Crystal and Molecular Structure of *NN'*-Dithiodisuccinimide

By **Mazhar-Ul-Haque** * and **Mohammad Behforouz**, Department of Chemistry, Pahlavi University, Shiraz, Iran

The crystal structure of the title compound has been determined from three-dimensional *X*-ray diffractometer data. Crystals are monoclinic with unit-cell dimensions, $a = 9{\cdot}913(2)$, $b = 6{\cdot}630(1)$, $c = 18{\cdot}390(3)$ Å, $\beta = 117{\cdot}33(1)^\circ$, space group $A2$, $Z = 4$, with two independent monomers in the asymmetric unit. The structure was solved by Patterson and heavy-atom methods. Full-matrix least-squares refinement, using 1108 independent reflections, has reduced R to 0·034.

In the attempted synthesis of *N*-(isobutyldithio)-succinimide by the reaction of isobutylthiosulphenyl chloride with succinimide in the presence of triethylamine,[1] *NN'*-dithiodisuccinimide was isolated as the sole product. This compound is the first example of an *NN'*-dithio-di-imide. *X*-Ray analysis was carried out to determine the disulphide dihedral angle and other molecular dimensions in this novel molecule.

EXPERIMENTAL

Preparation of NN'-Dithiodisuccinimide.—2-Methylpropane-1-thiol (9·0 g, 0·1 mol) in n-hexane (100 ml) was added dropwise to a stirred solution of sulphur dichloride (20·6 g, 0·2 mol) in n-hexane (100 ml) at −70 to −75 °C during 2 h. The excess of sulphur dichloride was evaporated at room temperature under reduced pressure in *ca.* 30 min. The resulting thiosulphenyl chloride solution was added dropwise to a stirred solution of succinimide (9·9 g, 0·1 mol) and triethylamine (30·3 g, 0·3 mol) in *NN*-dimethylformamide (80 ml) during 30 min at room temperature. The reaction mixture was transferred to a large beaker, cold water (800 ml) added with stirring, and the aqueous solution extracted with chloroform, dried (Na_2SO_4), and evaporated. Recrystallization of the yellow product gave white crystals (4·6 g, 35%), which were purified by further recrystallisation; m.p. 163·5—165 °C; δ ($CDCl_3$) 2·9 (s).

Crystal Data.—$C_8H_8N_2O_4S_2$, $M = 260{\cdot}3$. Monoclinic, $a = 9{\cdot}913(2)$, $b = 6{\cdot}630(1)$, $c = 18{\cdot}390(3)$ Å, $\beta = 117{\cdot}33(1)^\circ$, $U = 1073{\cdot}7$ Å^3, $D_m = 1{\cdot}61$, $Z = 4$, $D_c = 1{\cdot}609$ g cm^{-3}, $F(000) = 536$. Space group $A2$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 43·91 cm^{-1}.

Weissenberg and precession photographs showed systematic absences hkl, $k + l = 2n + 1$, consistent with space groups $A2$, Am, and $A2/m$. Statistical analysis of the E data and use of an $N(z)$ test gave conclusive evidence that the hkl reflections were acentric, and the $h0l$ reflections centric. The space group was thus identified uniquely as $A2$, and was confirmed by the solution and refinement of the structure. A crystal *ca.* 0·20 × 0·26 × 0·79 mm^3 was used for the collection of intensity data on a Siemens off-line four-circle diffractometer at Imperial College, London. Filtered Cu-K_α radiation and a Na(Tl)I scintillation counter were used. Accurate unit-cell dimensions were obtained by least-squares refinement of 20 high-angle α_1 reflections measured on the diffractometer. The intensities of 1109 independent reflections were measured by the θ—2θ scan technique with a five-value measuring procedure.[2] Only one reflection was unobserved, having a net count, N, $< 2{\cdot}58\sigma(N)$ (*i.e.* 99% confidence level). 1,0,10 was used as reference reflection and measured every 50 reflections, but showed no significant systematic trends during the course of data collection (*ca.* 2 days). The very small random variations in its intensity were used for adjustment of the scaling of the observed intensity data. Lorentz and polarization corrections were applied. Atomic scattering factors for non-hydrogen atoms were taken from ref. 3, and those for hydrogen atoms from ref. 4.

Structure Determination and Refinement.—The structure was solved and refined by use of the crystal-structure calculation system ' *X*-Ray '70 '.[5]

The three-dimensional $|F|^2$ and $E^2 - 1$ Pattersons showed that the two sets of (four) equivalent sulphur positions are such that each disulphide bond lies across a two-fold axis. The first difference-Fourier synthesis revealed all non-hydrogen atom portions. The presence of two independent sets of sulphur atoms in the space group ($A2$) was a great convenience since they destroyed the pseudo-mirror plane usually found in the first Fourier maps for $A2$ when phased by only one set of heavy atoms.

Three cycles of full-matrix least-squares refinement of atomic co-ordinates and individual isotropic temperature factors, reduced R to 0·134. Four more cycles of least-squares refinement of atomic co-ordinates and individual anisotropic temperature factors reduced R to 0·049. A difference-Fourier map at this stage revealed all hydrogen atom positions.

Data were corrected for absorption according to the method of Busing and Levy[6] by use of a 10 × 14 × 10 grid

[1] M. Behforouz, H. Firouzabadi, and A. A. Afzali, *J. Chem. Soc.* (*C*), 1971, 3550.

[2] F. H. Allen, D. Rogers, and P. G. H. Troughton, *Acta Cryst.*, 1971, **B27**, 1325.

[3] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[4] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[5] ' *X*-Ray '70 ' System of programs, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin, University of Maryland Technical Report TR 64 6, 1963, revised 1970.

[6] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

with pathlengths determined by the vector-analysis method of Coppens *et al.*[7] A weighting scheme suggested by Hughes[8] was applied, where $\sqrt{w} = 1$ for $|F_0| < P$, and $\sqrt{w} = P/|F_0|$ for $|F_0| \geqslant P$, with $P = 20$. Five cycles of full-matrix least-squares, refining non-hydrogen atoms anisotropically and hydrogen atoms isotropically, reduced R to a final value of 0·034.

RESULTS AND DISCUSSION

Final atomic positions of all non-hydrogen atoms are listed with their standard deviations in Table 1. Atomic co-ordinates of hydrogen atoms, with their isotropic temperature factors, are given in Table 2. Interatomic distances, and valence and torsion angles are in Tables 3—5, and the intermolecular contacts <3·5 Å in Table 6. Observed and calculated structure factors, and anisotropic thermal parameters of the non-hydrogen atoms, are listed in Supplementary Publication No. SUP 21090 (7 pp.).*

TABLE 1

Fractional co-ordinates for sulphur (×10^5) and non-hydrogen atoms (×10^4), with estimated standard deviations in parentheses

	Molecule (1)			Molecule (2)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
S	11092(11)	00000(0)	01332(5)	52261(9)	25967(19)	05923(5)
N	1878(3)	−1826(5)	0847(2)	6567(3)	4431(5)	1041(2)
C(1)	1939(4)	−3870(6)	0643(2)	6249(4)	6438(6)	1137(2)
C(2)	2656(5)	−5029(7)	1425(2)	7725)4)	7524(7)	1578(3)
C(3)	3244(5)	−3461(7)	2104(2)	8946(4)	5934(8)	1782(2)
C(4)	2634(4)	−1479(4)	1690(2)	8128(4)	4023(6)	1405(2)
O(1)	1450(3)	−4453(5)	−0045(2)	4990(3)	7092(5)	0904(2)
O(2)	2768(4)	0131(5)	2012(2)	8661(3)	2390(5)	1406(2)

TABLE 2

Fractional co-ordinates for hydrogen atoms (×10^3) and their isotropic temperature factors (Å^2), with estimated standard deviations in parentheses

	Molecule (1)			
Atom	*x*	*y*	*z*	*B*
H(21) [C(2)]	352(5)	−596(9)	136(3)	6·0(11)
H(22) [C(2)]	182(5)	−607(8)	149(3)	4·6(9)
H(31) [C(3)]	287(5)	−350(8)	254(3)	5·3(10)
H(32) [C(3)]	428(5)	−345(8)	237(3)	4·7(10)
	Molecule (2)			
	x	*y*	*z*	*B*
H(21) [C(2)]	779(5)	801(9)	211(3)	5·5(10)
H(22) [C(2)]	763(5)	854(9)	111(3)	5·5(11)
H(31) [C(3)]	955(5)	586(8)	234(3)	5·4(11)
H(32) [C(3)]	961(5)	616(8)	156(3)	4·5(9)

TABLE 3

Interatomic distances (Å), with estimated standard deviations in parentheses

	Molecule (1)	Molecule (2)
S–S′	2·022(2)	2·012(2)
S–N	1·688(3)	1·709(3)
N–C(1)	1·414(5)	1·397(5)
N–C(4)	1·397(4)	1·402(4)
C(1)–C(2)	1·492(5)	1·493(5)
C(1)–O(1)	1·192(5)	1·199(5)
C(2)–C(3)	1·521(6)	1·516(7)
C(3)–C(4)	1·500(6)	1·492(6)
C(4)–O(2)	1·198(5)	1·204(5)
C(2)–H(21)	1·11(6)	1·00(6)
C(2)–H(22)	1·12(5)	1·05(6)
C(3)–H(31)	1·03(6)	0·92(5)
C(3)–H(32)	0·92(5)	0·94(6)

TABLE 4

Valence angles (deg.), with estimated standard deviations in parentheses

	Molecule (1)	Molecule (2)
N–S–S′	103·9(2)	105·1(2)
S–N–C(1)	122·7(2)	124·6(2)
S–N–C(4)	124·4(3)	122·5(5)
C(1)–N–C(4)	112·7(3)	112·8(3)
N–C(1)–C(2)	107·3(3)	107·8(3)
N–C(1)–O(1)	123·1(4)	123·9(3)
C(2)–C(1)–O(1)	129·6(4)	128·3(4)
C(1)–C(2)–C(3)	105·8(4)	105·7(4)
C(2)–C(3)–C(4)	105·6(3)	105·9(3)
N–C(4)–C(3)	107·8(3)	107·6(3)
N–C(4)–O(2)	125·2(3)	124·2(3)
C(3)–C(4)–O(2)	127·1(3)	128·2(3)
C(1)–C(2)–H(21)	104(3)	107(3)
C(1)–C(2)–H(22)	112(2)	100(2)
C(3)–C(2)–H(21)	116(2)	107(3)
C(3)–C(2)–H(22)	111(3)	114(3)
H(21)–C(2)–H(22)	108(4)	121(5)
C(2)–C(3)–H(31)	119(3)	111(4)
C(2)–C(3)–H(32)	111(3)	115(3)
C(4)–C(3)–H(31)	102(3)	114(4)
C(4)–C(3)–H(32)	111(3)	106(3)
H(31)–C(3)–H(32)	107(4)	105(4)

TABLE 5

Torsion angles (deg.)

	Molecule (1)	Molecule (2)
C(4)–N–C(1)–C(2)	6·6	2·4
C(1)–N–C(4)–C(3)	−1·2	−0·1
N–C(1)–C(2)–C(3)	−9·2	−3·6
N–C(4)–C(3)–C(2)	−4·7	−2·1
C(1)–C(2)–C(3)–C(4)	8·4	3·4
C(1)–N–S–S′	88·6	92·7
C(4)–N–S–S′	−97·4	−91·8
N–S–S′–N′	−84·7	−85·0

TABLE 6

Intermolecular contacts <3·5 Å involving non-hydrogen atoms

Atoms *		Atoms *	
O(1′) ··· N$^{\mathrm{I}}$	3·12	N′ ··· O(1$^{\mathrm{II}}$)	3·33
O(2) ··· C(2$^{\mathrm{I}}$)	3·37	O(2′) ··· O(1$^{\mathrm{II}}$)	3·23
O(1′) ··· C(4$^{\mathrm{I}}$)	3·40	C(3′) ··· O(1$^{\mathrm{II}}$)	3·05
O(1′) ··· C(2$^{\mathrm{I}}$)	3·21	N′ ··· O(2$^{\mathrm{III}}$)	3·36
O(1′) ··· O(1$^{\mathrm{I}}$)	3·28	C(3′) ··· O(2$^{\mathrm{III}}$)	3·40
O(1′) ··· C(1$^{\mathrm{I}}$)	2·91	C(1′) ··· O(2$^{\mathrm{III}}$)	3·20
O(1′) ··· C(3$^{\mathrm{I}}$)	3·39	C(4′) ··· O(2$^{\mathrm{III}}$)	3·49
C(2′) ··· O(2′$^{\mathrm{I}}$)	3·41	C(2′) ··· O(2$^{\mathrm{III}}$)	3·26
C(4′) ··· O(1$^{\mathrm{II}}$)	2·90		

* Roman numeral superscripts denote the following equivalent positions: I, $x, 1 + y, z$; II, $1 - x, 1 + y, -z$; III, $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$. Primed atoms are in molecule (2), unprimed in molecule (1).

Figure 1 shows the structure and numbering scheme for molecule (1): the other is very similar. A stereodiagram[9] of the arrangement of the two independent molecules in the unit cell is shown in Figure 2. The two independent molecules lie in quite different orientations in the cell, but the geometry of both is in good agreement: the conformational details and even the dihedral angles match closely.

---

* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue.

[7] P. Coppens, L. Leiserowtz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

[8] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

[9] C. K. Johnson, ORTEP Thermal Ellipsoid Plotting Program, Oak Ridge National Laboratory Report ORNL 3794, 1965.

Structural data for molecules containing an X–S–S–Y bond have been reviewed by Hordvik,[10] who showed a correlation between S–S bond length and dihedral angle between the planes X–S–S and S–S–Y. The shortest bond lengths seem to correspond to dihedral angles of *ca.* 90°, and the longest to small dihedral angles. The dihedral angles in two independent molecules are −84·7 and −85·0° and the S–S bond lengths 2·022 and 2·012 Å, which fit very well with Hordvick's curve. Thus, in these S–S bonds the π-bonding is considerable, and represents about one-third double-bond character, if the single S–S bond is taken as 2·08 Å.

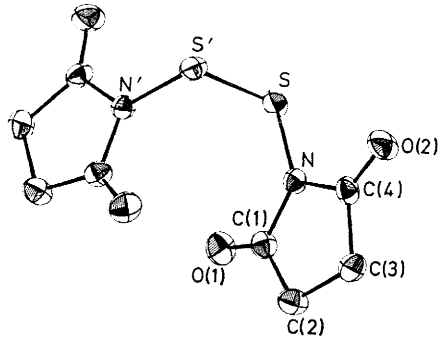


FIGURE 1 Perspective view of molecule (1), showing 30% probability thermal ellipsoids

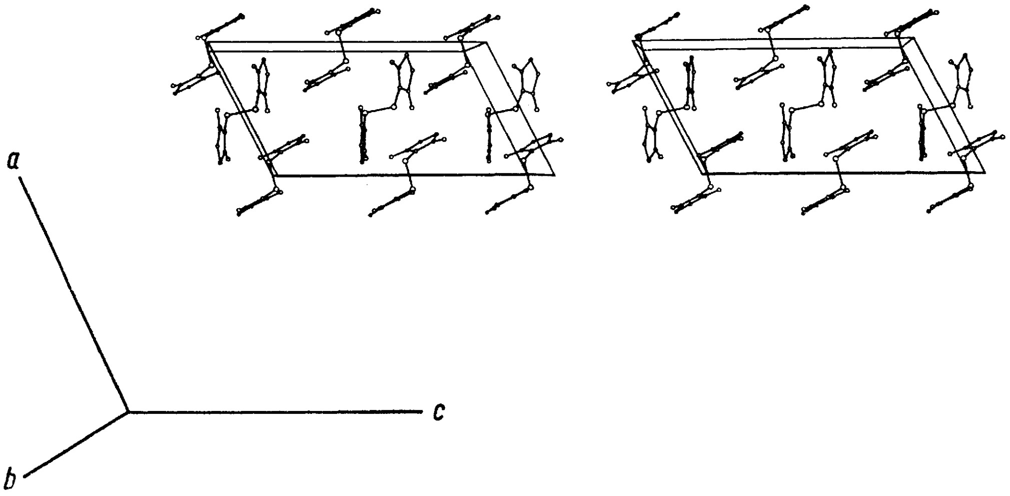
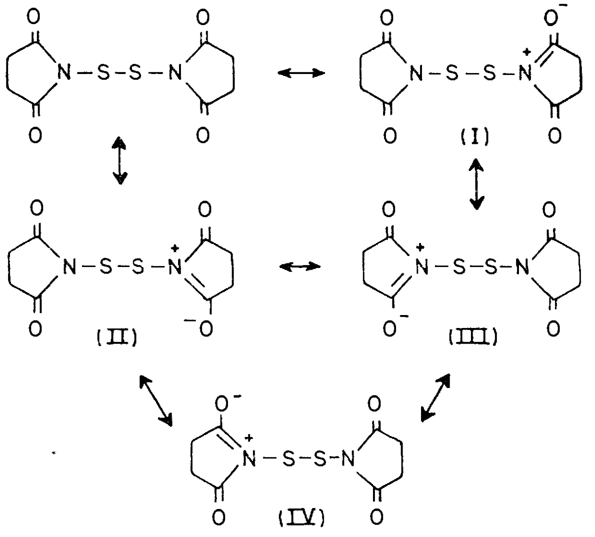


FIGURE 2 Stereoscopic view showing the packing of molecules

The N–S bond lengths (1·688 and 1·709 Å) in the two independent molecules are a little shorter than the sum of the Pauling covalent radii (1·74 Å), but even shorter N–S single-bond lengths (1·60—1·67 Å) have been observed.[11] The slight lengthening of the N–S bonds in the present compound may be due to shortening of the S–S bond length. The mean C–N distances (1·406 and 1·399 Å) in the two independent molecules are in good agreement with those in *N*-chlorosuccinimide (1·39 Å)[12] and in succinimide (1·385 Å).[13] If a C(sp^3)–N(sp^3) single-bond distance is taken[14] as 1·47 Å and a C(sp^2)–N(sp^2) double-bond as 1·29 Å,[14] the present C–N bonds possess 38% double-bond character. This is probably due to the contributions of the resonance structures (I)—(IV).

Mean C=O distances (1·195 and 1·202 Å) compare well, but are a little shorter than the typical value of 1·22 in *N*-chlorosuccinimide[12] and 1·23 Å in succinimide.[13] The values of the bond lengths C(1)–C(2) (1·492 and 1·493 Å) and C(3)–C(4) (1·500 and 1·492 Å) are between those for trigonally and tetrahedrally hybridized carbon atoms. Their values are in good agreement with those found by Brown[12] and by Mason[13] (1·48 and 1·506 Å). Such short C–C lengths adjacent to carbonyl groups are common. The C(2)–C(3) bond lengths (1·521 and 1·516 Å) are not significantly different from the accepted single-bond distances (1·541 Å). Mean C–H distances are 1·07 and 0·98 Å.

The valence angles in the two independent molecules



---

[10] A. Hordvick, *Acta Chem. Scand.*, 1966, **20**, 1885.

[11] 'Molecular Structures and Dimensions,' vol. AI, Interatomic Distances, 1960—1965, published for Crystallographic Data Centre, Cambridge and Internat. Union Crystallography by Oosthoek, Utrecht.

[12] R. N. Brown, *Acta Cryst.*, 1961, **14**, 711.

[13] R. Mason, *Acta Cryst.*, 1961, **14**, 720.

[14] L. Pauling, 'The Nature of Chemical Bond,' Cornell University Press, Ithaca, New York, 1967, p. 225.

match closely and are in good agreement with those in *N*-chlorosuccinimide [12] and succinimide.[13] The ring torsion angles are also in good agreement and match closely those in *N*-chlorosuccinimide.[12]

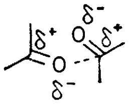
TABLE 7

Equations of planes in the form: $Px + Qy + Rz = S$ with x, y, z in fractional co-ordinates and P, Q, R, S in Å. Deviations of atoms are in Å × 10^{-4}.

	Molecule (1)			Molecule (2)		
	Plane (*A*)	Plane (*B*)	Plane (*C*)	Plane (*A*)	Plane (*B*)	Plane (C)
S	−105			128		
N	−433	−502	−225	−332	−249	−73
C(1)	6	−19	486	−129	−10	184
C(2)	−794	−738	−544	−249	−317	−216
C(3)	598	655	419	371	302	177
C(4)	45	20	−137	−39	−9	−72
O(1)	585	534		253	313	
O(2)	99	49		−2	60	
P	9·8115	9·8178	9·8221	−4·3739	−4·4115	−4·5615
Q	0·9402	0·9131	0·8510	−1·4473	−1·4790	−1·4500
R	−8·6201	−8·5628	−9·0559	17·9459	17·9265	17·9430
S	0·9840	1·0018	0·9445	−1·6115	−1·6605	−1·7622

The two independent monomers are slightly but significantly non-planar. Least-squares equations of the planes and atomic deviations from them are in Table 7.

There are certain intermolecular contacts (Table 6) which are less than the sum of the van der Waals radii given by Pauling. The close contacts between carbon and oxygen [O(1′) · · · C(1) 2·91, C(4) · · · O(1) 2·90 Å] may be explained by electrostatic attraction between a carbonyl carbon in one molecule and a carbonyl oxygen in another as in (V). Similar results have been observed and explained in this way.[15,16]



(V)

We thank Professor D. Rogers for the use of laboratory facilities and helpful discussion, the British Council for a Research Bursary, and Pahlavi University for leave of absence (to M. U. H.). We also thank the Imperial College and University of London Computing Laboratories for assistance, and Mr. D. J. Williams, who used his own program to carry out the statistical test. We thank Pahlavi University for Research grants (to M. U. H. and M. B.).

[3/2567 *Received*, 18*th December*, 1973]

---

[15] D. R. Davies and J. J. Blum, *Acta Cryst.*, 1955, **8**, 129.

[16] S. S. C. Chu, G. A. Geffrey, and T. Sakurai, *Acta Cryst.*, 1962, **15**, 661.