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## The Crystal and Molecular Structure of *N*-*tert*-Butyldithiophthalimide

BY MAZHAR-UL-HAQUE\*

*Department of Chemistry, University of Petroleum and Minerals, Dhahran, Saudi Arabia*

AND MOHAMMAD BEHFOROZ

*Department of Chemistry, Pahlavi University, Shiraz, Iran*

(Received 2 October 1978; accepted 11 December 1978)

### Abstract

$C_{12}H_{13}NO_2S_2$  is triclinic,  $a = 8.627$  (3),  $b = 8.994$  (2),  $c = 9.606$  (3) Å,  $\alpha = 103.17$  (3),  $\beta = 114.28$  (3),  $\gamma = 95.77$  (3)°, space group  $P\bar{1}$ ,  $Z = 2$ . The structure was refined to  $R = 0.033$  for 2023 observed reflections. The angle between the planes C–S–S and S–S–N is 97.8°, and the S–S bond length is 2.007 (1) Å.

and an S–S length of 2.02 Å, indicating the presence of a considerable amount of  $\pi$  character. In this investigation, another dithioimide, having a phthalimide and an alkyl group in place of the two succinimide moieties on the S–S bond, was studied to compare the effect of these groups on the bond lengths and angles.

### Introduction

We have already reported the structure of *N,N'*-dithiodisuccinimide (Mazhar-ul-Haque & Behforouz, 1974); it has an angle of about 85° between the two S–S–N planes

\* To whom correspondence should be addressed.

### Experimental

*N-tert*-Butyldithiophthalimide is a white crystalline material (m.p. 378–379 K), which was prepared by the reaction of *tert*-butylthiosulphenyl chloride with phthalimide in the presence of triethylamine (Behforouz, Firouzabadi & Ardakani, 1971).

*Crystal data*

$C_{12}H_{13}NO_2S_2$ ,  $M_r = 267.4$ , triclinic,  $a = 8.627(3)$ ,  $b = 8.994(2)$ ,  $c = 9.606(3)$  Å,  $\alpha = 103.17(3)$ ,  $\beta = 114.28(3)$ ,  $\gamma = 95.77(3)^\circ$ ,  $U = 645.5$  Å<sup>3</sup>,  $D_m$  (by flotation) = 1.37,  $Z = 2$ ,  $D_c = 1.376$  Mg m<sup>-3</sup>. Space group  $P1$ ; Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å,  $\mu = 0.392$  mm<sup>-1</sup>,  $F(000) = 280$ .

A crystal  $ca\ 0.35 \times 0.25 \times 0.35$  mm was used for intensity measurements on a Syntex  $P1$  diffractometer at a take-off angle of  $3^\circ$  with Mo  $K\alpha$  radiation filtered by a graphite incident-beam monochromator. 2975 independent reflections ( $2\theta < 55^\circ$ ) were measured by the  $\theta$ - $2\theta$  scan technique with a variable scan rate of 4–24° min<sup>-1</sup>; stationary-crystal stationary-counter background counts were taken at each end of the scan range. The ratio of scan time to background counting time was 2.0. 2023 reflections were judged to be observed, having  $I > 3\sigma(I)$ . Three representative reflections were measured periodically and showed no significant change. Scattering factors were from Cromer & Waber (1965), except those for H which were from Stewart, Davidson & Simpson (1965).

The structure was solved by the heavy-atom method. Isotropic least-squares refinement of the two S atoms gave  $R = 0.51$ . The remaining non-hydrogen atoms were located by Fourier synthesis, and block-diagonal isotropic refinement of all these atoms gave  $R = 0.124$ . Further anisotropic refinement reduced  $R$  to 0.057. At this stage a difference synthesis revealed all 13 H atoms. Finally the non-hydrogen atoms were refined anisotropically and the H atoms isotropically, which gave  $R = 0.033$ .\* A Hughes (1941) weighting scheme of the form  $w = 1$  for  $|F_o| \leq 15$ ,  $\sqrt{w} = 15/|F_o|$  for  $|F_o| > 15$  was used. A final difference synthesis was flat except for a few peaks of  $ca\ 0.5\ e\ \text{Å}^{-3}$  in the vicinity of the S atoms. An anomalous-dispersion correction for the S atoms was applied.

**Results and discussion of the structure**

Fig. 1 shows the structure and the atomic numbering, and Fig. 2 the [010] projection of the structure. Tables 1 and 2 list the coordinates of the non-hydrogen and the H atoms. Bond lengths and angles are listed in Table 3. Torsion angles and the intermolecular contacts  $< 3.6$  Å are given in Tables 4 and 5 respectively.

Hordvik (1966) has shown that, for molecules containing a disulfide group  $X-S^II-S^II-Y$ , the bond

\* Lists of structure factors and anisotropic temperature factors of the non-hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34087 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

length between two divalent S atoms varies with the angle between the  $X-S-S$  and  $S-S-Y$  planes. The shortest bond lengths correspond to dihedral angles of  $ca\ 90^\circ$ , while the longest correspond to smaller dihedral angles. The most favorable dihedral angle for  $\pi$ -bonding in these systems is  $90^\circ$ . The dihedral angle of  $97.8^\circ$  and the S–S length of 2.007(1) Å fit well with Hordvik's (1966) curve, as we observed previously for *N,N'*-dithiodisuccinimide (Mazhar-ul-Haque & Behforouz, 1974). If the length of a single S–S bond is taken as 2.08 and a double bond as 1.88 Å (Pauling, 1960) and we assume a linear relationship between bond length and bond order, a  $\pi$ -bond order of 0.365 fits well with Hordvik's (1966) proposed bond length/bond order curve.

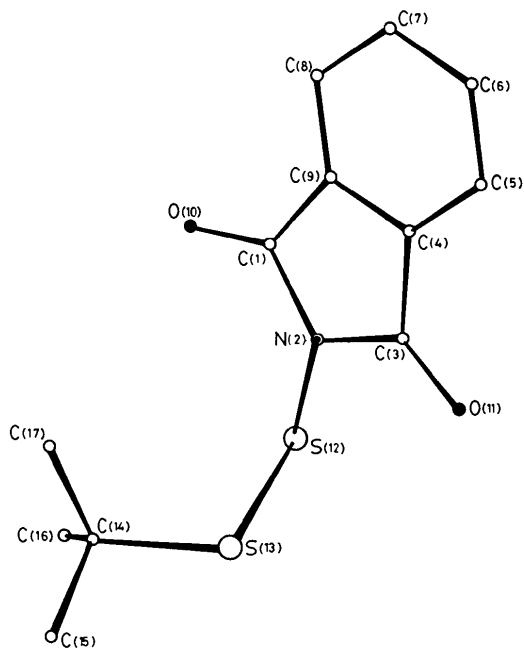


Fig. 1. Molecule of *N-tert*-butyldithiophthalimide, showing the numbering scheme.

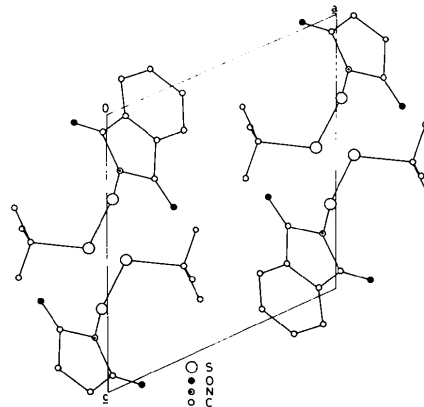


Fig. 2. The [010] projection showing the packing of molecules.

The S—N length of 1.702 Å is shorter than the sum of the Pauling covalent radii (1.74 Å), but agrees fairly well with the single-bond lengths (1.688 and 1.709 Å) in *N,N'*-dithiodisuccinimide (Mazhar-ul-Haque & Behforouz, 1974), but even shorter S—N single-bond lengths (1.60–1.67 Å) have been observed (*Molecular Structures and Dimensions*, 1972). The S—C length [1.853 (3) Å] is in good agreement with the accepted value of 1.812 Å (Pauling, 1960) and with the C(*sp*<sup>3</sup>)—S values of 1.823 and 1.843 Å (Mellor & Nyburg, 1971) and 1.82 Å found in other compounds (Abrahams, 1956). The mean C—N distance (1.414 Å) is in good agreement with those in *N*-chlorosuccinimide (1.39 Å) (Brown, 1961), in succinimide (1.385 Å) (Mason, 1961), and in *N,N'*-dithiodisuccinimide (1.406 and 1.399 Å) (Mazhar-ul-Haque & Behforouz, 1974). If a C(*sp*<sup>3</sup>)—N(*sp*<sup>3</sup>) single-bond distance is taken as 1.47 and a C(*sp*<sup>2</sup>)—N(*sp*<sup>2</sup>) double bond as 1.29 Å (Pauling, 1960), and assuming a linear relationship between bond length and bond order, the

Table 1. Fractional coordinates ( $\times 10^4$ ) for non-hydrogen atoms, with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	−230 (3)	1905 (2)	559 (2)
N(2)	589 (2)	2155 (2)	2223 (2)
C(3)	2065 (3)	3421 (3)	3002 (3)
C(4)	2196 (3)	3979 (2)	1715 (2)
C(5)	3422 (3)	5154 (3)	1794 (3)
C(6)	3222 (3)	5394 (3)	366 (3)
C(7)	1851 (4)	4510 (3)	−1078 (3)
C(8)	629 (3)	3335 (3)	−1146 (3)
C(9)	829 (3)	3084 (2)	268 (2)
O(10)	−1514 (2)	920 (2)	−378 (2)
O(11)	2955 (2)	3881 (2)	4418 (2)
S(12)	202 (1)	880 (1)	3169 (1)
S(13)	−931 (1)	1924 (1)	4461 (1)
C(14)	−3314 (3)	1148 (3)	3282 (3)
C(15)	−3986 (4)	1734 (4)	4497 (4)
C(16)	−3732 (3)	−616 (3)	2701 (3)
C(17)	−4021 (3)	1836 (3)	1900 (3)

Table 2. Fractional coordinates ( $\times 10^3$ ) and isotropic temperature factors for H atoms, with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
H(1) [C(5)]	436 (3)	576 (3)	278 (3)	3.7 (5)
H(2) [C(6)]	402 (4)	622 (3)	37 (3)	5.2 (6)
H(3) [C(7)]	176 (3)	468 (3)	−201 (3)	4.6 (6)
H(4) [C(8)]	−31 (3)	272 (3)	−211 (3)	3.6 (5)
H(5) [C(15)]	−355 (3)	131 (3)	532 (3)	5.2 (6)
H(6) [C(15)]	−377 (4)	293 (4)	487 (4)	6.7 (7)
H(7) [C(15)]	−516 (4)	149 (3)	410 (3)	6.3 (7)
H(8) [C(16)]	−326 (3)	−103 (3)	359 (3)	5.2 (6)
H(9) [C(16)]	−329 (3)	−99 (3)	191 (3)	5.0 (6)
H(10) [C(16)]	−497 (3)	−98 (3)	211 (3)	5.0 (6)
H(11) [C(17)]	−378 (4)	302 (3)	231 (3)	6.0 (7)
H(12) [C(17)]	−350 (4)	163 (3)	117 (3)	6.1 (7)
H(13) [C(17)]	−527 (4)	149 (3)	134 (3)	6.0 (7)

Table 3. Bond lengths and angles with *e.s.d.*'s in parentheses

## (a) Distances (Å)

C(1)—N(2)	1.408 (3)	C(8)—H(4)	0.94 (2)
C(1)—C(9)	1.479 (3)	S(12)—S(13)	2.007 (1)
C(1)—O(10)	1.200 (3)	S(13)—C(14)	1.853 (3)
N(2)—C(3)	1.419 (3)	C(14)—C(15)	1.521 (4)
N(2)—S(12)	1.702 (2)	C(14)—C(16)	1.508 (4)
C(3)—C(4)	1.476 (3)	C(14)—C(17)	1.517 (4)
C(3)—O(11)	1.196 (3)	C(15)—H(5)	0.92 (3)
C(4)—C(5)	1.383 (3)	C(15)—H(6)	1.03 (3)
C(4)—C(9)	1.386 (3)	C(15)—H(7)	0.90 (3)
C(5)—C(6)	1.381 (4)	C(16)—H(8)	0.96 (3)
C(5)—H(1)	0.95 (2)	C(16)—H(9)	1.00 (3)
C(6)—C(7)	1.383 (3)	C(16)—H(10)	0.96 (3)
C(6)—H(2)	0.96 (3)	C(17)—H(11)	1.02 (3)
C(7)—C(8)	1.386 (4)	C(17)—H(12)	0.97 (3)
C(7)—H(3)	0.91 (3)	C(17)—H(13)	0.96 (3)
C(8)—C(9)	1.371 (1)		

## (b) Angles (°)

N(2)—C(1)—C(9)	105.3 (2)	N(3)—S(12)—S(13)	106.4 (1)
N(2)—C(1)—O(10)	125.2 (2)	S(12)—S(13)—C(14)	107.3 (1)
C(9)—C(1)—O(10)	129.5 (2)	S(13)—C(14)—C(15)	102.5 (2)
C(1)—N(2)—C(3)	111.5 (2)	S(13)—C(14)—C(16)	110.7 (2)
C(1)—N(2)—S(12)	125.0 (2)	S(13)—C(14)—C(17)	109.8 (2)
C(11)—N(2)—S(12)	122.0 (2)	C(15)—C(14)—C(16)	111.0 (2)
N(2)—C(3)—C(4)	105.6 (2)	C(15)—C(14)—C(17)	111.1 (2)
N(2)—C(3)—O(11)	124.4 (2)	C(16)—C(14)—C(17)	111.4 (2)
C(4)—C(3)—O(11)	130.3 (2)	C(14)—C(15)—H(5)	110 (2)
C(3)—C(4)—C(5)	130.0 (2)	C(14)—C(15)—H(6)	113 (2)
C(3)—C(4)—C(9)	108.4 (2)	C(14)—C(15)—H(7)	114 (2)
C(5)—C(4)—C(9)	121.5 (2)	H(5)—C(15)—H(6)	113 (3)
C(4)—C(5)—C(6)	116.9 (2)	H(5)—C(15)—H(7)	107 (3)
C(4)—C(5)—H(1)	122 (2)	H(6)—C(15)—H(7)	100 (3)
C(6)—C(5)—H(1)	121 (2)	C(14)—C(16)—H(8)	110 (2)
C(5)—C(6)—C(7)	121.6 (3)	C(14)—C(16)—H(9)	111 (2)
C(5)—C(6)—H(2)	120 (2)	C(14)—C(16)—H(10)	109 (2)
C(7)—C(6)—H(2)	119 (2)	H(8)—C(16)—H(9)	112 (2)
C(6)—C(7)—C(8)	121.1 (3)	H(8)—C(16)—H(10)	111 (2)
C(6)—C(7)—H(3)	120 (2)	H(9)—C(16)—H(10)	105 (2)
C(8)—C(7)—H(3)	119 (2)	C(14)—C(17)—H(11)	110 (2)
C(7)—C(8)—C(9)	117.6 (2)	C(14)—C(17)—H(12)	115 (2)
C(7)—C(8)—H(4)	122 (2)	C(14)—C(17)—H(13)	109 (2)
C(9)—C(8)—H(4)	120 (2)	H(11)—C(17)—H(12)	105 (3)
C(8)—C(9)—C(1)	129.5 (2)	H(11)—C(17)—H(13)	106 (3)
C(8)—C(9)—C(4)	121.3 (2)	H(12)—C(17)—H(13)	111 (3)
C(4)—C(9)—C(1)	109.1 (2)		

Table 4. Torsion angles (°), with *e.s.d.*'s in parentheses

C(1)—N(2)—C(3)—C(4)	−1.4 (2)
C(1)—C(9)—C(4)—C(3)	−0.5 (2)
C(1)—N(2)—S(12)—S(13)	−113.3 (1)
N(2)—C(1)—C(9)—C(4)	−0.4 (2)
N(2)—S(12)—S(13)—C(14)	97.8 (1)
N(2)—C(3)—C(4)—C(9)	1.1 (2)
C(3)—N(2)—S(12)—S(13)	81.6 (1)
C(3)—N(2)—C(1)—C(9)	1.1 (2)
C(4)—C(5)—C(6)—C(7)	0.5 (3)
C(5)—C(6)—C(7)—C(8)	−0.6 (3)
C(6)—C(7)—C(8)—C(9)	0.1 (3)
C(7)—C(8)—C(9)—C(4)	0.4 (2)
C(8)—C(9)—C(4)—C(5)	−0.4 (2)
C(9)—C(4)—C(5)—C(6)	0.0 (2)

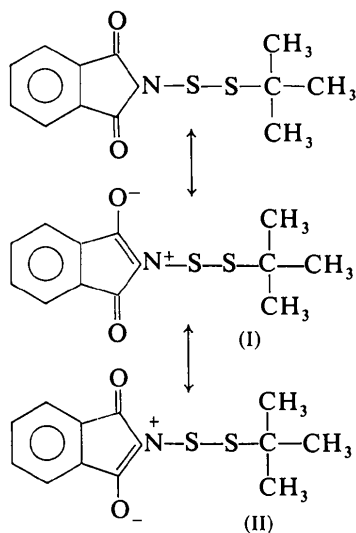
Table 5. Intermolecular contacts  $<3.6 \text{ \AA}$  involving non-hydrogen atoms

Atoms*	
C(1)···C(1 <sup>I</sup> )	3.465 (3)
C(1)···O(10 <sup>I</sup> )	3.088 (3)
N(2)···O(10 <sup>I</sup> )	3.286 (3)
C(5)···O(11 <sup>II</sup> )	3.525 (3)
C(6)···C(6 <sup>II</sup> )	3.520 (4)
C(8)···C(4 <sup>III</sup> )	3.573 (3)
C(9)···C(7 <sup>III</sup> )	3.514 (4)
O(10)···O(10 <sup>I</sup> )	3.154 (3)
O(11)···O(11 <sup>II</sup> )	3.471 (3)
S(12)···O(10 <sup>I</sup> )	3.461 (2)

\* Roman numeral superscripts denote the following equivalent positions, relative to the reference molecule at  $x, y, z$ .

- (I)  $-x, -y, -z$   
 (II)  $1-x, 1-y, 1-z$   
 (III)  $-x, 1-y, -z$

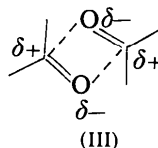
present C—N bond possesses 31% double-bond character. This may be due to the contributions of resonance structures (I) and (II).



The mean C=O distance ( $1.198 \text{ \AA}$ ) is a little shorter than the  $1.22 \text{ \AA}$  in *N*-chlorosuccinimide (Brown, 1961) and  $1.23 \text{ \AA}$  in succinimide (Mason, 1961), but agrees well with the mean C=O distances ( $1.195$  and  $1.202 \text{ \AA}$ ) in *N,N'*-dithiodisuccinimide (Mazhar-ul-Haque & Behforouz, 1974). The C(1)—C(9) ( $1.479 \text{ \AA}$ ) and C(3)—C(4) ( $1.476 \text{ \AA}$ ) lengths are in good agreement with those in *N,N'*-dithiodisuccinimide ( $1.492$  and  $1.493 \text{ \AA}$ , and  $1.500$  and  $1.492 \text{ \AA}$ ) and such short C—C lengths adjacent to carbonyl groups are common (Brown, 1961; Mason, 1961). The mean C—C length [ $1.382 (3) \text{ \AA}$ ] is close to the accepted value of  $1.395 (3)$

$\text{\AA}$  (*Molecular Structures and Dimensions*, 1972). The bond distances, bond angles and torsion angles are in good agreement with those in *N,N'*-dithiodisuccinimide.

There is only one short intermolecular contact less than the sum of van der Waals radii given by Pauling (1960). This close contact between C(1)···O(10) ( $3.088 \text{ \AA}$ ) may be explained by electrostatic interaction between a carbonyl C in one molecule and a carbonyl O atom in another as in (III). Similar results have been observed and explained in this way (Davies & Blum, 1955; Chu, Jeffrey & Sakurai, 1962).



All calculations were carried out on the University of Petroleum and Minerals IBM 370/158 computer with the NRC Crystallographic Programs (Ahmed, Hall & Pippy, 1966).

MUH thanks the University of Petroleum and Minerals for a research grant, and the staff of the computer center for their cooperation.

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