

Acta Cryst. (1975). B31, 895**Tetrasulphur Tetranitride-Bis(norbornadiene)**

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Abstract. $C_{14}H_{16}N_4S_4$, monoclinic, $C2/c$, $a = 16.69$ (2), $b = 8.57$ (1), $c = 10.96$ (1) Å, $\beta = 103.67$ (5)°, $U = 1523$ Å³, $Z = 4$, $D_x = 1.607$ g cm⁻³. One C=C bond in each diene molecule adds across an S-N-S unit to give a five-membered C-S-N-S-C- ring. The product retains the eight-membered (NS)₄ ring, and possesses a crystallographic centre of symmetry. Some mean bond lengths and angles are: S-N, 1.62 (2); S-C, 1.84 (2) Å; N-S-N, 118.0 (13); S-N-S, 126.4 (13) [eight-membered ring] and 118.5 (13)° [both rings]. The structure was refined to an R of 0.101 for 338 unique diffractometer data.

Introduction. Becke-Goehring & Schläfer (1968) found that S_4N_4 forms adducts with cyclopentadiene, norbornene and bicycloheptadiene, which they suggested were analogous to Diels-Alder products, the S_4N_4 acting as a diene to form six-membered C-C-N-S-N-S-rings whilst retaining an eight-membered (NS)₄ ring. Brinkman & Allen (1972) proposed structures involving five-membered C-C-N-S-N- rings on the basis of n.m.r., infrared, Raman and mass spectra. The structure determination reported here shows that both of these proposed structures are incorrect.

Intensities were determined with an automated Stoe two-circle diffractometer, Mo $K\alpha$ radiation, graphite monochromator, and two crystals of approximate dimensions $0.048 \times 0.053 \times 0.139$ mm (layers $h0l$ to $h6l$) and $0.033 \times 0.033 \times 0.285$ mm (layers $hk0$ to $hk9$). The compound was prepared by refluxing a 1:2 molar ratio of S_4N_4 and norbornadiene in benzene, and recrystallized from nitrobenzene. [Found: C 45.7%, H 4.38%, N 15.4%, S 35.1%; calculated for $C_{14}H_{16}N_4S_4$: C 45.7%, H 4.35%, N 15.2%, S 34.8%.] Interlayer scale factors were derived by a linear least-squares analysis of common reflexions; 1112 reflexions with intensities greater than 3σ based on counting statistics were merged to give 338 unique observed reflexions. Cell dimensions were obtained from diffractometer zero-layer ω angle measurements.

The structure was solved by multiresolution tangent refinement in the space group Cc , but the best E map, which revealed all but one atom, corresponded to the centrosymmetric space group $C2/c$. This space group was confirmed by the successful refinement of the structure; the molecule possesses a crystallographic centre of symmetry, and the asymmetric unit consists of half of one molecule. Hydrogen atom coordinates were calculated geometrically, and the structure refined with the constraint that the C-H vectors were fixed in

magnitude and direction but with the carbon atoms free to move (Sheldrick, 1975). The final weighted residual $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o|$ was 0.088, with a corresponding unweighted residual R of 0.101. The weighting scheme employed was $w = [\sigma^2(N) + 0.001N^2]^{-1} / (41.98 + |F_o| + 0.00687 F_o^2)$, where N is the net peak count and the summation is over equivalent reflexions. Complex neutral-atom scattering factors were used (Cromer, 1965; Cromer & Waber, 1965). Final atomic coordinates are given in Table 1 and the resulting interatomic distances and angles in Tables 2-4.*

Discussion. The molecule possesses a unique and unexpected fused-ring system. The planes of the two five-membered C-C-S-N-S- rings are almost perpendicular

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30658 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atom coordinates ($\times 10^4$) and isotropic temperature factors ($\text{Å}^2 \times 10^3$)*

	x/a	y/b	z/c	U
S(1)	181 (4)	2933 (8)	4247 (6)	†
S(2)	1234 (4)	5196 (8)	5544 (7)	†
N(1)	-814 (12)	3282 (25)	4008 (18)	59 (6)
N(2)	776 (10)	4380 (21)	4216 (16)	39 (6)
C(1)	1071 (14)	938 (28)	6158 (22)	43 (7)
H(1)	838 (14)	-17 (28)	5531 (22)	57 (30)‡
C(2)	501 (12)	2442 (22)	5921 (16)	22 (6)
H(2)	-74 (12)	2321 (22)	6201 (16)	57 (30)
C(3)	1074 (15)	3691 (29)	6675 (22)	48 (7)
H(3)	855 (15)	4238 (29)	7422 (22)	57 (30)
C(4)	1895 (14)	2742 (32)	7195 (22)	54 (7)
H(4)	2437 (14)	3454 (32)	7524 (22)	57 (30)
C(5)	1655 (13)	1601 (27)	8089 (22)	42 (7)
H(5)	1834 (13)	1683 (27)	9100 (22)	57 (30)
C(6)	1199 (13)	547 (30)	7460 (21)	44 (7)
H(6)	944 (13)	-447 (30)	7843 (21)	57 (30)
C(7)	1932 (15)	1590 (29)	6116 (22)	59 (8)
H(7)	1939 (15)	2156 (29)	5238 (22)	57 (30)
H(8)	2427 (15)	748 (29)	6338 (22)	57 (30)

† Anisotropic temperature factors were employed for S(1) and S(2) in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$. For S(1), U_{11} to U_{12} were 84 (5), 27 (4), 31 (4), -15 (4), 12 (4) and -10 (5) Å² × 10³ respectively, and for S(2), U_{11} to U_{12} were 42 (4), 40 (5), 80 (6), 16 (5), 6 (4) and -6 (4) Å² × 10³ respectively.

‡ An overall isotropic hydrogen atom temperature factor was employed.

Table 2. Bond lengths (Å)

S(1)—N(1)	1.65 (3)	C(1)—C(6)	1.43 (3)
S(1)—N(2)	1.59 (2)	C(1)—C(7)	1.55 (3)
S(2)—N(1)	1.61 (3)	C(2)—C(3)	1.54 (3)
S(2)—N(2)	1.63 (2)	C(3)—C(4)	1.58 (4)
S(1)—C(2)	1.83 (3)	C(4)—C(5)	1.50 (4)
S(2)—C(3)	1.85 (3)	C(4)—C(7)	1.55 (4)
C(1)—C(2)	1.59 (3)	C(5)—C(6)	1.27 (3)

Table 3. Bond angles (°)

N(2)—S(1)—N(1)	117.7 (13)	C(3)—C(2)—S(1)	112.0 (17)
N(1')—S(2)—N(2)	118.2 (13)	C(3)—C(2)—C(1)	101.8 (19)
S(1')—N(1')—S(2)	126.4 (13)	C(1)—C(2)—S(1)	111.8 (17)
S(2)—N(2)—S(1)	118.5 (13)	C(2)—C(3)—S(2)	107.1 (18)
C(2)—S(1)—N(1)	104.2 (13)	C(4)—C(3)—C(2)	102.2 (21)
C(2)—S(1)—N(2)	99.4 (12)	C(4)—C(3)—S(2)	110.6 (19)
N(1')—S(2)—C(3)	102.6 (13)	C(5)—C(4)—C(3)	103.2 (20)
C(3)—S(2)—N(2)	100.8 (13)	C(7)—C(4)—C(5)	98.5 (23)
		C(7)—C(4)—C(3)	103.9 (22)
C(7)—C(1)—C(6)	101.1 (22)	C(6)—C(5)—C(4)	109.1 (24)
C(7)—C(1)—C(2)	103.1 (21)	C(5)—C(6)—C(1)	107.6 (26)
C(6)—C(1)—C(2)	107.2 (21)	C(4)—C(7)—C(1)	90.1 (22)

Table 4. Intra- and intermolecular distances

Short intramolecular distances (<3.7 Å)			
S(1)—S(2)	2.77	N(2)—C(2)	2.62
S(1')—S(2)	2.91	N(2)—C(3)	2.69
S(1')—N(2)	3.46	N(2)—C(4)	3.64
S(2')—N(2)	3.44	N(2)—C(7)	3.45
N(1')—N(2)	2.78	N(2')—C(2)	3.44
N(2')—N(2)	3.59	N(2')—C(3)	3.43
N(1)—N(2)	2.77		
		C(1)—C(3)	2.43
S(1)—C(1)	2.84	C(1)—C(4)	2.20
S(1)—C(3)	2.80	C(1)—C(5)	2.19
S(1)—C(7)	3.35	C(2)—C(4)	2.43
S(1')—C(3)	3.57	C(2)—C(5)	2.78
S(2)—C(2)	2.73	C(2)—C(6)	2.43
S(2')—C(2)	3.59	C(2)—C(7)	2.46
S(2)—C(4)	2.82	C(3)—C(5)	2.42
S(2)—C(7)	3.31	C(3)—C(6)	2.82
N(1)—C(2)	2.75	C(3)—C(7)	2.47
N(1')—C(2)	3.70	C(4)—C(6)	2.27
N(1')—C(3)	2.71	C(5)—C(7)	2.32
N(2)—C(1)	3.60	C(6)—C(7)	2.31
Intermolecular distances (<3.8 Å)			
S(1 ⁱ)—S(1)	3.73	N(1 ^{iv})—C(1)	3.64
S(2 ⁱⁱ)—C(5)	3.69	N(1 ^{iv})—C(6)	3.64
N(1 ⁱ)—N(2)	3.67	C(7 ^v)—C(7)	3.77
N(2 ⁱⁱⁱ)—C(3)	3.37		
Intermolecular H...H distances (<2.8 Å)			
H(7 ^v)—H(7)	2.14	H(1 ^{iv})—H(1)	2.76
H(4 ⁱⁱ)—H(8)	2.31	H(2 ^{vi})—H(2)	2.80
H(2 ^{vi})—H(3)	2.76		
Intermolecular distances to hydrogen (<3.2 Å)			
S(1 ^{iv})—H(1)	3.06	C(4 ⁱⁱ)—H(8)	3.10
S(1 ^{vi})—H(6)	3.07	H(2 ^{vi})—C(5)	2.99
N(1 ^{iv})—H(1)	2.85	H(2 ^{vi})—C(6)	3.05
N(1 ^{iv})—H(6)	3.14	H(4 ⁱⁱ)—C(6)	2.89
N(2 ⁱⁱⁱ)—H(3)	2.33	H(4 ⁱⁱ)—C(7)	3.13
H(1 ^{iv})—C(2)	3.19	C(7 ^v)—H(7)	2.78

Key to symmetry transformations. Superscript: (i) $-x, y, \frac{1}{2}-z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, 1\frac{1}{2}-z$; (iii) $x, 1-y, \frac{1}{2}+z$; (iv) $-x, -y, 1-z$; (v) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (vi) $-x, y, 1\frac{1}{2}-z$; (vii) $x, -y, \frac{1}{2}+z$.

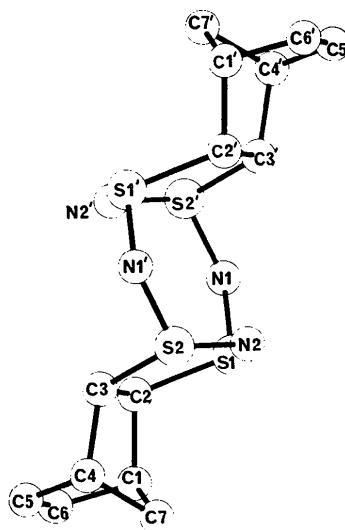


Fig. 1. One molecule of the adduct.

to the approximate plane containing six of the eight atoms in the (SN)₄ ring (Fig. 1). In retrospect, the n.m.r. spectrum and decoupling experiments of Brinkman & Allen (which we have confirmed) are consistent with either N...N or S...S addition, but not N...S addition. In contrast to the structures of N₄S₄F₄ (Wiegiers & Vos, 1963) and N₄S₄[ON(CF₃)₂]₄ (Forder & Shelldrick, 1971), the conformation of the eight-membered ring is also quite different from that in these two structures, with a centre of symmetry rather than a crystallographic inverse tetrad axis. The S—N bond lengths (mean 1.62 (2) Å) are close to the mean value in S₄N₄ of 1.616 (10) Å (Sharma & Donohue, 1963), indicating appreciable multiple-bond character, but the N—S—N and S—N—S angles are wider. There are no particularly short intermolecular distances (Table 4).

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