Fig. 2. A view of the packing of the molecules in the unit cell.

1·415 (7) Å; 1·375 (5), 1·381 (5) Å; and 117·7 (4), 117·9 (4)° respectively].

The crystal structure is stabilized by two hydrogen bonds (Table 3) which form a linear O—H···O—H···O—H chain running parallel to the crystallographic a axis. A view of the packing of the molecules is shown in Fig. 2.

References

ALLEN, F. H., BELLARD, S., BRICE, M. D., CARTWRIGHT, G. A., DOUBLEDAY, A., HIGGS, H., HUMMELINK, T., HUMMELINK-PETERS, B. J., KENNARD, O., MOTHERWELL, W. D. S., RODGERS, J. R. & WATSON, D. G. (1979). Acta Cryst. B35, 2331–2339.

CHATTERJEE, A. & PARTHASARATHY, R. (1983). Program and Abstracts, Am. Crystallogr. Assoc., Vol. 11, Series 2, p. 12.

COHEN-ADDAD, C., LEHMANN, M. S., BECKER, P., PÁRKÁNYI, L. & KÁLMÁN, A. (1984). J. Chem. Soc. Perkin Trans. 2, pp. 191–196.

FRENZ, B. A. (1979). Structure Determination Package. Enraf-Nonius, Delft, The Netherlands.

GURU ROW, T. N. & PARTHASARATHY, R. (1981). J. Am. Chem. Soc. 103, 477–479.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

KÁLMÁN, A. & PÁRKÁNYI, P. (1980). Acta Cryst. B36, 2372–2378.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.

PLETCHER, J., SAX, M., BLANK, G. & WOOD, M. (1977). J. Am. Chem. Soc. 99, 1396–1403.

ROSENFIELD, R. E. JR, PARTHASARATHY, R. & DUNITZ, J. D. (1977). J. Am. Chem. Soc. 99, 4860–4862.

SHIN, W., PLETCHER, J. & SAX, M. (1979). J. Am. Chem. Soc. 101, 4365–4371.

ULMAN, A. & MANASSEN, J. (1979). J. Chem. Soc. Perkin Trans. 1, pp. 1066–1069.

Structure of Bis(2-benzimidazolyl) Disulfide

BY V. GANESH AND M. SESHASAYEE

Department of Physics, Indian Institute of Technology, Madras 600 036, India

SP. CHIDAMBARAM AND G. ARAVAMUDAN

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

AND H. SCHENK

Laboratorium voor Kristallografie, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Abstract. $C_{14}H_{10}N_4S_2$, $M_r = 298.40$, orthorhombic, Pcc2, $a = 9.964$ (3), $b = 9.967$ (3), $c = 12.890$ (3) Å, $V = 1280.26$ Å^3, $Z = 4$, $D_x = 1.548$, $D_m = 1.540$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 3.56$ mm^{-1}, $F(000) = 632$, $T = 293$ K, $R = 0.053$, $wR = 0.046$ for 1089 observed reflections. The S—S bond length is 2·077 (3) Å, longer than those in most disulfides which is indicative of the title compound's instability in

solution. The two benzimidazole groups are planar with maximum deviations 0·012 (6) and 0·008 (4) Å. The interplanar angle is 27·5°. Hydrogen bonds between N atoms regulate the crystal packing.

Introduction. Bis(2-benzimidazolyl) disulfide $(L-L)$ is the first-step oxidation product of 2-benzimidazolethione (L). Treatment of L with mild oxidizing agents such as hydrogen peroxide and tellurium(IV) in methanolic solution (Rout, Seshasayee, Aravamudan & Sowrirajan, 1984) precipitated $L-L$ as a polycrystalline material. The compound is indefinitely stable in the solid state and decomposes only above 473 K. Unlike most other disulfides, this compound is unstable in acidic methanolic media. Though documented by Hofmann (1953), no reason was given for this unusual instability. Therefore, a crystal-structure study was attempted after preparing the single crystal with great difficulty, as described in the following with a probable reason for the instability.

Experimental. Recrystallization from powdery $L-L$ was not successful in obtaining single crystals. $L-L$ has an interesting solubility and stability behaviour. It is insoluble in most solvents, e.g. dilute mineral acids and methanol, but readily dissolves in a mixture of the two. On gradual evaporation of methanol $L-L$ is not recovered but only its decomposition products, namely L, benzimidazole and SO_2 are obtained. Single crystals of $L-L$ could, however, be obtained in very low yield (< 1%) by the slow aerial oxidation of 0·2 M methanolic solution of L kept in a 1 L flask for four months. Single crystals in a better yield but of poorer quality were obtained by aerial oxidation of 0·2 M methanolic solution of L catalysed by the addition of 0·005 M Cu^{2+} and 0·5 M NH_3.

Pale-yellow needle-shaped crystals, crystal size 0·1 × 0·1 × 0·4 mm; density measured by flotation; data collection by Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Cu $K\alpha$ radiation; lattice parameters from least-squares analysis of 25 high-angle reflections ($60 < 2\theta < 90°$); ω–2θ scan, $2\theta_{max} = 140°$, index range $0 \le h \le 12$, $0 \le k \le 12$, $0 \le l \le 15$; standard reflections $15\bar{1}$ and $33\bar{1}$ monitored every hour showed no significant variation; 1440 reflections measured, 1089 with $I \ge 3\sigma(I)$; Lorentz and polarization corrections applied, no absorption correction. Structure solution using direct methods [$SHELX86$ (Sheldrick, 1986)]; anisotropic temperature factors for non-H atoms, H atoms from difference Fourier map were refined with isotropic temperature factors, structure refined using full-matrix least squares on F [$SHELX76$ (Sheldrick, 1976)]; final $R = 0·053$, $wR = 0·046$ for 1089 observed reflections, weighting scheme used $w = 1·00/[\sigma^2(F_o) + 0·0472|F_o|^2]$, (shift/e.s.d.)$_{max} = 0·031$ for all non-H atoms, reflection/parameter ratio 6·05, max. height in final difference

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* $(\text{Å}^2 \times 10^3)$ *for the non-*H *atoms with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3} \sum_{i=1}^{3} U_{ii}.$$

	x	y	z	U_{eq}
S(1)	0·7392 (1)	1·2079 (1)	0·0035	37 (1)
S(2)	0·7078 (1)	1·2389 (1)	−0·1540 (2)	37 (1)
N(1)	0·6353 (3)	0·9588 (4)	0·0436 (4)	32 (2)
N(2)	0·8583 (3)	0·9593 (4)	0·0176 (4)	30 (2)
C(1)	0·7456 (3)	1·0322 (5)	0·0192 (4)	30 (3)
C(2)	0·8194 (5)	0·8317 (5)	0·0412 (4)	29 (2)
C(3)	0·8936 (5)	0·7142 (5)	0·0495 (5)	35 (3)
C(4)	0·8230 (6)	0·5971 (6)	0·0740 (5)	40 (3)
C(5)	0·6864 (6)	0·5972 (5)	0·0912 (5)	41 (3)
C(6)	0·6103 (5)	0·7149 (5)	0·0833 (5)	37 (3)
C(7)	0·6804 (5)	0·8318 (6)	0·0570 (4)	30 (2)
C(8)	0·5325 (6)	1·2446 (4)	−0·1704 (4)	29 (3)
N(3)	0·4608 (4)	1·3590 (3)	−0·1678 (3)	31 (2)
N(4)	0·4604 (4)	1·1353 (3)	−0·1936 (4)	33 (2)
C(9)	0·3316 (5)	1·3195 (5)	−0·1909 (4)	29 (2)
C(10)	0·2127 (5)	1·3936 (5)	−0·1996 (5)	38 (3)
C(11)	0·0977 (5)	1·3227 (6)	−0·2253 (5)	39 (3)
C(12)	0·0986 (5)	1·1859 (6)	−0·2420 (5)	40 (3)
C(13)	0·2137 (5)	1·1116 (5)	−0·2342 (5)	36 (3)
C(14)	0·3315 (6)	1·1807 (5)	−0·2079 (4)	30 (2)

Fourier map < 1 e Å^{-3}. Atomic scattering factors from Cromer & Mann (1968) for non-H atoms and Stewart, Davidson & Simpson (1965) for H; anomalous-dispersion-correction factors from Cromer & Liberman (1970).

Discussion. The refined atomic parameters for non-H atoms are listed in Table 1. The bond lengths and bond angles involving non-H atoms are given in Table 2.* Figs. 1 and 2 show the *ORTEP* plot (Johnson, 1976) of this molecule and packing of the molecules in the unit cell, respectively. The S(1)–S(2) bond length is 2·077 (3) Å, which is longer than those reported for other disulfides, namely bis[morpholino(thiocarbonyl)]disulfane, 2·009 (5) Å (Rout, Seshasayee & Aravamudan, 1982), 3,3'-dithiodipropionic acid, 2·033 (1) Å (Appa Rao, Seshasayee, Aravamudan, Nageswara Rao & Venkatasubramanian, 1982) and 3,3'-dihydroxydi-2-pyridyl disulfide, 2·018 (7) Å (Higashi, Lundeen & Seff, 1978). These compounds, unlike the title compound, are stable in solution also. Thus the longer S—S bond length is one of the contributing factors towards the instability of the title compound in solution.

The two benzimidazole (mbi) groups are planar with maximum deviations 0·012 (6) and 0·008 (4) Å. The interplanar angle is 27·5°. S—C bond lengths are

---

* Lists of structure factors, H-atom parameters, bond lengths and bond angles involving H atoms and anisotropic thermal parameters of non-H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51431 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and bond angles* (°)
involving non-H *atoms with e.s.d.'s in parentheses*

S(1)–S(2)	2·077 (3)	S(1)–C(1)	1·764 (5)
C(1)–N(1)	1·358 (5)	C(1)–N(2)	1·338 (5)
N(1)–C(7)	1·355 (7)	N(2)–C(2)	1·363 (6)
C(2)–C(3)	1·390 (7)	C(3)–C(4)	1·399 (8)
C(4)–C(5)	1·379 (9)	C(5)–C(6)	1·401 (7)
C(6)–C(7)	1·400 (8)	C(7)–C(2)	1·400 (7)
S(2)–C(8)	1·761 (6)	C(8)–N(3)	1·345 (6)
C(8)–N(4)	1·339 (6)	N(3)–C(9)	1·379 (6)
N(4)–C(14)	1·374 (7)	C(9)–C(10)	1·400 (7)
C(10)–C(11)	1·387 (7)	C(11)–C(12)	1·380 (9)
C(12)–C(13)	1·369 (7)	C(13)–C(14)	1·402 (8)
C(14)–C(9)	1·401 (7)		

|			
S(2)–S(1)–C(1)	105·4 (2)	S(1)–S(2)–C(8)	105·8 (3)
S(1)–C(1)–N(1)	122·2 (4)	S(1)–C(1)–N(2)	124·6 (4)
N(1)–C(1)–N(2)	113·0 (4)	C(1)–N(1)–C(7)	105·3 (4)
C(1)–N(2)–C(2)	105·3 (3)	N(2)–C(2)–C(3)	130·7 (4)
N(2)–C(2)–C(7)	108·3 (4)	C(7)–C(2)–C(3)	121·0 (4)
C(2)–C(3)–C(4)	116·9 (4)	C(3)–C(4)–C(5)	122·1 (5)
C(4)–C(5)–C(6)	121·6 (5)	C(5)–C(6)–C(7)	116·4 (4)
C(6)–C(7)–C(2)	121·9 (4)	N(1)–C(7)–C(2)	108·1 (4)
N(1)–C(7)–C(6)	130·0 (4)	S(2)–C(8)–N(3)	123·4 (4)
S(2)–C(8)–N(4)	122·2 (4)	N(3)–C(8)–N(4)	114·2 (4)
C(8)–N(3)–C(9)	104·4 (4)	C(8)–N(4)–C(14)	105·3 (4)
N(3)–C(9)–C(10)	131·0 (4)	N(3)–C(9)–C(14)	108·4 (4)
C(14)–C(9)–C(10)	120·5 (4)	C(9)–C(10)–C(11)	116·7 (4)
C(10)–C(11)–C(12)	122·3 (5)	C(11)–C(12)–C(13)	121·9 (5)
C(12)–C(13)–C(14)	116·9 (4)	C(13)–C(14)–C(9)	121·6 (4)
N(4)–C(14)–C(9)	107·7 (4)	N(4)–C(14)–C(13)	130·8 (4)
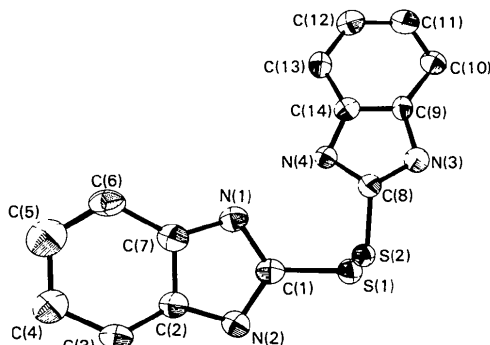
Fig. 1. *ORTEP* plot of the molecule.
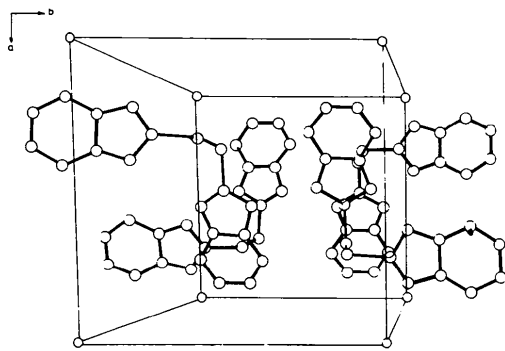
Fig. 2. Molecular packing in the unit cell.

normal. The C(1)–N(1), C(1)–N(2), C(8)–N(3) and C(8)–N(4) bond lengths with an average of 1·345 (6) Å show partial double-bond character. This is in keeping with resonance in the benzimidazole group. Bond parameters involving C atoms are normal.

The average N—H and C—H bond lengths are 0·81 and 0·95 (6) Å respectively. Though according to stoichiometry, each one of the two benzimidazole rings should have one deprotonated nitrogen and one NH nitrogen, due to extensive delocalization in the N—C—N bond, the two N atoms become equivalent and interestingly this is reflected in the positions occupied by the H atoms in the structure. Hydrogen peaks appear around both the N atoms in each ring with short H···H distances between equivalent positions related by the symmetry operation $(-x, -y, z)$: H(1)··· H(1′) = 1·272, H(2)···H(2′) = 1·519, H(7)···H(7′) = 1·157 and H(8)···H(8′) = 1·271 Å. Hence these hydrogen positions were given a fixed occupancy factor of 0·50. All these H atoms take part in hydrogen bonds between the N atoms in neighbouring mbi's, with $(N···N)_{av} = 2·871$ (4) Å and the angle $(N—H···N)_{av} = 167·3$ (3)°. Crystal packing is due to these three-dimensional hydrogen-bonding networks.

The C—S—S—C dihedral angle is 90·6 (2)° and is comparable to those reported for other disulfides (78–101°). An empirical relationship between the S—S bond length and X—C—S—S torsion angle has been reported (Higashi *et al.*, 1978) where X is C or N in these symmetric disulfides with S atoms bonded to sp^2 C atoms. When the X—C—S—S angle is within about 90 ± 20°, the average S—S bond length is 2·08 Å. In the present compound this relationship is also held, since the N—C—S—S torsion angles are −93·1 (4), 93·0 (4), 92·3 (4) and −92·3 (4)°.

References

APPA RAO, G. V. N., SESHASAYEE, M., ARAVAMUDAN, G., NAGESWARA RAO, T. & VENKATASUBRAMANIAN, P. N. (1982). *Acta Cryst.* B38, 2852–2855.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* 53, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.

HIGASHI, L. S., LUNDEEN, M. & SEFF, K. (1978). *J. Am. Chem. Soc.* 100, 8101–8106.

HOFMANN, K. (1953). *Imidazole and its Derivatives*, Part I, p. 292. New York: Interscience.

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

ROUT, G. C., SESHASAYEE, M. & ARAVAMUDAN, G. (1982). *Cryst. Struct. Commun.* 11, 1389–1393.

ROUT, G. C., SESHASAYEE, M., ARAVAMUDAN, G. & SOWRIRAJAN, S. (1984). *Polyhedron*, 3, 921–927.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1986). *SHELX*86. Program for the solution of crystal structures from diffractometer data. Univ. of Göttingen, Federal Republic of Germany.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.