Synthesis and Crystal Structure of $(S_3N_3O_4)_2S$,† a Compound with Two Six-membered Rings bridged by a Sulphur Atom

Herbert W. Roesky,* William Clegg, Jürgen Schimkowiak, Martin Schmidt, Michael Witt, and George M. Sheldrick *
Institut für Anorganische Chemie der Universität, Tammannstrasse 4, D-3400 Göttingen, West Germany

---

The compound $S_4N_4O_2$ reacts with SO_2 under mild conditions to yield $(S_3N_3O_4)_2S$, a new bicyclic system with a skeleton consisting only of sulphur and nitrogen atoms. Crystals of this compound are tetragonal, space group $P\bar{4}2_1m$, with $a = b = 1\,183.8(2)$, $c = 493.5(1)$ pm, and $Z = 4$. The structure has been refined to $R = 0.027$ for 637 unique observed reflexions. The molecule possesses crystallographic *mm* symmetry, with both mirror planes passing through the sulphur atom which links the two six-membered rings. The bond lengths and angles are consistent with the presence of localised sulphur–di-imide (–N=S=N–) units, the remaining sulphur–nitrogen bonds being essentially single bonds.

While interest in sulphur–nitrogen compounds has been maintained for many years,[1] little effort has been directed towards the preparation of sulphur-bridged rings. The only derivatives previously described were obtained by coupling two S_7NH molecules with SCl_2, S_2Cl_2, S_3Cl_2, and S_5Cl_2, in the presence of a stoicheiometric amount of pyridine, giving $(S_7N)_2S$, $(S_7N)_2S_2$, $(S_7N)_2S_3$, and $(S_7N)_2S_5$, respectively.[2]

It has recently been shown that tetrasulphur tetranitride reacts with SO_3 to yield the 1 : 1 Lewis adduct.[3] We have therefore studied the analogous reaction between $S_4N_4O_2$ and SO_3.

Experimental

Preparation of $(S_3N_3O_4)_2S$.—The compound $S_4N_4O_2$ was prepared from $SO_2(NH_2)_2$ and $S_3N_2Cl_2$ in carbon tetrachloride.[4] It (1.5 g) was then placed in a dried Schlenk apparatus equipped with a frit. The apparatus was evacuated and SO_3 (1.44 g) as well as SO_2 (30 cm^3) condensed in using liquid N_2. The mixture was warmed slowly to 0 °C and stirred at this temperature for another hour. Sulphur dioxide and unreacted SO_3 were removed under vacuum. The residue was extracted twice with SO_2 (30 cm^3). A brown solid remained. After slowly removing the SO_2 from the filtrate, pale yellow needles formed, which were purified by recrystallisation from SO_2. Yield: 60%, m.p. 101—120 °C (decomp.) (Found: N, 19.4; S, 51.2. $N_6O_8S_7$ requires N, 19.25; S, 51.4%). The i.r. spectrum of a Nujol mull was recorded in the range 400—4 000 cm^{-1} on a Perkin-Elmer 257 spectrometer: 1 428vs, 1 405vs, 1 221s, 1 200vs, 1 136s, 1 100vs, 930w, 840s, 800m, 720vs, 640s, 615w, 546s, 520w, and 450s cm^{-1}.

X-Ray Structural Analysis.—Intensities were collected at 17 °C by a real-time profile-fitting procedure[5] on a Stoe-Siemens four-circle diffractometer with graphite-monochromated Mo-K_α radiation and a crystal of approximate dimensions 0.6 × 0.2 × 0.2 mm (sealed in a Lindemann-glass capillary). 2 208 Reflexions were measured in the range $7 < 2\theta < 50°$. After application of Lorentz, polarisation, and empirical absorption corrections (based on 400 measurements of equivalent reflexions at different azimuthal angles) the data were merged to yield 637 unique reflexions with $F > 4\sigma(F)$, which were employed for all calculations. The unit cell was determined by a least-squares fit to the optimum angles for 40 strong reflexions, 2θ values being determined from ω measurements at ±2θ.

Crystal data. $N_6O_8S_7$, Tetragonal, space group $P\bar{4}2_1m$, $a = b = 1\,183.8(2)$, $c = 493.5(1)$ pm, $U = 0.6916$ nm^3, $Z = 4$, $D_c = 2.525$ Mg m^{-3}, $F(000) = 436$, Mo-K_α radiation, $\lambda = 71.069$ pm, $\mu = 1.14$ mm^{-1}.

The structure was solved by multisolution tangent refinement, all the atoms being present in the best E map, although because of the special positions involved the molecule was not immediately recognised. Least-squares refinement, with all atoms anisotropic, complex neutral-atom scattering factors, and the weighting scheme $w = [\sigma^2(F) + 0.0002F^2]^{-1}$, converged to $R' = \Sigma w^{\frac{1}{2}}|\Delta|/\Sigma w^{\frac{1}{2}}|F_o| = 0.028$ and $R = 0.027$. A final difference map showed no peaks higher than 0.42×10^{-6} e nm^{-3}. The results are given in Tables 1 and 2 and the Figure. Calculations were performed using the SHELXTL program system (written by G. M. S.).

Table 1. Atomic co-ordinates (× 10^4)

Atom	x	y	z
S(1)	5 000	0	4 219(3)
N(1)	4 204(2)	796(2)	2 108(8)
S(2)	2 885(1)	379(1)	1 136(2)
O(1)	2 650(2)	−647(2)	2 455(6)
O(2)	2 820(3)	463(3)	−1 697(5)
N(2)	2 077(2)	1 348(3)	2 436(6)
S(3)	2 421(1)	2 579(1)	3 002(3)

Table 2. Bond lengths (pm) and angles (°)

S(1)–N(1)	169.1(2)	N(1)–S(1)	170.7(3)
S(2)–O(1)	140.5(3)	S(2)–O(2)	140.4(3)
S(2)–N(2)	162.5(3)	N(2)–S(3)	153.9(3)
N(1)–S(1)–N(1a)	104.0(2)	S(1)–N(1)–S(2)	121.5(2)
S(1)–N(1)–S(2a)	121.5(2)	S(2)–N(1)–S(2a)	116.8(1)
N(1)–S(2)–O(1)	107.5(1)	N(1)–S(2)–O(2)	108.0(2)
O(1)–S(2)–O(2)	120.8(2)	N(1)–S(2)–N(2)	102.9(1)
O(1)–S(2)–N(2)	108.1(2)	O(2)–S(2)–N(2)	108.1(2)
S(2)–N(2)–S(3)	125.8(2)	N(2)–S(3)–N(2a)	117.9(2)

---

† 2,2′-Thiobis(1,1,3,3-tetraoxo-$1\lambda^6,3\lambda^6,5\lambda^4$,2,4,6-trithiatriazine).
Supplementary data available (No. SUP 23366, 6 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

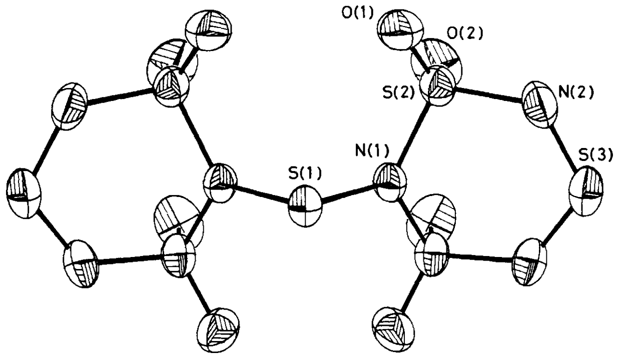
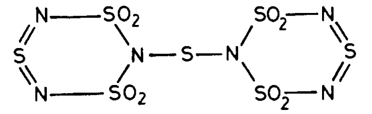


Figure. The molecule of $(S_3N_3O_4)_2S$ showing 50% probability thermal ellipsoids

Results and Discussion

We reported recently[6] that the reaction of $S_4N_4O_2$ with excess of SO_3 at room temperature results in the formation of $S_3N_2^+$-$S_3N_3O_4^-$ and $S_3N_2O_5$. The present study shows that at lower temperature and with a smaller quantity of SO_3 the primary product isolated is $(S_3N_3O_4)_2S$, in which two six-membered rings are linked by a sulphur atom. This intermediate may provide a convenient route to the preparation of organometallic derivatives containing the $S_3N_3O_4$ ring.

The $(S_3N_3O_4)_2S$ molecule exhibits crystallographic *mm* symmetry. The six-membered rings lie perpendicular to one mirror plane, and the bridging sulphur atom lies on the line of intersection of the mirror planes. There are thus seven crystallographically independent atoms, two of which lie on special positions of *m* symmetry and one on a special position of *mm* symmetry. The sulphur atom [S(3)] furthest from the bridge makes the shortest S–N bonds [153.9(3) pm] and has the largest N–S–N angle [117.9(2)°], and as a first approximation may be considered to take part in a sulphur-di-imide system with localised S=N double bonds, as shown below.



Conjugation of the sulphur–nitrogen bonds is then broken by the ' saturated ' sulphurs of the SO_2 groups. However, the triply connected nitrogen lies only 5.7(6) pm out of the plane of the three sulphur atoms to which it is bonded, which might also be taken to imply some degree of N–S π bonding. This nitrogen atom lies 73.1(5) pm out of the plane of the other five ring atoms, which themselves are effectively coplanar (root-mean-square deviation 1.1 pm). This distortion from planarity and the accompanying rotations of the SO_2 units enables the molecule to increase the O(1) ··· O(1′) distance between the rings, which would otherwise be very short, to 285.3(4) pm. At the same time the distance O(2) ··· O(2″) across the ring is reduced to 287.3(4) pm. It is likely that these short O ··· O contacts impose a relatively rigid and symmetrical conformation on the molecule.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft and to the Fonds der Chemischen Industrie for financial support.

References

1 H. W. Roesky, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 239.
2 H. G. Heal, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 375.
3 A. Gieren, B. Dederer, H. W. Roesky, N. Amin, and O. Petersen, *Z. Anorg. Allg. Chem.*, 1978, **440**, 119.
4 H. W. Roesky, M. Witt, M. Diehl, J. W. Bats, and H. Fuess, *Chem. Ber.*, 1979, **112**, 1372.
5 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
6 H. W. Roesky, M. Witt, J. Schimkowiak, M. Schmidt, M. Noltemeyer, and G. M. Sheldrick, *Angew. Chem.*, 1982, **94**, 541.

Received 22*nd March* 1982; *Paper* 2/494