

Crystal Structure of Diethyl 1,2,3,4-Tetrathiepane-6,6-dicarboxylate and Structural Aspects of S₄-Containing Ring Systems

Sine Larsen[†] and Lene Teuber

Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

Larsen, S. and Teuber, L., 1994. Crystal Structure of Diethyl 1,2,3,4-Tetrathiepane-6,6-dicarboxylate and Structural Aspects of Containing Ring Systems. – Acta Chem. Scand. 48: 652–656 © Acta Chemica Scandinavica 1994.

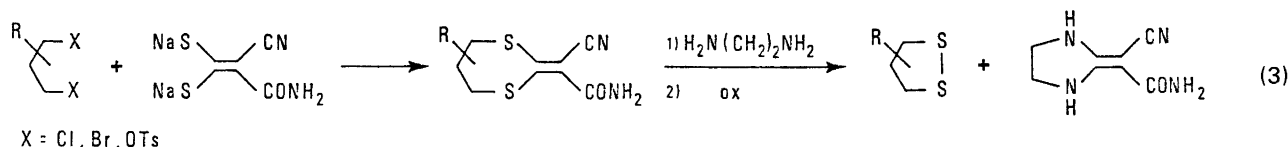
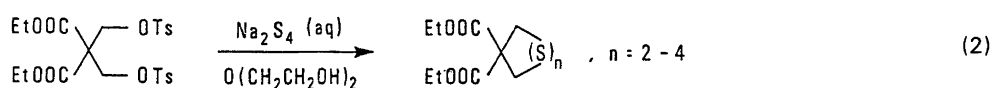
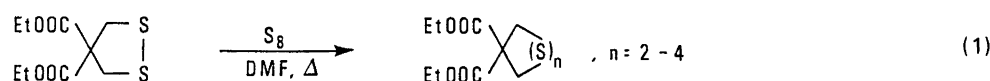
The crystal structure of the title compound has been determined from low-temperature (110 K) X-ray diffraction data. The compound crystallizes in the orthorhombic space group *Pbca* with $a = 20.351(3)$, $b = 14.773(3)$ and $c = 9.3588(13)$ Å, $Z = 8$. Using 2159 reflections the structure was refined to $R = 0.060$.

Two intramolecular contacts 3.124 and 3.188 Å, between the two carbonyl oxygen atoms and the two terminal sulfur atoms, are somewhat shorter than the sum of their van der Waals radii (3.25 Å). These interactions appear to be important for the stabilization of the molecule. The geometry of C–S–S–C fragments observed in six- to sixteen-membered ring systems, revealed that the torsion angles C–S–S–S and S–S–S–S vary with the size of the ring system and with a distinctly preferred conformation for each size of the ring.

The synthesis of the title compound, which contains the previously unknown tetrathiepane ring, has recently been described.¹ We were able to prepare diethyl 1,2,3,4-tetrathiepane-6,6-dicarboxylate either from the corresponding 1,2-dithiolane [eqn. (1)] or by alkylation of the tetrasulfide ion [eqn. (2)].

1,2,3,4-tetrathiepanes by the reaction with elemental sulfur have so far been futile.

In an alternative approach the oxidation step of eqn. (3) was omitted, and the resulting 1,3-dithiols were treated with sulfur monochloride.³ Again the title compound was the only isolated 1,2,3,4-tetrathiepane.



This result prompted a search for additional compounds containing this new heterocyclic ring. A number of 1,2-dithiolanes have been prepared according to eqn. (3),^{2,3} but all efforts to transform these products into

The products from all other substrates tested were 1,2-dithiolanes and 1,2,3-trithianes. Occasionally mass spectrometric analysis of the crude product mixtures indicated the presence of 1,2,3,4-tetrathiepanes in trace amounts. However, the attempted isolation of these compounds led to the formation of S₈ and the smaller ring analogues. In an attempt to trace the unique stability of

[†] To whom correspondence should be addressed.

diethyl 1,2,3,4-tetrathiepane-6,6-dicarboxylate, we have carried out a structure determination by X-ray diffraction methods. The results from this structure determination are related to other structures containing the tetrasulfane moiety in rings.

Experimental

Preparation. Diethyl 1,2,3,4-tetrathiepane-6,6-dicarboxylate was prepared by the reaction in eqn. (2) as described in Ref. 1. The following modifications were made in the purification procedure to obtain crystals of a quality suitable for X-ray analysis. The crude product was eluted through silica gel (25 g silica gel swelled in hexane per g crude product) with hexane until complete removal of S_8 . Elution was continued with a hexane/ CH_2Cl_2 mixture in the ratio 9:1. The first band was collected. Evaporation of solvent left an oily residue, which was triturated with pentane and stored at $-16^\circ C$ overnight to complete crystallization. The crystals were collected, redissolved in a small volume of hexane and recrystallized by addition of pentane in the cold. This procedure was repeated twice.

X-Ray crystallography. A single plate-shaped crystal $0.22 \times 0.04 \times 0.64$ mm bounded by the faces $\{100\}$, $\{010\}$ and $\{001\}$ was selected for the data collection performed with an Enraf-Nonius CAD4 diffractometer using graphite monochromated $CuK\alpha$ radiation. The crystal was

Table 1. Crystal data and a summary of results from data collection and structure refinement.

Formula	$C_9H_{14}O_4S_4$
Formula weight/g mol $^{-1}$	314.47
Crystal system	Orthorhombic
Space group	$Pbca$
Radiation/ λ	$CuK\alpha/1.54184 \text{ \AA}$
Cell parameters at 110 K:	
$a/\text{\AA}$	20.351(3)
$b/\text{\AA}$	14.773(3)
$c/\text{\AA}$	9.3588(13)
$V/\text{\AA}^3$	2813.5(14)
Z	8
$d_{cal}/g \text{ cm}^{-3}$	1.485
μ/cm^{-1}	61.55
$\Delta\omega/^\circ$	$1.2 + 0.15 \tan\Theta$
Octants measured	$h k \pm l / h - k \pm l$ (partly)
Θ interval/ $^\circ$	1–75
Max. scan time/s	60
No. of measured reflections	10972
No. of independent reflections	2902
R_{int}	0.026
No. of contributing reflections, n ($ F ^2 > 3\sigma(F ^2)$)	2159
w^{-1}	$\sigma_{cs}^2(F) + 9 \times 10^{-4} F ^2$
No. of variables, m	154
R	0.060
R_w	0.087
$S = \left(\frac{\sum w \Delta F^2}{n - m} \right)^{1/2}$	2.2

cooled to ca. 110 K during the data collection on an Enraf-Nonius gas flow low-temperature device. The temperature monitored with a thermocouple placed a few centimetres above the crystal in the exhaust pipe was constant within 1 K. The unit-cell parameters were determined from a least-squares refinement of the setting angles for 25 reflections ($38.7 < \theta < 46.0^\circ$). The crystal data and a summary of the results from data collection, data reduction and structure refinement are listed in Table 1. Based on an analysis of reflection profiles the ω - 2θ scan mode and the scan interval were selected. During the data collection the intensities of three standard reflections were measured every 10^4 s, after every 300 reflections the orientation of the crystal was checked. These repeated measurements showed that no mis-setting or deterioration of the crystal had occurred. The space group was determined from the systematically absent reflections derived from the diffractometer list. Data reduction included corrections for Lorentz, polarization, background and absorption effects. The latter correction was performed using the Gaussian integration procedure, and the transmission factors were between 0.153 and 0.783. Symmetry-related reflections were averaged $R_{int} = 0.026$ to give 2902 independent reflections, of these 2159 with $|F|^2 > 3\sigma(|F|^2)$ were considered observed and used for the subsequent structure solution and refinement. The structure was solved by direct methods;⁴ a standard run gave starting coordinates for all the non-hydrogen atoms in the structure. It was refined by least-squares minimization $\sum w(|F_o| - |F_c|)^2$. After anisotropic displacement parameters had been introduced the difference electron density showed the positions of the hydrogen atoms. They were introduced in idealized positions with a common isotropic displacement parameter $B = 3.0 \text{ \AA}^2$. The maximum shift after the final refinement cycle was 0.01σ . The residual electron density had peaks in the range -0.70 to

Table 2. Position parameters and equivalent isotropic displacement parameters.

Atom	x	y	z	$B_{iso}/\text{\AA}^2$ ^a
C1	0.8477(2)	0.3928(3)	0.2359(4)	1.48(7)
C11	0.7845(2)	0.3641(3)	0.3155(5)	1.62(7)
S11	0.72964(6)	0.29013(8)	0.2149(1)	1.97(2)
S12	0.74933(6)	0.16733(8)	0.3053(1)	2.37(2)
C12	0.8930(2)	0.4391(3)	0.3439(4)	1.61(7)
O11	0.9472(2)	0.4116(3)	0.3738(4)	2.60(7)
O12	0.8634(2)	0.5097(2)	0.4021(3)	1.84(5)
C13	0.8991(2)	0.5637(3)	0.5055(5)	2.41(9)
C14	0.9293(3)	0.6442(4)	0.4368(8)	4.7(1)
C21	0.8848(2)	0.3152(3)	0.1615(5)	1.91(8)
S21	0.90369(6)	0.21851(8)	0.2757(1)	2.16(2)
S22	0.83516(7)	0.12653(8)	0.2065(1)	2.47(2)
C22	0.8301(2)	0.4632(3)	0.1217(4)	1.62(7)
O21	0.7754(2)	0.4779(2)	0.0796(4)	2.16(6)
O22	0.8847(2)	0.5022(2)	0.0727(3)	2.14(6)
C23	0.8757(2)	0.5722(3)	-0.352(5)	2.10(8)
C24	0.9430(3)	0.6019(4)	-0.0791(6)	3.0(1)

$$^a B_{iso} = \frac{8 \pi^2}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

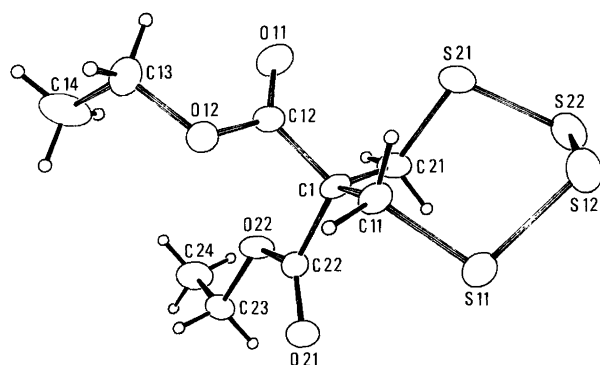


Fig. 1. ORTEP drawing of diethyl 1,2,3,4-tetrathiepane-6,6-dicarboxylate, showing the atomic labelling. The thermal ellipsoids enclose 50% probability. The hydrogen atoms are illustrated as spheres with a fixed radius.

$0.67 \text{ e } \text{\AA}^{-3}$ with the largest peaks close to the sulfur atoms. The SDP-system⁵ was used for crystallographic computations, the atomic scattering factors including corrections for anomalous dispersion were from Ref. 6 and used as contained in the program. The final positional parameters are listed in Table 2. Anisotropic displacement parameters and positional parameters for the hydrogen atoms and lists of observed and calculated structure amplitudes may be obtained from one of the authors (S. L.).

Results and discussion

The molecular geometry is illustrated by the ORTEP drawing in Fig. 1 and by the bond lengths, bond and

torsion angles listed in Table 3. It is apparent that apart from the ethyl groups the overall molecular symmetry is close to C_2 . The seven-membered tetrathiepane ring adopts a chair-like conformation.

Two equivalent short S–O interatomic distances (less than the sum of the van der Waals radii, 3.25 Å) are observed in the molecule, S11–O21 and S21–O11, which are 3.188(3) and 3.124(3) Å, respectively, with the corresponding O···S–S angles 151.7(1) and 152.9(1)°. It seems likely that the unusual stability of the tetrathiepane ring system observed for the investigated compound may have its origin in these interactions.

Our attempted preparations included asparagusic acid analogues, i.e. compounds having only one carboxylic function. The fact that we were unable to isolate the desired products could indicate that the presence of two such functions is essential for a successful preparation. We interpret these short S–O contacts as attractive interactions that are important for the stabilization of the ring system. This is supported by the observation that similar non-bonded interactions have been observed in other compounds containing the S_4 system.⁷ The intramolecular contact distances are significantly shorter than the intermolecular contact distances between oxygen atoms and the central sulfur atoms, which are S12–O12($1/2 - x, y - 1/2, z$) = 3.392(2) Å, S12–O21($x, 1/2 - y, 1/2 + z$) = 3.387(3) Å and S22–O21($1/2 - x, y - 1/2, z$) = 3.361(3) Å. The crystal packing is illustrated by the stereo pair in Fig. 2.

With the aim of investigating whether the small numerical value of the S11–S12–S22–S21 torsion angle is a consequence of constraints of the ring system, a search was made in the Cambridge Structural Database.⁸ The

Table 3. Bond lengths (in Å), bond and torsion angles (in °).

C1–C11	1.545(4)	C1–C21	1.539(4)
C11–S11	1.825(3)	C21–S21	1.826(3)
S11–S12	2.0417(12)	S21–S22	2.0522(13)
S12–S22	2.0664(13)	C1–C22	1.534(4)
C1–C12	1.529(4)	C22–O21	1.201(4)
C12–O11	1.208(4)	C22–O22	1.333(4)
C12–O12	1.322(4)	O22–C23	1.457(4)
O12–C13	1.450(4)	C23–C24	1.493(5)
C13–C14	1.485(5)		
C11–C1–C21	115.0(3)	C12–C1–C22	107.4(3)
C11–C1–C12	107.8(2)	C21–C1–C22	107.7(2)
C1–C11–S11	115.1(2)	C1–C21–S21	114.9(2)
C11–S11–S12	101.40(11)	C21–S21–S22	100.98(12)
S11–S12–S22	103.85(5)	S21–S22–S12	103.818(5)
C1–C12–O11	123.6(3)	C1–C22–O21	124.6(2)
C1–C12–O12	110.6(3)	C1–C22–O22	109.7(2)
O11–C12–O12	125.8(13)	O21–C22–O22	125.6(3)
C12–O12–C13	118.8(2)	C22–O22–C23	116.1(2)
O12–C13–C14	110.1(3)	O22–C23–C24	106.5(3)
C1–C11–S11–S12	102.8(3)	C1–C21–S21–S22	104.5(3)
C11–S11–S12–S22	–80.4(2)	C21–S21–S22–S12	–78.5(2)
C11–C1–C12–O12	–58.3(4)	C21–C1–C22–O22	–67.3(4)
C1–C12–O12–C13	–178.7(4)	C1–C22–O22–C23	–178.9(3)
C12–O12–C13–C14	96.5(5)	C22–O22–C23–C24	–177.0(4)
S11–S12–S22–S21	66.13(8)		

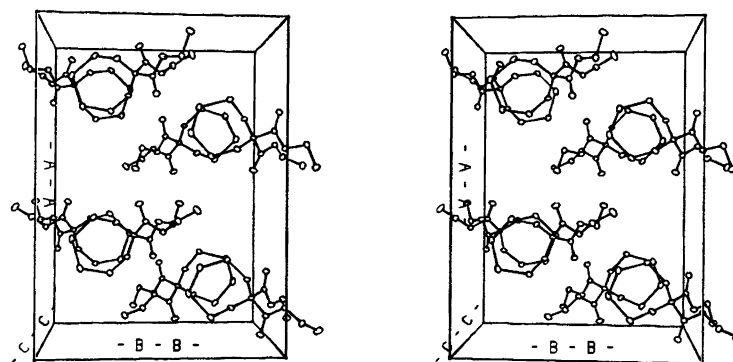


Fig. 2. A stereo pair illustrating the molecular packing viewed along the crystallographic *c*-axis.

C–S–S–S–C moiety was found as part of a ring system in 19 structures listed in the database. The ring systems in these structures were all even numbered with $2n = 6, 8, 12$ and 16 . The compound investigated represents the only case where the C–S–S–S–C fragment is part of an odd-membered ring. The analysis of the geometries of the C–S–S–S–C fragments with the GSTAT⁸ program gave some interesting results that are summarized in Table 4. The bond lengths and angles do not vary systematically, but as shown in Table 4 the con-

formation of the C–S–S–S–C fragment displays significant variations with the size of the ring system. In six-membered rings the torsion angles C–S–S–S and S–S–S–S are virtually numerically equivalent. Compared to this the C–S–S–S angle is significantly increased in the seven-membered ring system that is the subject of the present investigation.

The conformations of the C–S–S–S–C fragment in eight-membered rings fall into two groups. If there is conjugation within the fragment, as indicated by shorter

Table 4. Geometries of (C–S_{term}–S_{int}–S_{int}–S_{term}–C) moieties extracted from the Cambridge Structural Database.⁸

Refcode	(C–S _{term}) /Å	(S _{ter} –S _{int}) /Å	(S _{int} –S _{int}) /Å	(C–S _{ter} –S _{int} –S _{int}) /°	(S _{ter} –S _{int} –S _{int} –S _{ter}) /°	(S _{int} –S _{int} –S _{ter} –C) /°
6-Membered ring						
CUVYEX	1.82	2.04	2.07	66	–68	65
JEJBAB ^a	1.84	2.04	2.06	67	–69	66
TSDECA10	1.81	2.05	2.06	68	–69	66
7-Membered ring						
Present study	1.83	2.045	2.065	–81	66	–79
8-Membered ring						
CEZDUG ^a	1.90	2.03	2.09	69	–105	72
DIDXOD ^a	1.90	2.00	2.08	71	–105	73
GETKOF	1.83	2.03	2.06	–65	104	–73
HYALTS	1.90	2.02	2.09	71	–103	73
JUSSAR	1.73	2.08	2.03	89	–75	91
METHPZ10	1.87	2.03	2.08	69	–105	69
MTKPIN	1.90	2.01	2.08	72	–106	67
SPORGE10	1.88	2.02	2.08	–67	107	–72
SOJTIU	1.72	2.07	2.02	–91	78	–89
SOJTOA	1.78	2.08	2.04	–89	79	–90
VAXCIG	1.73	2.08	2.04	–89	78	–89
VEBCEK	1.73	2.08	2.03	89	–76	89
VIDKOI	1.75	2.07	2.02	88	–76	90
VIWBOS	1.75	2.07	2.02	–89	82	–91
12-Membered ring						
HMHTMC10 ^a	1.79	2.06	2.07	–98	108	–98
16-Membered ring						
TEOSHE10 ^a	1.78	2.03	2.07	–87	93	–88

^a The values are averaged over the independent molecules in the asymmetric unit.

C-S_{ter} and S_{int}-S_{int} bond lengths, the three torsion angles (-90 , 78 and -90°) are very different from the values found in non-conjugated systems (-69 , 104 and -69°). The torsion angles in the 12- and 16-membered rings are distinctly different from those found in the other ring systems.

This analysis of the structural data indicates that the C-S-S-S-C moiety is a fairly rigid fragment that has a distinctly preferred conformation depending on the size of the ring system of which it is part.

Acknowledgements. The authors thank Mr. Flemming Hansen for help with the experimental crystallographic work, and Dr. Lars Henriksen for valuable discussions. This work was supported through grants from The Carlsberg Foundation and the Danish Natural Science Research Council.

References

1. Teuber, L. and Christophersen, C. *Acta Chem. Scand., Ser. B* 42 (1988) 620.
2. Teuber, L. and Christophersen, C. *Acta Chem. Scand., Ser. B* 42 (1988) 629.
3. Teuber, L. *Ph.D. Thesis*, Department of Chemistry, University of Copenhagen, Copenhagen 1994.
4. Sheldrick, G. M. *Acta Crystallogr., Sect. A* 46 (1990) 467.
5. *SDP-Plus Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands 1985.
6. *International Tables for X-ray Crystallography*. Vol. IV, Kynoch Press, Birmingham 1974.
7. Mott, A. W. and Barany, G. *J. Chem. Soc., Perkin Trans. 1* (1984) 2615.
8. *Cambridge Structural Database*. Version 5, Cambridge Crystallographic Data Centre, Cambridge, UK 1993.

Received January 24, 1994.