(6) Protopova, T. V.; Skoldinov, A. P. *Zh. Obsch. Khim.* **1959,** *29*, 963; *Chem. Abstr.* **1960,** *54* 1288d.

(7) NMR data for **11:** δ ($CDCl_3$) 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^{-1}.

(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:** δ ($CDCl_3$) −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^{-1}.

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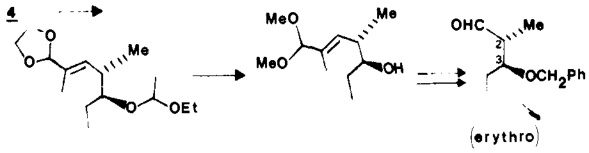
(11) Structure assignment was made by Raney Ni desulfurization of **4** followed by acetal exchange (MeOH, pyridinium tosylate), benzylation (NaH, $PhCH_2Br$), and ozonolysis (O_3, Me_2S) as shown. Both isomers of **18** were



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.

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(14) Use of the mangesio 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 (±)-**2** (vide infra).

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(17) IR 1700, 1648, 1602, 1575 cm^{-1}; NMR ($CDCl_3$) δ 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.

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(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 $(SN)_x$ Vapor. Evidence for a Nonpolar Tetramer

Sir:

Polymeric sulfur nitride ($(SN)_x$) is a prototype "nonmetallic" metal.[1] 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.[2] The predominant species in the vapor has been shown[3] to be a tetramer $(SN)_4$, distinct from the known S_4N_4 molecule, but the isomeric form of this tetramer has not been established. Both linear and cyclic forms have been postulated.[3,4] Here we report a study of the electrical polarity of the $(SN)_x$ vapor using the molecular beam electric deflection method.[5,6]

The $(SN)_x$ 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 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. Mass Spectrum and Electric Deflection Analysis

	source, T = 460 K		source, T = 420 K	
ion (m/e)	intensity	% focused	intensity	% focused
S_8^+ (256)	0.7			
$(SN)_4^+$ (184)	(1.0)	defocused	(1.0)	defocused
$S_4N_2^+$ (156)	2.6	32	0.8	40
$(SN)_3^+$ (138)	4.6	defocused	13	defocused
$S_3N_2^+$ (124)	0.7	13	1.7	13
S_3N^+ (110)	5.3	12	1.7	17
$S_2N_2^+$ (92)	7.8	3	18	12
S_2N^+ (78)	7.9	4	20	5
S_2^+ (64)	5.2	6	12	6
SN^+ (46)	33	4	100	4

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,[3] our results indicate the vapor consists predominantly of a tetramer species, $(SN)_4$. We find that $(SN)_4$ is nonpolar and also observe smaller contributions from one or more polar species. All of the mass peaks that show focusing have been observed[7] in the mass spectrum of S_4N_2, with the exception of the weak $S_3N_2^+$ peak. Differences in the intensity distribution and the presence of $S_3N_2^+$ can both be ascribed to differences in the fragmentation of S_4N_2 in our ionizer. The S_4N_2 molecule is polar and is known as a degradation product.[3,8] Likewise, the weak S_8^+ peak indicates that some decomposition of the sample occurred. Our results are also compatible with previous evidence[3,9] that a number of minor species (S_4N_4, S_4N_2, S_3N_3, S_3N_2, S_2N_2, S_2N, SN) may exist in the vapor of $(SN)_x$ even at modest temperatures.

The only mass peaks which yield information regarding the $(SN)_4$ component are the $(SN)_4^+$ and $(SN)_3^+$ 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_4N_2 (and possibly other minor polar species) and nonpolar $(SN)_4$ 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 $S_4N_2^+$ has not been convoluted with a fragment from $(SN)_4^+$, 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 $(SN)_4$ in the vapor exceeded ~85% under comparable conditions.[3]

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[3] indicate that $(SN)_4$ differs structurally from the known "cradlelike" and nonpolar cyclic molecule S_4N_4. The fragmentation pattern indeed suggests a "quasilinear", open-chain structure for $(SN)_4$. 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 (≲200 cm^{-1}) that are thermally excited (at 420 K), the net Stark effect could be reduced below the level of detectability.[10] The small vapor-

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ization coefficient[4] ($\sim 2 \times 10^{-3}$) and the magnitude of the heat of vaporization[3,4] (30 kcal mol^{-1}, compared with ~50-60 kcal mol^{-1} for the S-N bond strength) both suggest that the vapor species does not have the open-chain structure of the solid polymer but involves an exothermic rearrangement such as ring formation.[4] A comprehensive molecular orbital treatment[11] of the $(SN)_4$ tetramer has described several possible cyclic isomers. Some of these, such as the "chair" form, should have a dipole moment but again might be rendered nonpolar by low frequency vibrations or pseudorotation. There are also two cyclic isomers that lack a dipole moment (and are distinct from S_4N_4); both of these are predicted to have a triplet ground state. Future experiments can test the role of vibrations by cooling the vapor in a supersonic expansion and can look for triplet character by use of magnetic deflection analysis.

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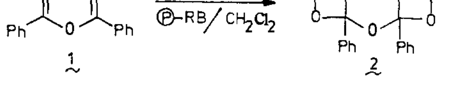
A Stable Bisdioxetane[1]

Sir:

Singlet oxygenation of tetraphenyl-*p*-dioxin (**1**) affords the bisdioxetane **2** (eq 1). This unusual "high energy" substance (a) represents the first authentic and stable bisdioxetane that has been prepared, isolated, and characterized; (b) is unusually stable, melting with decomposition at 103-104 °C, $t_{1/2} = 36$ min at 80 °C, and $E_a = 26 \pm 1$ kcal/mol; (c) affords quantitatively benzoic anhydride on thermal decomposition; (d) produces triplet excited benzoic anhydride in 22 ± 1%, as determined by the triplet-selective benzonorbornadiene titrimetric method;[2] and (e) results in a triplet–singlet excited states ratio $\phi^T/\phi^S \sim 2000$, using the DPA/DBA method.[3] To the best of our knowledge, this novel hyperenergetic molecule is the most efficient chemical source[4] for triplet excited anhydrides.

(eq 1)



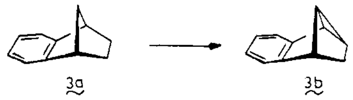
Irradiation of a 0.1 M CH_2Cl_2 (freshly distilled from EDTA disodium salt) solution of *p*-dioxin **1**, prepared by *p*-toluenesulfonic acid catalyzed cyclization of benzoin,[5] with a General Electric 150-W sodium street lamp at −78 °C for 2 h in the presence of polymer-bound Rose Bengal[6] under a continuous stream of dry oxygen gas, afforded the crude bisdioxetane **2** quantitatively after rotoevaporation (0 °C at 10 Torr) of the CH_2Cl_2, positive peroxide test (KI/HOAc). Low temperature (−50 °C) silica gel chromatography, eluting with CH_2Cl_2, afforded analytically pure bisdioxetane **2** (Atlantic Analytical Laboratories, Atlanta, Ga.), mp 103-104 °C (decomposition with light emission), in 70% yield. The structural assignment is based on the following spectral data: ^1H NMR ($CDCl_3$, Me_4Si) δ 7.05 (12 H, meta and para aromatic protons, m), 7.40 ppm (8 H, ortho aromatic protons, m);[7] IR ($CHCl_3$) 3020, 1600, 1470, 1450, 1380, 1175, 910, 690, 640 cm^{-1}. Furthermore, on thermolysis at 80 °C in C_6H_6 benzoic anhydride is formed quantitatively with light emission, as confirmed by comparison of ^1H NMR and IR spectra and TLC (silica gel, CH_2Cl_2 eluant) retention times with those of the authentic material. The above data clearly establish the bisdioxetane structure; however, the stereochemistry of the phenyl substituents, i.e. all syn or syn-anti, is unknown.

On thermal decomposition of 0.0001 M C_6H_6 (freshly distilled from EDTA disodium salt) solutions of **2**, direct chemiluminescence can be visibly observed in a dark room. The direct chemiluminescence emission intensity, monitored on a Mitchell-Hastings photometer,[8] decays via first-order kinetics, affording a rate constant $k_1 = (3.83 \pm 0.10) \times 10^{-4}$ s^{-1} at 80 °C ($t_{1/2} = 36$ min) and an activation energy $E_a = 26 \pm 1$ kcal/mol. Thus, the stability of this novel bisdioxetane is comparable with that of the monodioxetanes such as tetramethyl-1,2-dioxetane.[9]

The direct chemiluminescence efficiency was calculated[9] to be $\phi^{DC} = 7.70 \times 10^{-7}$ einstein/mol from the total initial intensity $I_0 = 4.16 \times 10^{-14}$ einstein/L s, initial bisdioxetane concentration $[\mathbf{2}]_0 = 1.41 \times 10^{-4}$ M, and the first-order rate constant $k_1 = 3.83 \times 10^{-4}$ s^{-1} at 80 °C in C_6H_6. Unfortunately, no photophysical data appears to be published on the fluorescence or phosphorescence of benzoic anhydride to permit estimating the excitation yield from the above ϕ^{DC} data.

For this reason we decided to determine the triplet yield of benzoic anhydride by means of the recently established[2] triplet-selective titrimetric method, in which benzonorbornadiene (**3a**) is converted into its tricyclic isomer **3b** (eq 2) under triplet sensitization. After heating solutions of **2** ([**2**] = 0.0273 M) and **3** ([**3a**] = 0.211-0.529 M) in C_6H_6 at 80 °C in sealed tubes for 4 h to assure complete decomposition of the bisdioxetane **2**, the ratios of [**3b**] to [**3a**] as a function of [**3a**] were determined by GLC.[10] A double reciprocal plot of the chemical yield of **3b** vs. [**3a**] afforded an intercept value of 9.0 ± 0.3 on triplicate analysis. Using the literature value[11] of 0.50 for the photoisomerization yield of **3b** from **3a**, the triplet benzoic anhydride yield from **2** was determined to be 22 ± 1%.

(eq 2)



We then proceeded to determine the triplet/singlet ratio, i.e., ϕ^T/ϕ^S, employing the well-established DPA vs. DBA enhanced chemiluminescence technique.[3] Using C_6H_6 solutions which contained [**2**] = 1.45×10^{-5} M and [DPA] = [DBA] = $(1.0\text{-}10.0) \times 10^{-3}$ M, the enhanced chemiluminescence yields (ϕ^{EC}) for DPA and DBA were separately de-

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