The *X*-Ray Crystal and Molecular Structure of Tetrasulphur Dinitride

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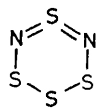
Summary A low-temperature (−100 °C) *X*-ray crystallographic analysis of S_4N_2 shows that it consists of a six-membered ring in a 'half-chair' conformation, with the nitrogen atoms in the 1,3-positions.

THE existence of tetrasulphur dinitride, S_4N_2, has been known since the last century.[1,2] The compound can be prepared *via* a wide variety of methods,[3] and is also found as a contaminant in the thermal decomposition of S_4N_4 to S_2N_2.[4] However, because of its low melting point (23 °C) and thermal instability, precise structural information on the molecule has been difficult to obtain. Using the results of mass, vibrational, and ^{14}N n.m.r. spectroscopy and dipole-moment measurements, Nelson and Heal reduced the number of structural alternatives to the structure (**1**), but could make no firm assignment regarding the conformation.[5] In 1972 Jolly suggested a conformation in which the central atom of the S–S–S unit was tilted out of the plane of the other five atoms.[6] Subsequently, however, CNDO/2 calculations by Adkins and Turner indicated such an arrangement to be less stable than the completely planar ring.[7] In order to resolve this controversy, we have carried out a low-temperature crystal structure determination of S_4N_2.



(1)

Crystals of S_4N_2 suitable for *X*-ray work were obtained by recrystallization of a freshly sublimed sample (prepared by the reaction of *cyclo*-S_8 and S_4N_4 in toluene)[8] from diethyl ether at −20 °C. *Crystal data*: S_4N_2, M = 156·25, tetragonal, space group $P4_2nm$, $a = b$ = 11·146(4), c = 3·773(1) Å, U = 468·7 Å^3, Z = 4, D_c = 2·21 g cm^{-3}; crystal dimensions: 0·1 × 0·2 × 0·2 mm, μ(Mo-K_α) = 17·68 cm^{-1}. A total of 914 reflections were measured at −100(5) °C and averaged to give 438 unique reflections of which 295 had $I \geqslant 3\sigma(I)$. The data were collected on a CAD4F diffractometer equipped with a graphite monochromator with Mo-K_α radiation (λ 0·71069 Å) and operated in the $\omega/2\theta$ scan mode. The structure was solved by direct methods and refined by full-matrix least-squares techniques to give a final, unweighted R of 0·021.†

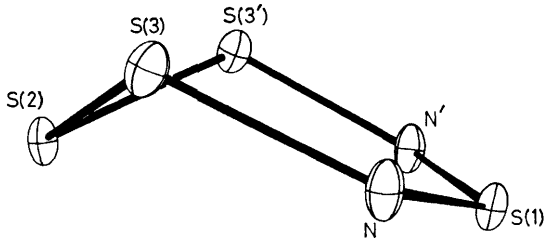


FIGURE. ORTEP drawing (50% probability ellipsoids) of S_4N_2 showing the atomic numbering scheme. Bond distances and angles (e.s.d.s in parentheses) are: S(1)–N 1·561(4), N–S(3) 1·676(4), and S(3)–S(2) 2·061(2) Å; angles at S(1) 122·9(2), N 126·7(2), S(2) 102·9(1), and S(3) 103·4(2)°.

† The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

The structure of S_4N_2 is shown in the Figure. There are no intermolecular contacts shorter than 3·32 Å. The molecule consists of a six-membered ring with the two nitrogen atoms occupying the 1,3-positions. At least from a descriptive point of view, the molecule adopts a conformation which is intermediate between the chair shape of S_6[9] and the planar $S_3N_3^-$ anion.[10] Thus, the S(3)–N–S(1)–N′–S(3′) unit is planar to within 0·03 Å, with the S(3)–S(2)–S(3′) plane rotated away from it by an angle of 54·9°. As suggested by Jolly, this geometry probably reduces lone-pair repulsions on adjacent sulphur atoms and alleviates the angle strain at S(2).[6] The S(2)–S(3) bonds [2·061(2) Å] and the S(3)–S(2)–S(3′) angle [102·9(1)°] are very similar to the corresponding parameters in S_6 [*d*(S–S) 2·06 Å, angle at S 102°) and the internal angles at S(1) [122·9(2)°] and N [126·7(2)°] are not much larger than those found in $S_3N_3^-$ (angles at S 117°, N 123°). The S–N bond lengths, however, do deviate significantly from the value found for $S_3N_3^-$ (1·60 Å). The S(1)–N bonds are shortened to 1·561(4) Å, approaching the S–N distance in Me–N=S=N–Me (1·53 Å)[11], and the S(3)–N bonds are lengthened to 1·676(4) Å, a trend which is in agreement with the π-bond orders calculated by Adkins and Turner.[7] The apparent weakness of the S(3)–N bonds may provide some insight into the mechanism of the thermal decomposition of the molecule. Thus, cleavage of these two bonds would generate an S_3 and an N_2S unit; the latter rapidly disproportionates into dinitrogen and sulphur,[12] the known decomposition products of S_4N_2.[8] Such a pathway is consistent with several other thermal transformations undergone by conjugated S–N systems, all of which proceed *via* the elimination of N_2S.[13]

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