entirely, to the variable rate of $^{10}B$ and $^{11}B$ quadrupole relaxation, which progressively "washes out" the boron-hydrogen spin-spin coupling. The boron spin-lattice relaxation follows an $\tilde{\eta}/T$ dependence, which implicates hydrodynamic (frictional) effects in the description of molecular reorientation leading to quadrupole relaxation, though inertial effects are also probably operating. Computation of the molecular correlation time based on a hydrodynamic model allows a reasonably accurate estimation of the nuclear quadrupole coupling constants, which are identical for I and II: $^{10}B$, 3.5 ± 0.6 MHz; $^{11}B$, 1.7 ± 0.3 MHz. These values indicate the metal-ligand bonding deviates significantly from an ionic description, and are qualitatively in accord with the covalent properties of the molecules. The Arrhenius activation energies for molecular reorientation are, within experimental error, the same for $Zr(BH_4)_4$ and $Hf(BH_4)_4$, 3.1 ± 0.1 kcal/mol. There is no evidence that an intramolecular rearrangement process is rapid enough to compete with molecular tumbling as a mechanism for quadrupolar relaxation.

**Acknowledgments.** We thank the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank the Vogelback Computation Center for a generous grant of computer time, the Office of Research Coordination for a summer grant-in-aid (T. J. M.), and W. R. Grace and Co. for generous gifts.

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# Reaction of Tetrasulfur Tetranitride with Strained Olefins[1]

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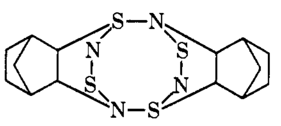
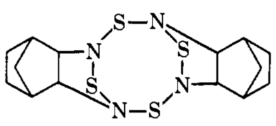
*Received July 8, 1971*

**Abstract:** Tetrasulfur tetranitride has been shown to undergo cycloaddition reactions with strained, rigid bicyclic olefins such as norbornene and other [2.2.1] bicyclic systems. The nmr, ir, and mass spectra of the resulting bis cycloadducts indicate that the norbornyl unit is bonded to $S_4N_4$ through the nitrogen atoms and has the exo-cis stereochemistry. Total exchange in solution of one norbornyl unit for another was demonstrated, and competition experiments enabled the establishment of a relative reactivity sequence.

The study of the chemistry of tetrasulfur tetranitride, $S_4N_4$, has revealed an intriguing and complex pattern of structure and reactivity.[2-4] Tetrasulfur tetranitride has been shown to undergo Lewis acid-base, redox, and ring contraction reactions. Becke-Goehring and Schwarz have reported some novel adducts which are formed from $S_4N_4$ and norbornene, norbornadiene, and cyclopentadiene in an apparent cycloaddition reaction.[5] They proposed a 1,4-cycloaddition wherein the olefin is bonded to alternate sulfur and nitrogen atoms, as in **1**. However, no convincing evidence was presented to support this proposed structure. Josey has shown that the interaction of $S_4N_4$ with substituted acetylenes leads to 1,2,5-triadiazoles;[6] this suggests attack solely on nitrogen (as in **2**) as a possibility for the olefin system. Recent MO calculations coupled with orbital symmetry considerations suggest attack solely on sulfur (as in **3**).[7] Since, with the exception of the work of Becke-Goehring and Schwarz, cycloaddition reactions are unknown for inorganic heterocycles which contain multiple bonds, such as $S_4N_4$, we have investigated this system in order to establish the effect of reaction conditions on the nature of the product, the type of olefin capable of undergoing this reaction, and the structures of the products.



**1**



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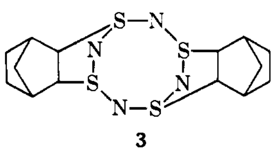

**3**

## Experimental Section

**Materials.** Tetrasulfur tetranitride[8] and 2,3-trithianorbornane, $C_7H_{10}S_3$,[9] were prepared by published procedures. All other reactants and solvents were available commercially and used without further purification.

**Measurements.** The 60-MHz proton nuclear magnetic resonance (nmr) spectra were recorded on a Varian A-60 spectrometer and the 100-MHz nmr spectra on a JEOL MH-100 spectrometer. All nmr spectra were run in deuteriochloroform with TMS as an internal standard. Mass spectra were obtained with a Perkin-Elmer RMU-4 mass spectrometer operating at 70 eV and 130°. Infrared spectra were recorded on Perkin-Elmer Model 51 and Beckman Model 5A (CsBr) spectrophotometers. Raman spectra were recorded on a JEOL JRS-S1 Laser Raman spectrometer using an Ar-ion laser. Photolysis reactions were carried out using

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(1) Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April 1971.

(2) M. Becke-Goehring, *Progr. Inorg. Chem.*, **1**, 207 (1959).

(3) C. W. Allen, *J. Chem. Educ.*, **44**, 38 (1967).

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(6) A. D. Josey, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Division of Organic Chemistry, p 14.

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(8) M. Villena-Blanco and W. L. Jolly, *Inorg. Syn.*, **9**, 98 (1967). *Caution should be exercised in handling $S_4N_4$ due to its explosive nature.*

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**Table I.** Melting Point and Analytical Data for $S_4N_4[olefin]_2$

| Olefin | Mp, °C | Calculated, % C | Calculated, % H | Calculated, % N | Calculated, % S | Found, % C | Found, % H | Found, % N | Found, % S |
|---|---|---|---|---|---|---|---|---|---|
| Norbornene, $C_7H_{10}$ | 143 | 45.16 | 5.38 | | | 45.23 | 5.12 | | |
| Norbornadiene, $C_7H_8$ | 199 | 45.65 | 4.35 | | | 45.23 | 4.43 | | |
| Dicyclopentadiene, $C_{10}H_{12}$ | 145 | 53.57 | 5.36 | | | 53.95 | 5.69 | | |
| 5-Norbornenol, $C_7H_9OH$[a] | 160 | 41.58 | 4.95 | 13.86 | 31.68 | 41.86 | 5.24 | 13.69 | 32.15 |
| 5-Methylenenorbornene, $C_8H_{10}$ | 135 | 48.48 | 5.05 | 14.14 | 32.32 | 47.91 | 5.25 | 14.21 | 32.00 |

[a] Extreme insolubility prevented normal purification of this compound.

the Nester-Faust-400 power supply unit with the NFUV-300 low-pressure mercury lamp. Melting points were determined on a Thomas-Hoover melting point apparatus and were not corrected. Elemental analyses were carried out by the Galbraith and Robertson Laboratories.

**Syntheses.** All of the adducts could be prepared by the same procedures, so only the synthesis of the bisnorbornene adduct, $S_4N_4(C_7H_{10})_2$, will be described. All the adducts are white solids obtained in 94–98% yield. For a particular olefin, identical products are formed (as indicated by mixture melting points and infrared and nmr spectroscopy), independent of the mode of synthesis. Melting points and analytical data for the products may be found in Table I.

**Preparation of $S_4N_4(C_7H_{10})_2$. Procedure 1.** To a mixture of 1.84 g (0.01 mol) of $S_4N_4$ in 75 ml of anhydrous diethyl ether was added 4.70 g (0.05 mol) of norbornene. The mixture was refluxed for 24 hr. A white solid was formed and collected by filtration. The solid was washed with three 20-ml portions of anhydrous ether. The yield was 3.60 g (96.7% of theory). The white solid was dissolved in chloroform, and several drops of anhydrous diethyl ether were added. A white crystalline compound slowly came out of solution. Similar results were obtained using benzene as the solvent.

**Procedure 2.** A 150-ml Erlenmeyer flask was charged with 1.85 g (0.01 mol) of $S_4N_4$ and a large excess of norbornene (18.8 g, 0.1 mol). The solid mixture was heated to 65° in a water bath to melt the norbornene. The mixture was stirred; after two minutes the orange mixture turned white. The white solid was allowed to cool to room temperature and then 100 ml of anhydrous diethyl ether was added. The excess norbornene was dissolved in the ether, and the white solid was isolated by filtration. Further purification of the white solid was carried out as described in Procedure 1.

**Procedure 3.** To a solution of 0.92 g (0.005 mol) of $S_4N_4$ in 300 ml of dry chloroform was added 2.35 g (0.25 mol) of norbornene. The solution was then placed in a standard photolysis cell, and a quartz finger containing a mercury lamp was inserted. The entire photolysis cell was submerged in an ice–water bath contained in a 20-l. dewar bottle. The photolysis was allowed to continue for 2 hr, after which time a heavy, white flocculent matter was observed to be suspended in the chloroform. The reaction was stopped and the solution filtered, leaving approximately 0.1 g of light brown powder. The powder decomposed at 450° and was assumed to be polymeric. The solution was evaporated to dryness and the remaining solid washed with three 25-ml portions of anhydrous diethyl ether to remove excess norbornene. The remaining product was purified as described in Procedure 1.

**Unreactive Systems.** A wide variety of olefins were allowed to react with $S_4N_4$ by procedures 1, 2, and 3. In each case only $S_4N_4$ and unreacted olefin, or hydrocarbon degradation products were obtained. Unreactive olefins included cyclohexene; cyclopentene; 1,5-cyclooctadiene; maleic anhydride; dichloromaleic anhydride; tetracyanoethylene; bicyclo[2.2.2]oct-2-ene; 3-methyl-1,3-butadiene; 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hepta-2,3-diene; 5-norbornene-2,3-dicarboxylic anhydride; 3-bromotricyclo[2.2.1.0$^{2,6}$]-heptane; and methylenecyclobutane.

**Olefin Exchange Reactions.** A mixture of any of the olefin adducts with an excess of any other of the reactive olefins found in Table I resulted in the quantitative formation of the adduct of the free olefin. A typical reaction, the exchange reaction between $S_4N_4(C_7H_{10})_2$ and $C_8H_{10}$, is described as follows. To a solution of 0.37 g (0.001 mol) of $S_4N_4(C_7H_{10})_2$ in 10 ml of chloroform was added 3.96 g (0.01 mol) of $C_8H_{10}$. Upon addition of the $C_8H_{10}$, the red color immediately disappeared and the solution remained colorless. Within 5 min, a white solid came out of solution. The white solid was collected by filtration and was washed with three 10-ml portions of anhydrous diethyl ether and was shown to be $S_4N_4(C_8H_{10})_2$ by its nmr spectrum and melting point.

**Competition Reactions.** A series of reactions was carried out in which $S_4N_4$ was allowed to react with two olefins simultaneously. These reactions are detailed in Table II. A typical reaction, the reaction of $S_4N_4$ with $C_7H_{10}$ and $C_{10}H_{12}$, is described as follows. To a mixture of 1.84 g (0.01 mol) of $S_4N_4$ in 90 ml of anhydrous diethyl ether were added 1.88 g (0.02 mol) of $C_7H_{10}$ and 2.44 g (0.02 mol) of $C_{10}H_{12}$. The mixture was stirred under refluxing conditions for 10 hr. The resulting white solid was purified by the method described in Procedure 1. The remaining solution was evaporated to dryness and the resulting solid was purified as described in Procedure 1. The solids were identical (mp 126°). *Anal.* Calcd for $S_4N_4 \cdot C_7H_{10} \cdot C_{10}H_{12}$:[10] C, 49.76; H, 5.35. Found: C, 49.25; H, 5.34.

**Table II.** Competition Reactions, $S_4N_4 + 2L + 2L'$

| L | L′ | Product |
|---|---|---|
| $C_7H_{10}$ | $C_8H_{10}$ | $S_4N_4 \cdot C_7H_{10} \cdot C_8H_{10}$ |
| $C_7H_{10}$ | $C_7H_8$ | $2S_4N_4(C_7H_8)_2 : 1S_4N_4(C_7H_{10})_2$[a] |
| $C_8H_{10}$ | $C_{10}H_{12}$ | $S_4N_4 \cdot C_8H_{10} \cdot C_{10}H_{12}$ |
| $C_7H_8$ | $C_{10}H_{12}$ | $S_4N_4(C_7H_8)_2$ |
| $C_7H_8$ | $C_8H_{10}$ | $S_4N_4(C_7H_8)_2$ |

[a] Ratio assigned by integrated area of former olefinic and bridgehead proton in nmr spectra.

## Results and Discussion

**Structure of the Adducts.** The nmr spectra of the olefins and the adducts were found to be most helpful in determining the structure of the adducts. The chemical shifts ($\delta$)[11] in parts per million of the protons for the olefinic centers in the norbornyl-type olefins and in the adducts can be found in Table III. (Numbering is as in I.) In all cases, the absorption assigned to the protons on the olefinic center disappear upon adduct

**Table III.** Selected $^1H$ Nmr Data of $S_4N_4$ Adducts[a]

| Free olefin | $\delta^b$ | Adduct | $\delta^b$ |
|---|---|---|---|
| $C_7H_{10}$ | 5.95 | $S_4N_4(C_7H_{10})_2$ | 4.20 |
| $C_7H_8$ | 6.70 | $S_4N_4(C_7H_8)_2$ | 4.40 |
| $C_{10}H_{12}$ | 5.90 | $S_4N_4(C_{10}H_{12})_2$ | 4.18 |
| $C_8H_{10}$ | 6.05 | $S_4N_4(C_8H_{10})_2$ | 4.32 |

[a] There are no data available for $S_4N_4(C_7H_{10}O)_2$ owing to the insolubility of the adduct. [b] Chemical shifts correspond to positions 2 and 3 of the free olefin and in the adduct (for numbering of compound, see structure I).

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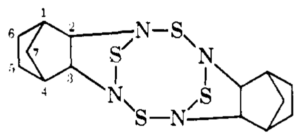
(10) We have formulated these products as the mixed adduct based on the nmr spectra and elemental analyses. An alternate formulation would be an equimolar mixture of the appropriate symmetrically substituted diadducts, *e.g.*, $S_4N_4(C_7H_{10})_2$ and $S_4N_4(C_{10}H_{12})_2$.

(11) There is no significant variation in chemical shift with concentration. If excess olefin is added to a solution of the adduct, one can observe both the free and reacted olefinic centers each unshifted upon mixing. Thus, ligand exchange is slow on the nmr time scale.



I

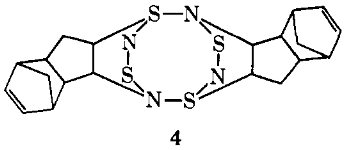
formation. Concomitantly, a new peak appears in the region of 4.2–4.4 ppm. This peak is assigned to the protons at the former olefinic bond. The integrated area of this peak is equal to the area for the methine protons at positions 1 and 4, indicating that this peak represents two protons.

In the nmr spectra (60 and 100 MHz) of $S_4H_4(C_7H_{10})_2$, there is only a single line for the protons at the former olefinic bond, implying a symmetrical structure, *i.e.*, either **2** or **3**. Norbornanes which are N substituted in the 2 and 3 positions have chemical shifts for the protons in the 2 and 3 positions around 4.5 ppm, while the corresponding substitution of sulfur gives shifts from 3.0 to 3.6 ppm.[9,12,13] Therefore, the chemical shifts for all the adducts in Table III indicate a norbornyl unit attached to nitrogen atoms at the 2 and 3 positions as in structure **2**. This single peak also rules out the trans isomer, since the protons in the 2 and 3 positions would have observably different chemical shifts for the trans isomer.[14]

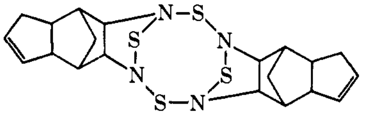
The nmr spectrum of $S_4N_4(C_7H_8)_2$ indicated one olefinic center has reacted while the other remains. The splitting in the doublet arising from the protons at the former olefin bond is constant (~2 Hz) at 60 and 100 MHz, indicating that it arises from spin–spin coupling. Decoupling experiments show that the coupling is not with the methine protons (1 and 4), so it is assumed to be due to the proton in the 7 position; this is in accord with previous observations. Higher multiplicity is obtained in the case of the endo-cis isomers of 2,3-dibromonorbornane and 5,6-dibromonorbornene. The exo-cis isomers invariably show a doublet.[15] Therefore, the exo-cis configuration has been assigned to the adducts.

The olefinic protons at positions 2 and 3 in the nmr spectrum of $C_8H_{10}$ absorb at 6.05 ppm. The exocyclic olefinic protons at position 5 are nonequivalent and absorb at 4.69 and 4.95 ppm. The nmr spectrum of $S_4N_4(C_8H_{10})_2$ clearly shows that the carbon atoms at positions 2 and 3 are the ones bonded to $S_4N_4$, since the exocyclic olefinic protons are present in the adduct.

Becke-Goehring suggests that the interaction of $S_4N_4$ and cyclopentadiene results in initial formation of $S_4N_4(C_5H_6)_2$ followed by a cycloaddition reaction between the remaining olefinic center in $S_4N_4(C_5H_6)_2$ and cyclopentadiene to give **4**.[5] However, cyclopentadiene dimerization is fast compared to the $S_4N_4$ cycloaddition reaction and furthermore, one obtains the same product from either cyclopentadiene or dicyclopentadiene. We also noted that the remaining olefinic center in $S_4N_4(C_7H_8)_2$ was unreactive in further cycloaddition reactions with either $S_4N_4$ or cyclopentadiene. In the nmr spectrum, the protons at the former olefinic bond of $S_4N_4(C_{10}H_{12})_2$ did not show the complexity which one would associate with **4**. Based on these observations, we assigned structure **5** to $S_4N_4(C_{10}H_{12})_2$.



**4**



**5**

The mass spectrum of $S_4N_4(C_7H_{10})_2$ contains neither the parent ion nor $S_4N_4^+$. Furthermore, it does not contain the $S_3N_2^+$ ion which is very prominent in the spectrum of $S_4N_4$.[16] It does, however, contain the principal peak at *m/e* 66 which is the $C_5H_6^+$ ion usually found in the mass spectra of norbornyl molecules. In addition, there are peaks at *m/e* 42, 43, 44, 56, and 57, which are common to amines.[17,18] There are no peaks in the mass spectrum of $S_4N_4(C_7H_{10})_2$ that could be attributed to a fragment containing carbon–sulfur bonds.

The infrared spectra (4000–280 cm$^{-1}$) of the adducts listed in Table I are all similar, the only differences being due to changes in the parent olefin. There is a medium-weak band at approximately 670 cm$^{-1}$ in $C_7H_{10}S_3$ which can be assigned to a carbon–sulfur stretching mode in a 2,3-substituted norbornane. There is no corresponding band in $S_4N_4(C_7H_{10})_2$. There are several weak bands in the carbon–nitrogen region (1220–1020 cm$^{-1}$) in both $C_7H_{10}S_3$ and $S_4H_4(C_7H_{10})_2$, so nothing can be concluded about carbon–nitrogen stretching modes. Carbon–sulfur stretching modes appear as intense bands in Raman spectra; the Raman spectrum of $S_4N_4(C_7H_{10})_2$ showed no evidence for a carbon–sulfur stretching mode. Unfortunately, however, some of the region of interest was obscured by solvent absorption.

The only sulfur–nitrogen stretching mode which can be clearly identified in the olefin adducts is the band which appears at 705 cm$^{-1}$ in $S_4N_4$.[19] This band is shifted to 690 cm$^{-1}$ in the adducts, suggesting a weakening of the sulfur–nitrogen bond on adduct formation.

In $S_4N_4$ there is an SSN bending mode at 341 cm$^{-1}$;[19] this band occurs at 327 cm$^{-1}$ in the olefin adducts. This decrease suggests a moving away from the rigid cage structure found in $S_4N_4$. In tetrasulfur tetraimide, $S_4N_4H_4$, this band is shifted to approximately 300 cm$^{-1}$.[20]

The accumulated spectroscopic evidence indicates a structure in which the norbornane unit is bonded to the sulfur–nitrogen ring at nitrogen centers and has the exo-cis configuration. If we assume that the cycloaddition reaction is a concerted one, then attack on

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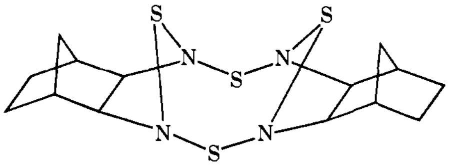
consecutive nitrogen atoms is the most reasonable situation. The high value of the ring bending modes for the adducts compared to $S_4N_4H_4$ suggests a less drastic reorganization of the $S_4N_4$ structure than that observed for $S_4N_4H_4$[21] and for the Lewis acid adducts $S_4N_4 \cdot SbCl_5$[22] and $S_4N_4 \cdot BF_3$.[23] Therefore, we propose a structure[24] such as **6** for the $S_4N_4 \cdot$ olefin adducts.



**6**

**Synthesis and Reactivity.** As opposed to many cycloaddition reactions, the synthesis of $S_4N_4$ olefin adducts does not show any sensitivity to solvent polarity. The same products and the same yields were obtained by using diethyl ether, benzene, or the olefin as the solvent. Furthermore, identical products were obtained in both thermal and photochemical reactions. This observation is of interest in that orbital symmetry arguments not only predicted attack on the sulfur atoms but also that photochemical and thermal reactions would be mutually exclusive.[7]

The fact that normally reactive olefins such as maleic anhydride, dichloromaleic anhydride, and tetracycanoethylene are not reactive toward $S_4N_4$ implies that $S_4N_4$ is an electron-poor species.[25] Since no reaction took place with cyclohexene, cyclopentene, or cycloocta-1,5-diene, it appears that ring size alone is not the determining factor. The lack of reactivity of an exocyclic olefin such as methylenecyclobutane, and the exocyclic bond in $C_8H_{10}$, indicates that acyclic olefins are not good substrates. Even alterations in the norbornyl unit resulted in lack of adduct formation, as evidenced by the lack of reactivity of 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hepta-2,3-diene and 5-norbornene-2,3-dicarboxylic anhydride. Changes in the carbocyclic structure of the norbornene nucleus also resulted in a lack of reactivity, as indicated by the behavior of bicyclo[2.2.2]oct-2-ene. The failure of 2-methyl-1,3-butadiene to form a cycloadduct shows the unreactivity of a conjugated acyclic olefin. It was also shown in the case of 3-bromotricyclo[2.2.1.0$^{2,6}$]heptane that a strained $\sigma$ bond is also unreactive. Therefore, based on the nature of the olefins which do undergo adduct formation and the dipolar character of the sulfur–nitrogen bonds in $S_4N_4$,[2,3] it appears that the observed reactions be considered to be examples of 1,3-dipolar additions to a class of dipolarophilic olefins.

Competition experiments (Table II) indicate that $S_4N_4(C_7H_8)_2$ is always formed when $C_7H_8$ is present. The fact that some $S_4N_4(C_7H_{10})_2$ is formed when both $C_7H_8$ and $C_7H_{10}$ are present, whereas $C_8H_{10}$ and $C_{10}H_{12}$ cannot compete with $C_7H_8$, places $C_7H_{10}$ higher than the latter two olefins in the reactivity sequence. Mixtures of $S_4N_4$ with $C_8H_{10}$ and $C_{10}H_{12}$ yield the mixed adduct (or mixture of adducts), indicating similar reactivities. Hence, the following order of reactivity was established

$$C_7H_8 > C_7H_{10} > C_8H_{10} \sim C_{10}H_{12}$$

The fact that $C_7H_8$ is the most reactive member of the series may reflect simply a frequency factor; however, inductive effects are suggested by the differential reactivity of the other olefins. Further work is in progress to clarify this matter and to establish that this is a kinetic and not a thermodynamic phenomenon.

When the norbornyl adducts listed in Table I were dissolved in any solvent, the initially colorless solution turned to canary yellow and then to red at room temperature. If the solution was heated immediately upon dissolution, the color change was rapid. This observation suggests that the cycloadducts were dissociating in solution to give the olefin and $S_4N_4$. The color of the adducts in solution is attributed to $S_4N_4$, which results from this dissociation, since it has been established that $S_4N_4$ exhibits thermochromism in solution.[26] If so, then the observed color change is not due to the formation of a charge-transfer complex as postulated by Becke-Goehring.[5] Further work is in progress to clarify this point.

It was shown by total exchange reactions that there is a certain degree of dissociation in solution. This reaction is slow on the nmr time scale. The isolation of the adduct of the olefin in excess can be interpreted as simply a mass action effect on the equilibrium.

**Acknowledgment.** The Raman spectrum and the 100-MHz nmr spectra were obtained courtesy of JEOL Corp. The mass spectrum was obtained courtesy of Perkin-Elmer Corp. Support form an NSF institutional grant is gratefully acknowledged.

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(24) The chair form, which differs from **6** by interchanging a sulfur atom and a norbornane ring with respect to the plane of the nitrogen atoms, is also possible. Structure **6**, however, requires less reorganization of the $S_4N_4$ unit upon adduct formation.

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