<sub>4</sub> molecule, but the isomeric form of this tetramer has not been established. Both linear and cyclic forms have been postulated.<sup>3,4</sup> Here we report a study of the electrical polarity of the (SN)<sub>x</sub> vapor using the molecular beam electric deflection method.<sup>5,6</sup>

The (SN)<sub>x</sub> vapor was generated from a Knudsen effusion source operated at 420–460 K. The source was made from a Teflon tube with a 12.7-mm i.d. and a 0.34-mm orifice diameter. The vapor was collimated into a beam during passage through two differentially pumped regions and then traversed a quadrupole electric field of 34-cm length and an 0.261-cm

Table I. Mass Spectrum and Electric Deflection Analysis

| ion ( $m/e$ )                                    | source, $T = 460$ K |           | source, $T = 420$ K |           |
|--|---------------------|-----------|---------------------|-----------|
|  | intensity           | % focused | intensity           | % focused |
| S <sub>8</sub> <sup>+</sup> (256)                | 0.7                 |           |                     |           |
| (SN) <sub>4</sub> <sup>+</sup> (184)             | (1.0)               | defocused | (1.0)               | defocused |
| S <sub>4</sub> N <sub>2</sub> <sup>+</sup> (156) | 2.6                 | 32        | 0.8                 | 40        |
| (SN) <sub>3</sub> <sup>+</sup> (138)             | 4.6                 | defocused | 13                  | defocused |
| S <sub>3</sub> N <sub>2</sub> <sup>+</sup> (124) | 0.7                 | 13        | 1.7                 | 13        |
| S <sub>3</sub> N <sup>+</sup> (110)              | 5.3                 | 12        | 1.7                 | 17        |
| S <sub>2</sub> N <sub>2</sub> <sup>+</sup> (92)  | 7.8                 | 3         | 18                  | 12        |
| S <sub>2</sub> N <sup>+</sup> (78)               | 7.9                 | 4         | 20                  | 5         |
| S <sub>2</sub> <sup>+</sup> (64)                 | 5.2                 | 6         | 12                  | 6         |
| SN <sup>+</sup> (46)                             | 33                  | 4         | 100                 | 4         |

effective aperture. A beam stop located at the field exit conceals the detector entrance slit from direct view of the vapor source. When electrostatic potentials of up to 20 kV are applied to the quadrupole electrodes, molecules in positive energy Stark states are deflected or "focused" around the beam stop and enter the mass spectrometer detector. The spectrometer comprises a high-intensity electron bombardment ionizer operated at ~80 eV and a 60° sector electromagnet.

Table I lists the relative intensities observed at 10 mass peaks and the corresponding percentage of the signal at each peak which can be focused by the electric field. In agreement with previous mass spectral work,<sup>3</sup> our results indicate the vapor consists predominantly of a tetramer species, (SN)<sub>4</sub>. We find that (SN)<sub>4</sub> is nonpolar and also observe smaller contributions from one or more polar species. All of the mass peaks that show focusing have been observed<sup>7</sup> in the mass spectrum of S<sub>4</sub>N<sub>2</sub>, with the exception of the weak S<sub>3</sub>N<sub>2</sub><sup>+</sup> peak. Differences in the intensity distribution and the presence of S<sub>3</sub>N<sub>2</sub><sup>+</sup> can both be ascribed to differences in the fragmentation of S<sub>4</sub>N<sub>2</sub> in our ionizer. The S<sub>4</sub>N<sub>2</sub> molecule is polar and is known as a degradation product.<sup>3,8</sup> Likewise, the weak S<sub>8</sub><sup>+</sup> peak indicates that some decomposition of the sample occurred. Our results are also compatible with previous evidence<sup>3,9</sup> that a number of minor species (S<sub>4</sub>N<sub>4</sub>, S<sub>4</sub>N<sub>2</sub>, S<sub>3</sub>N<sub>3</sub>, S<sub>3</sub>N<sub>2</sub>, S<sub>2</sub>N<sub>2</sub>, S<sub>2</sub>N, SN) may exist in the vapor of (SN)<sub>x</sub> even at modest temperatures.

The only mass peaks which yield information regarding the (SN)<sub>4</sub> component are the (SN)<sub>4</sub><sup>+</sup> and (SN)<sub>3</sub><sup>+</sup> peaks. The observation that these peaks are defocused by the electric field indicates the neutral precursor is a nonpolar molecule. The presence of fragments from both polar S<sub>4</sub>N<sub>2</sub> (and possibly other minor polar species) and nonpolar (SN)<sub>4</sub> accounts for the wide variation in focusing behavior observed at the lighter mass peaks. Although our ionizer produces rather severe cracking, we can obtain a crude estimate of the ratio of the polar and nonpolar precursors in the parent beam. If we assume that the 40% focusing observed for S<sub>4</sub>N<sub>2</sub><sup>+</sup> has not been convoluted with a fragment from (SN)<sub>4</sub><sup>+</sup>, we find the lower focusing percentages observed for the lighter mass peaks are consistent if ~85–95% of the parent beam is nonpolar. Previous work estimated that the fraction of (SN)<sub>4</sub> in the vapor exceeded ~85% under comparable conditions.<sup>3</sup>

The isomeric form of the nonpolar tetramer remains an open question. Marked contrasts in the cracking patterns for both electron-bombardment and field ionization mass spectra<sup>3</sup> indicate that (SN)<sub>4</sub> differs structurally from the known "cradlelike" and nonpolar cyclic molecule S<sub>4</sub>N<sub>4</sub>. The fragmentation pattern indeed suggests a "quasilinear", open-chain structure for (SN)<sub>4</sub>. Such a structure would have an electric dipole moment and thus appears inconsistent with our results. However, the open-chain form cannot definitely be ruled out. The dipole moment may be small, and, if there exist a number of low-frequency vibrational modes ( $\leq 200$  cm<sup>-1</sup>) that are thermally excited (at 420 K), the net Stark effect could be reduced below the level of detectability.<sup>10</sup> The small vapor-