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An Addition Compound of Tetrasulfur Dinitride and Dicyclopentadiene

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Introduction

Previous investigations have suggested that the structure of tetrasulfur dinitride is most likely that of a cyclic molecule with the nitrogen atoms located in the 1,3 positions with perhaps a small degree of non-planarity [1–3]. The reactive nature of this material as well as its physical properties, a red oil at ordinary temperatures, make X-ray structural studies of the material difficult [4]. In this note we report the synthesis of and a partial structure elucidation for the dicyclopentadiene addition compound of tetrasulfur dinitride. Some structural information about the parent compound S_4N_2 can be inferred from the structure of the adduct.

Experimental

Freshly distilled dicyclopentadiene was introduced into a hexanes solution of tetrasulfur dinitride [5]. The solution was refluxed for 48 hours, filtered and poured over a column of silica gel. The silica gel had been previously heated at 200 °C for 17 hours. The column was eluted with a mixture of hexanes–CCl_4 (1:1 by volume). The addition compound was the third material eluted from the column (R_f value 0.17) being preceded by dicyclopentadiene (R_f = 0.90) and S_4N_2 (R_f = 0.50). The R_f value of S_8 was taken as 1.00. The solvent was removed by vacuum and the material taken up and recrystallized from benzene. The material is a bright red crystalline solid (m.p. 129–131 °C with decomposition). *Anal.*: carbon calc. 41.6, found 43.3; hydrogen calc. 4.19, found 4.40; nitrogen calc. 9.71, found 9.44; sulfur calc. 44.46, found 42.17. $S_4N_2C_{10}H_{12}$ is soluble in benzene. The infrared spectra were recorded on a Beckman Model IR 12 infrared spectrometer over the range 650–4000 cm^{-1}. A KBr pellet technique was used.

TABLE I. Mass Spectrum of Adduct of Tetrasulfur Dinitride and Dicyclopentadiene[a].

m/e	Relative Intensity	m/e	Relative Intensity
288	2	209	17
258	27	208	11
257	14	196	19
256	28	195	15
230	43	194	32
229	43	193	7
228	100	192	79
226	18	164	51
224	15	163	100
212	7	162	9
211	7	161	5
210	48	160	80

[a] The spectrum consisted of peaks of high relative intensity from m/e ratio 159 to 1.

The mass spectra were measured on a CEC Model 110 mass spectrometer using a 7ev ionizing potential.

Results and Discussion

It is significant that the organic olefin adds to tetrasulfur dinitride as the dimer unit and not as a monomer unit. All attempts to synthesize a compound of the form S_4N_2(cp) or S_4N_2(cp)(cp)′ failed [6]. If addition of two monomer units had occurred one would expect to observe an $S_4N_2(C_5H_6)$ fragment unit in the mass spectrum. The peak (mass number 222) was never observed. This can be compared with the behavior of tetrasulfur tetranitride where cycloaddition reactions have been observed with [2.2.1]bicyclic olefins. The same product is obtained from the reaction of N_4S_4 and cyclopentadiene starting with either the monomer or dicyclopentadiene [7, 8].

Table I contains the mass spectrum of the material for the m/e range of 160–288. In Figure 1 we illustrate nine possible structures for the 1:1 adduct. D denotes the dicyclopentadiene moiety. The presence

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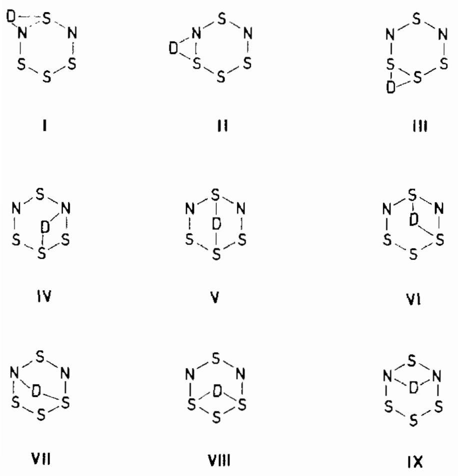

Figure 1. Possible structures of $S_4N_2 \cdot C_{10}H_{12}$ adduct.

TABLE II. IR Spectrum of Adduct of Tetrasulfur Dinitride and Dicyclopentadiene[a].

cm^{-1}			
2950 (s)	1441 (m)	991 (w)	742 (s)
2920 (s)	1351 (w)	941 (m)	702 (m)
2850 (m)	1266 (w)	790 (w)	678 (m)
1458 (m)	1103 (s)	770 (w)	615 (w)

[a] w, weak; m, medium; s, strong.

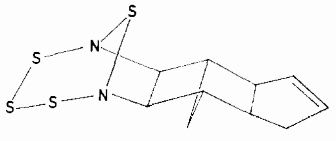

Figure 2. Proposed structure for the dicyclopentadiene adduct of tetrasulfur dinitride.

of the 256 peak and the 228 peak (DS_3) indicate a structure with the capability of losing either a sulfur atom or a SN_2 fragment. This observation eliminates all structures which contain the diene bonded to the S_4N_2 molecule forming a –S–D–N– bridge. Thus structures III, VIII, and IX are viable possibilities. Of these structures, III and VIII should readily give NS in a primary fragmentation process and give a 242 ($C_{10}H_{12}S_3N$) peak in the spectrum. Absence of a 242 peak argues against structures III and VIII. On the other hand, the high intensity of the 228 peak (DS_3) strongly argues for structures VIII or IX. Of these only structure IX can account for the 160 peak (DN_2), unless one admits the possibility of ion rearrangement reactions occurring upon fragmentation of VIII. On the basis of mass spectra we are unable to clearly define the structure of the adduct although the possibilities seem to be limited to an adduct which involves either 3,4 addition to adjacent sulfur atoms; 3,5 addition to sulfur atoms, or 2,6 addition across the ring *via* nitrogen atoms.

The infrared spectrum of the adduct is shown in Table II. One should be able to observe either C–N or C–S modes depending upon the nature of the bond to the diene. The infrared spectrum shows a strong band at 1103 cm^{-1} which might be indicative of a carbon–nitrogen bond. Neither tetrasulfur dinitride or dicyclopentadiene absorb in this region. Aliphatic amines generally absorb in the 1020–1220 range. The remaining absorptions (678, 702, 941, 1441, 1458, 2920, 2952) can be traced to cyclopentadiene or S_4N_2 [2]. Thus the IR spectrum supports structure IX and excludes the possibility of addition between sulfur atoms. A tentative structure is illustrated in Figure 2.

Griffin and Sheldrick have shown by X-ray that tetrasulfur tetranitride and norbornadiene form an adduct in which the diene adds so as to form a five membered, –C–S–N–S–C– ring [9]. This is to be contrasted with the work of Brinkman and Allen who concluded that addition was through the two nitrogen atoms.

It appears that the later is preferred in the cycloaddition of dicyclopentadiene to S_4N_2.

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