

The Structure of *N*-Methyl-1,4-dithiane-2,3-dicarboximide

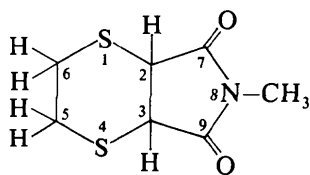
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Abstract. $C_7H_9NO_2S_2$, monoclinic, $P2_1/c$, $a = 13.55$ (2), $b = 6.34$ (2), $c = 10.08$ (2) Å, $\beta = 90.0$ (5)°, $V = 865.94$ Å³, $D_x = 1.56$, $D_m = 1.52$ Mg m⁻³, $Z = 4$, $F(000) = 424$, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu_{\text{av}} = 0.5$, $\mu(\text{Cu } K\alpha) = 4.94$ mm⁻¹. The structure was solved by direct methods and refined by least-squares methods with anisotropic temperature factors to an R of 0.07 for 662 observed reflections. The 1,4-dithiane ring has a boat conformation, with asymmetry parameters $\Delta C_s(1) = 6.60$, $\Delta C_s(2,3) = 8.91$ °. The imide ring is nearly planar and nearly perpendicular to the C(2)–C(3)–C(5)–C(6) plane in the boat ring.

Introduction. We are studying the structures of *N*-substituted derivatives of 5,6-dihydro-1,4-dithiin-2,3-dicarboximide and 1,4-dithiane-2,3-dicarboximide (Bukowska-Strzyżewska, Dobrowolska & Pniewska, 1979; Bukowska-Strzyżewska & Pniewska, 1979*a,b*). The compounds were obtained in the Department of Chemistry at Łódź University during a search for new heterocyclic compounds possessing high biological activity (Hahn & Ryczyński, 1971, 1976). The most interesting problems in the present work were the determination of the conformation of the 1,4-dithiane ring and its mode of combination with the imide ring. The existence of two isomers of the investigated compound suggested that they differed in the *cis*–*trans* arrangement of the H atoms at the carbons joining the two rings. The present paper includes the results of the investigation of the structure of one of these isomers; its formula and atom numbering are given below.



The *cis* isomer of the title compound crystallizes from ethanol in the monoclinic system. The cell dimensions were determined from Weissenberg photographs taken with Cu radiation. The density was determined by flotation in CH_3I solution in benzene.

Equi-inclination Weissenberg film data were collected with the multiple-film technique on the 0 to 4 and 0 to 6 layers around the y and z crystal axes respec-

tively. The intensities were visually estimated with a calibrated intensity scale. In total 662 reflections were collected. No absorption correction was made.

The structure was solved by direct methods using the *SIGMA 2* and *PHASE* programs of the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) on a RIAD 32 computer. The three-dimensional Fourier synthesis located the remaining atoms. The positional and isotropic thermal parameters were refined by the full-matrix least-squares method. Positions of H atoms were determined from geometric considerations. The final refinement was carried out including H atoms with isotropic temperature factors. The final R value for all observed reflections was 0.07. Form factors for neutral atoms were taken from Doyle & Turner (1968) and for H from *International Tables for X-ray Crystallography* (1962). The final positional parameters are listed in Table 1.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34729 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic positional parameters with *e.s.d.*'s in parentheses ($\times 10^4$) and isotropic thermal parameters

The positional parameters are from the anisotropic refinement. Isotropic temperature factors are from the last cycle of isotropic refinement with $R = 0.079$.

	x	y	z	B (Å ²)
S(1)	1572 (2)	8200 (4)	8141 (3)	3.06 (7)
S(4)	1142 (2)	4082 (6)	6526 (4)	4.17 (9)
O(1)	3759 (5)	7213 (13)	9175 (10)	4.15 (20)
O(2)	3238 (6)	1702 (15)	6355 (10)	5.64 (26)
N(8)	3651 (6)	4226 (15)	7951 (10)	3.79 (23)
C(2)	2632 (6)	7040 (15)	7273 (12)	3.00 (24)
C(3)	2384 (7)	5074 (15)	6381 (13)	3.27 (26)
C(5)	1038 (7)	3754 (19)	8278 (15)	4.14 (33)
C(6)	1166 (8)	5892 (20)	9067 (14)	4.72 (33)
C(7)	3430 (7)	6277 (16)	8222 (12)	2.98 (26)
C(9)	3141 (8)	3408 (21)	6846 (13)	3.34 (26)
C(10)	4471 (7)	3095 (19)	8596 (15)	4.97 (35)
H(21)	2877	8336	6660	
H(31)	2430	5488	5343	
H(51)	1599	2660	8603	
H(52)	318	3115	8499	
H(61)	465	6270	9509	
H(62)	1705	5616	9840	

Discussion. Fig. 1 presents a general view of the molecule showing the conformations and mutual positions of the rings and the location of the H atoms. The 1,4-dithiane ring has a boat conformation; the imide ring is nearly planar and almost perpendicular to the central plane of the boat. The angle between the C(2)–C(3)–C(5)–C(6) and C(2)–C(3)–C(7)–N(8)–C(9) planes is 89.5°. H(21) and H(31) are in the *cis* position. The molecule has a 'compact' shape with clearly shortened intramolecular distances between the S atoms, but no interactions between the S atoms and the C atoms of the imide ring. Table 2 presents some of the intramolecular distances between the non-bonded atoms. The shortest distances are S(1)⋯C(7) = 2.799 (11), S(4)⋯C(9) = 2.762 (12), C(6)⋯C(7) = 3.190 (15), C(5)⋯C(9) = 3.202 (16), S(1)⋯S(2) = 3.131 (8) Å. Bond lengths and valency angles are presented in Fig. 2; mean standard deviations take the following values: S–C 0.011, C–C 0.016, C–O 0.016, C–N 0.015 Å, C–S–C 0.5, C–N–C 1.0, S–C–C 0.8, C–C–C 0.8, O–C–C 1.0, O–C–N 1.1, C–C–N 1.0°.

The 1,4-dithiane ring has a boat conformation which is unusual in 1,4-dithiane crystal structures. It gives rise to a considerable shortening of the distance between the S atoms within the ring (3.131 Å), compared with those in 1,4-dithiane rings in chair conformations, which range from 3.45 to 3.48 Å. Fig. 3 presents torsion and dihedral angles in the 1,4-dithiane ring. Asymmetry parameters (Duax & Norton, 1975) calculated for the ring are: $\Delta C_s(1) = 6.60$ and $\Delta C_s(2,3) = 8.91^\circ$. Thus the ring is a slightly deformed boat. Dihedral angles between the base of the boat C(2)–C(3)–C(5)–C(6) and the planes C(2)–S(1)–C(6) and C(3)–S(4)–C(5) are 45.85 and 49.88° respectively.

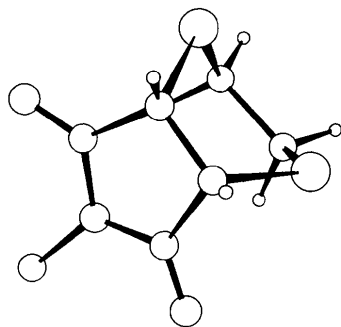


Fig. 1. A general view of *N*-methyl-1,4-dithiane-2,3-dicarboximide.

Table 2. Intramolecular non-bonding distances (Å)

S(1)⋯C(7)	2.799 (11)	C(5)⋯C(9)	3.202 (16)
S(1)⋯O(1)	3.203 (8)	C(5)⋯N(8)	3.568 (14)
S(4)⋯C(9)	2.762 (12)	C(6)⋯C(7)	3.190 (15)
S(4)⋯O(2)	3.221 (10)	C(6)⋯N(8)	3.700 (15)

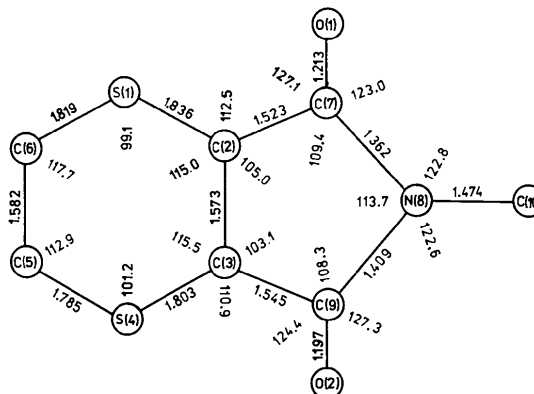


Fig. 2. Intramolecular bond lengths (Å) and angles (°).

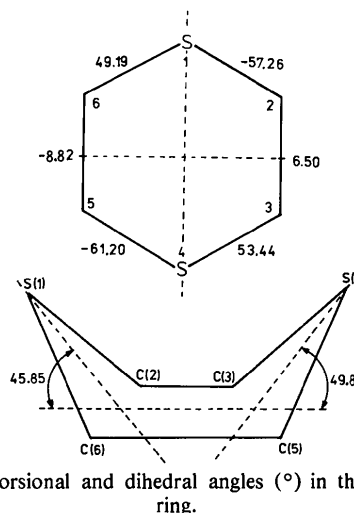


Fig. 3. The torsional and dihedral angles (°) in the 1,4-dithiane ring.

Bond lengths and valency angles agree with values reported previously. In the investigated structure the lengths of the C_{sp^2} –S bonds are 1.836 (10), 1.819 (14), 1.803 (10) and 1.785 (10) Å and in spite of the spread of about 5σ they are within the bond-length range found previously for a number of compounds (Montgomery, 1960; Kalf & Romers, 1965, 1966; Marsh, 1955; Carey, Smith, Maher & Bryan, 1977; McPhail, Onan & Koskimies, 1976; Bukowska-Strzyżewska & Pniewska, 1979a,b; Chao & McCullough, 1960; Kobayashi & Iitaka, 1977). Literature values for the C_{sp^2} –S bonds are in the range 1.770 (30)–1.843 (2) Å. A slight difference in the C–S length in the investigated structure may be a result of intramolecular stress between the dithiane and imide rings. Valency angles at the S atoms are 99.08 and 101.22° which are in agreement with those of known structures containing 1,4- and 1,3-dithiane rings with chair conformations. Literature values of the angles range from 96.4 to 101.5°.

The imide ring is nearly planar. Table 3 shows the deviations of its atoms from their best plane. In spite of

Table 3. Least-squares plane of imide ring and deviations of atoms (Å) from the plane

Equation of the plane in the standard orthogonal system:

$$0.6907X + 0.3181Y - 0.6494Z = -0.9133.$$

C(2)	0.0183 (15)	N(8)	-0.0322 (15)
C(3)	-0.0343 (14)	O(1)*	-0.1132 (16)
C(7)	0.0068 (16)	O(2)*	0.1236 (13)
C(9)	0.0414 (16)	C(10)*	0.0616 (18)

$$\chi^2 = 38.8$$

$$\alpha \leq 0.01$$

* Not included in the calculation of the plane.

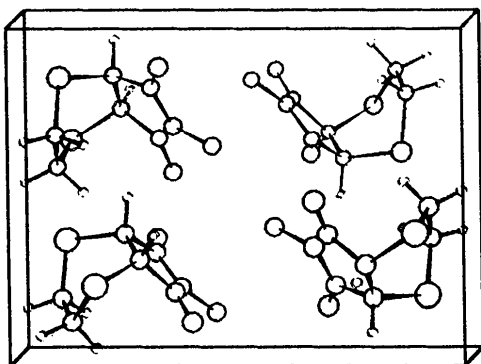


Fig. 4. Molecular packing.

the fact that the greatest deviation is only 0.041 Å, the ring cannot be considered ideally planar. The function $\chi^2 = \sum d_m^2/\sigma^2$ reaches the value 38.8, there being only a minimal probability that the ideal planar system of five atoms located with our accuracy would result in such a high χ^2 value ($\alpha < 0.01$). The O atoms and the CH₃ group clearly deviate from the best plane of the ring. The deviation from planarity of the bonds to the C_{sp²} atoms may be determined by the intramolecular repulsion between the S and O atoms in this 'compact' form of the molecule. The deviation of the CH₃ group from the plane of the imide ring indicates partial tetrahedral hybridization of the valency electrons of the N atom. The bond lengths observed in the imide ring agree with the literature data (Mason, 1961; Kirfel, Will & Fickentscher, 1975; Argay & Kálmán, 1973; Kirfel, 1975; Argay, Simon & Kálmán, 1974; Kaftory, 1978). Our C_{sp²}-N bond lengths are 1.362 (14) and 1.409 (16) Å and the difference between them is not more than 3σ. The bonds C_{sp²}-C_{sp²} [1.523 (15) and 1.545 (16) Å] are considerably shorter than the C_{sp²}-C_{sp³} bond [1.573 (15) Å].

The molecular packing within the unit cell is presented in Fig. 4. Intermolecular distances do not indicate any interactions stronger than normal van der Waals. The shortest intermolecular distances, C-C, C-S, C-O, O-O and S-S, are 3.574, 3.598, 3.204, 3.390, 3.734 Å respectively. Thus the shape of the molecule was not likely to be strongly influenced by intermolecular interactions.

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