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1,3,4-Thiadiazole at 220 K

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Abstract. $C_2H_2N_2S$, tetragonal, $P4_12_12$ or its enantiomorph; $a=5{\cdot}324$, $c=12{\cdot}643$ Å. Cell dimensions indicate a stacking of the molecules along the c axis. No intermolecular contacts seem to occur in the crystalline state, in agreement with the relatively low melting point and observed diffuse scattering of X-rays at room temperature. The calculated density assuming 4 molecules/cell is $\varrho=1{\cdot}60$ g cm^{-3}. It was difficult to measure the density because of the limited amount and size of the material provided; it was, however, possible to observe crystals in gravitational equilibrium in CCl_4 ($\varrho=1{\cdot}6$ g cm^{-3}) before they dissolved.

Introduction. A small sample of crystals, of which three were suitable for diffraction work, was kindly provided by Dr L. Nygaard. The crystals were prismatic with dimensions $0{\cdot}2\times0{\cdot}2\times0{\cdot}3$ mm. As the crystals were very hygroscopic they were sealed in glass capillaries under dry nitrogen. It was decided to use this compound as a test for a low-temperature device built by the author, because of its low melting point (303 K) and high volatility at room temperature.

Preliminary precession photographs showed the symmetry $4/mmm$ and systematic absences $00l$: $l\neq4n$ and $h00$, $0k0$: $h,k\neq2n$, indicating the tetragonal space groups $P4_12_12$ or $P4_32_12$, and with unit-cell dimensions $a=5{\cdot}33$ and $c=12{\cdot}7$ Å. Because of the limited number of crystals available, data were collected at only one temperature, 220 K. No space-group transition occurred in the temperature range 220–300 K.

Three-dimensional film data were collected at 220 K on a Supper–Buerger precession camera using Zr-filtered Mo radiation. The temperature was monitored continuously with an iron–constantan thermocouple placed in such a way that the crystal was positioned between the cold-nitrogen nozzle and the thermocouple. Variations in temperature never exceeded 3 °C.

The crystal used for data collection was mounted with the direction [110] along the spindle. Two exposures, of 4 and 8 h, with two films in the cassette were taken for each level and optical densities were measured using a manually operated Nonius densitometer. The films within each level were scaled together using the Hamilton, Rollett & Sparks (1965) least-squares procedure, corrected for Lorentz and polarization effects and finally scaled three-dimensionally and symmetry-averaged. Due to the cooling device only about 60% of the 350 independent reflexions out to $2\theta=60°$ were accessible. Of these, 45 reflexions were recorded as unobserved, and 30 reflexions were discarded due to either spot doubling or poor agreement in scaling and symmetry averaging. Only the remaining 109 independent structure-factor amplitudes were used in solving and refining the structure.

Since the unit cell contains only 4 sulphur atoms, these must occupy the 4 special equivalent positions. A three-dimensional Patterson synthesis revealed, in addition to the three S–S Harker peaks, the S–C and S–N peaks. A structure-factor calculation using the positions from the Patterson map, and isotropic B values of 2 Å^2 for sulphur and 3 Å^2 for carbon and nitrogen, showed an agreement between observed and calculated structure factors of $R=0{\cdot}18$ $\{R=[\sum(|F_o|-|F_c|)^2/\sum|F_o|^2]^{1/2}\}$ after the observations were put on the absolute scale derived from a Wilson plot. Subsequent least-squares refinement reduced the R value to 0·082, where in the last cycle the scale factor, atomic positions and isotropic thermal parameters were refined. The scattering factors were those of Cromer & Waber (1974). The hydrogen-atom bound to carbon was placed at the expected position and given a temperature factor of 5 Å^2. Two more cycles refining the scale factor and positional and thermal parameters for the nonhydrogen atoms converged with an R value of 0·072. Refinement of hydrogen atom parameters was not attempted.

The following computer programs were used in solving and refining the structure.

DATARED: an Algol program, written by the author, for converting raw film densities to three-dimensional structure-factor amplitudes.

FOURIER: a crystallographic Fourier summation program based on the logic of A. Zalkin's program *FORDAP*.

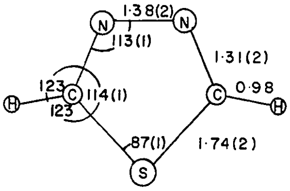

Fig. 1. The molecular geometry of 1,3,4-thiadiazole. The numbers in parentheses are standard deviations in the least significant digits.

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NUCLS: a full-matrix least-squares program based on Busing and Levy's *ORFLS* and revised by Doedens and Ibers.

ORFFE: a crystallographic function and error program written by Busing, Martin and Levy and containing W. C. Hamilton's least-squares plane routine.

Table 1. *Least-squares parameters and their estimated standard deviations*

Parameters for hydrogen were not refined.

	x	y	z	B_{iso}
S	0·2145 (5)	0·2145 (5)	0·0	0·81 (9) Å^2
C	0·5273 (26)	0·2369 (28)	0·0377 (11)	2·4 (3)
N	0·6273 (18)	0·4571 (21)	0·0199 (10)	1·9 (3)
H	0·61	0·1	0·065	5·0

Results and discussion. Table 1 shows the refined parameters and their estimated standard deviations.*

Fig. 1 shows the geometry of the molecule. An unweighted least-squares plane through the 5 non-hydrogen atoms has the equation $-1\cdot472X+1\cdot472Y+11\cdot636Z=0\cdot0$ and makes an angle of 10° with the *ab* plane. Considering the quality of the data, the molecule is assumed to be planar and to have symmetry C_{2v}, since all the atoms are closer than 0·02 Å to the plane.

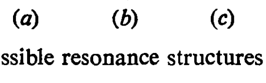
This implies that the atoms in the ring are sp^2 hybridized, with a possible exception of sulphur. Hence a high degree of electron delocalization must take place with the effect of bond shortening as compared to non-aromatic 5-membered rings.

In a recent paper, Downie, Harrison, Raper & Hepworth (1972) describe the structure of a derivative of 1,3,4-thiadiazole (5-amino-2-thiol-1,3,4-thiadiazole). Owing to asymmetric substitution at the two carbon atoms, the molecule they describe no longer possesses C_{2v} symmetry. However, part of the molecule, the S(1)–C(1)–N(1)–N(2) sequence, seems to have the same electron distribution in the bonds as that found in the present study.

Downie *et al.* found the following bond distances: S(1)–C(1): 1·746, C(1)–N(1): 1·305 and N(1)–N(2): 1·382 Å, in good agreement with the unsubstituted molecule. They conclude that the C–N bond has a 60% double-bond character based on Wheatley's (1955) order/length curve for C–N bonds, and the C–S bond has about 50% double character based on Abrahams's (1956) scale.

This means that the predominant structures are those shown in Fig. 2(*a*) and (*b*). The contribution of (*c*) is of minor importance owing to the greater electronegativity of N compared with C, thereby making structure (*b*) more favourable than (*c*). The high degree of double-bond character in the C–N bond might reflect the ability of the lone-pair electrons on nitrogen to interfere with the distribution of the electrons in the ring by 'pushing' bonding electrons into the C–N bond. At the same time repulsive forces between the nitrogen lone-pair orbitals would increase the N–N bond length. This explanation is in agreement with observations on the crystal structure of pyrazole (la Cour & Rasmussen, 1973), where a hydrogen atom is bound to one of the nitrogen atoms and the other nitrogen atom is involved in a relatively strong hydrogen bond. Here the observed bond lengths are N–N: 1·352 (3) and N–C: 1·33 (1) Å, *i.e.* there is a lengthening of the C–N bond and a shortening of the N–N bond by engaging lone-pair electrons in bonding.

It is a well-known fact that molecular geometry as determined by X-ray diffraction methods, especially where a substantial fraction of the electrons are distributed asymmetrically around the atomic nucleus, reflects the positions of electron-density centroids rather than those of the nuclei. However, these ambiguities do not weaken the observations described in the present work on thiadiazole and the previously mentioned work on pyrazole, since both molecules have been studied by microwave techniques by Bak, Nygaard, Pedersen & Rastrup-Andersen (1966) and Nygaard, Lykke Hansen, Tormod Nielsen, Rastrup-Andersen, Sørensen & Steiner (1972) and their results are in agreement with the X-ray structures.



(*a*) (*b*) (*c*)

Fig. 2. The possible resonance structures of thiadiazole.

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* A table of observed and calculated structure-factor amplitudes has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30366 (2pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.