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## Structure of N-(2-Nitrophenylthio)phthalimide. Intramolecular S...O Interaction

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**Abstract.**  $C_{14}H_8N_2O_4S$ ,  $M_r = 300.29$ , monoclinic,  $P2_1/c$ ,  $a = 12.037$  (1),  $b = 13.710$  (2),  $c = 7.858$  (1) Å,  $\beta = 99.94$  (1)°,  $V = 1277.4$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.561$  Mg m<sup>-3</sup>,  $Mo K\alpha_1$ ,  $\lambda = 0.70926$  Å,  $\mu = 0.258$  mm<sup>-1</sup>,  $F(000) = 616$ ,  $T = 293$  K,  $R = 0.041$  for 2405 observed reflexions. The molecule is composed of two planar sections, the thiophthalimido and 2-nitrophenylthio groups, which form a dihedral angle of 83.3 (3)°, and has an approximate mirror plane coinciding with the 2-nitrophenyl plane and bisecting

the phthalimido group. A short intramolecular contact [2.501 (2) Å] is found between the O atom of the nitro group and S. The angle O...S–N is 175.7 (1)°. The calculation of the total energy by the CNDO/2 method as a function of torsion angle ( $\varphi$ ) of the nitro group shows a minimum value at  $\varphi = -10^\circ$ , which is consistent with the observed angle of  $-3.8$  (3)°.

**Introduction.** The title compound was synthesized by Oae & Kodaera (1983). For the 2-nitrophenylthio group a short intramolecular S...O interaction is expected. An X-ray analysis was undertaken to investigate the structural features of this compound.

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Table 1. Positional parameters ( $\times 10^5$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2$ ) for non-H atoms
$$B_{eq} = \frac{1}{3} \sum_i \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}$
S	70813 (4)	86912 (5)	39961 (6)	3.6
N(1)	83351 (14)	86966 (14)	53607 (23)	3.4
C(2)	88927 (18)	95497 (16)	60912 (28)	3.4
C(3)	99266 (17)	92008 (16)	72259 (28)	3.3
C(4)	107575 (21)	97263 (19)	82714 (34)	4.3
C(5)	116363 (23)	91985 (22)	92190 (36)	4.9
C(6)	116801 (22)	81947 (23)	91164 (37)	5.0
C(7)	108413 (21)	76682 (19)	80676 (34)	4.4
C(8)	99659 (17)	81923 (16)	71422 (28)	3.4
C(9)	89358 (18)	78419 (16)	59749 (29)	3.5
O(2)	85497 (16)	103618 (12)	57992 (25)	4.8
O(9)	86252 (16)	70272 (13)	56106 (25)	4.9
C(11)	61510 (16)	87263 (15)	55119 (24)	3.0
C(12)	49767 (17)	87256 (16)	50109 (26)	3.2
C(13)	42343 (18)	87937 (18)	61650 (32)	4.0
C(14)	46606 (22)	88507 (21)	79062 (34)	4.6
C(15)	58145 (22)	88331 (20)	84518 (29)	4.4
C(16)	65424 (18)	87710 (18)	72894 (26)	3.7
N(2)	45037 (17)	86494 (15)	31860 (25)	4.1
O(21)	51637 (16)	86414 (16)	21663 (21)	5.3
O(22)	34865 (16)	85845 (19)	27390 (27)	6.5

**Experimental.** Yellow plates,  $0.20 \times 0.20 \times 0.25$  mm, unit-cell parameters by least squares from 25 reflexions ( $66 < 2\theta < 73^\circ$ ,  $\text{Cu K}\alpha_1$ ,  $\lambda = 1.54051 \text{ \AA}$ ), Rigaku AFC4 diffractometer, graphite monochromator,  $2 \leq 2\theta \leq 65^\circ$ ,  $h = 0-18$ ,  $k = 0-20$ ,  $l = -12-12$ ,  $\omega-2\theta$  scan, scan range  $\Delta\omega = 1.3^\circ + 0.5^\circ \tan\theta$ , scan speed  $2^\circ \text{ min}^{-1}$  in  $2\theta$ , three reflexions monitored (600, 180, 204) every 50 reflexions, variations within 3%. 5230 measured, 4663 unique, 2405 observed [ $|F_o| \geq 3\sigma(F)$ ] reflexions. Structure solved by *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). All non-H atoms obtained from *E* map. H atoms from difference map. Block-diagonal least squares with anisotropic temperature factors for non-H and isotropic for H.  $\sum w(|F_c| - k^{-1}|F_o|)^2$  minimized.  $w = 1 / (0.17251 + 0.01011|F_o| + 0.00025|F_o|^2)$ . Absorption correction applied numerically. Extinction parameter  $g = 7 \times 10^{-7}$ . 10 reflexions omitted from final refinement and final difference synthesis.  $\Delta\rho(\text{max.}) = 0.22 \text{ e \AA}^{-3}$  between C(8) and C(9),  $\Delta/\sigma(\text{max.}) = 0.24$ .  $R = 0.041$ ,  $wR = 0.054$ ,  $S = 1.053$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All computations performed on HITAC M180 computer of the Data Processing Center of the University with programs *UNICSIII* (Sakurai & Kobayashi, 1978), *MULTAN78* and *ORTEPII* (Johnson, 1971). The final atomic parameters are given in Table 1.\*

\* Lists of structure factors, anisotropic temperature factors and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42485 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Discussion.** The molecular structure with the atom numbering is shown in Fig. 1. Bond distances and angles are listed in Table 2. The molecule consists of two planes: the thiophthalimido and the *o*-nitrophenylthio groups. The dihedral angle between these two planes is  $83.3(3)^\circ$ . The large rotation angle around the N—S bond suggests that no conjugation exists between the phthalimido  $\pi$  system and the N—S—C grouping.

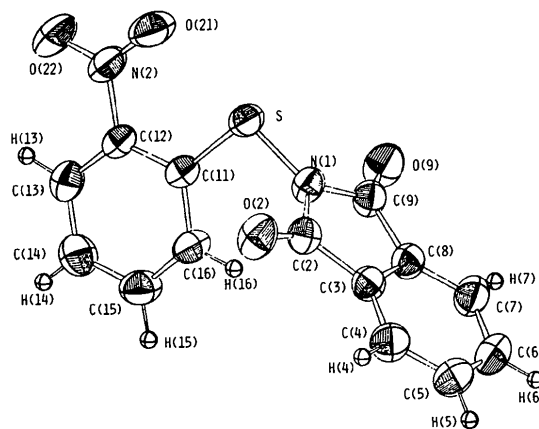


Fig. 1. *ORTEPII* (Johnson, 1971) drawing with atomic numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability.

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) of non-hydrogen atoms and dimensions about the S...O contact

S—N(1)	1.694 (2)	C(8)—C(9)	1.489 (3)
S—C(11)	1.771 (2)	C(9)—O(9)	1.197 (3)
N(1)—C(2)	1.420 (3)	C(11)—C(12)	1.400 (3)
N(1)—C(9)	1.417 (3)	C(11)—C(16)	1.396 (3)
C(2)—C(3)	1.480 (3)	C(12)—C(13)	1.382 (3)
C(2)—O(2)	1.196 (3)	C(12)—N(2)	1.452 (3)
C(3)—C(4)	1.382 (3)	C(13)—C(14)	1.378 (4)
C(3)—C(8)	1.385 (3)	C(14)—C(15)	1.381 (4)
C(4)—C(5)	1.388 (4)	C(15)—C(16)	1.373 (4)
C(5)—C(6)	1.380 (4)	N(2)—O(21)	1.222 (3)
C(6)—C(7)	1.390 (4)	N(2)—O(22)	1.217 (3)
C(7)—C(8)	1.375 (3)		
N(1)—S—C(11)	99.9 (1)	N(1)—C(9)—C(8)	105.4 (2)
S—N(1)—C(2)	124.5 (2)	N(1)—C(9)—O(9)	124.8 (2)
S—N(1)—C(9)	124.0 (2)	C(8)—C(9)—O(9)	129.9 (2)
C(2)—N(1)—C(9)	111.5 (2)	S—C(11)—C(12)	122.4 (2)
N(1)—C(2)—C(3)	105.5 (2)	S—C(11)—C(16)	122.1 (2)
N(1)—C(2)—O(2)	124.5 (2)	C(12)—C(11)—C(16)	115.5 (2)
C(3)—C(2)—O(2)	130.0 (2)	C(11)—C(12)—C(13)	123.4 (2)
C(2)—C(3)—C(4)	129.5 (2)	C(11)—C(12)—N(2)	118.8 (2)
C(2)—C(3)—C(8)	109.0 (2)	C(13)—C(12)—N(2)	117.7 (2)
C(4)—C(3)—C(8)	121.4 (2)	C(12)—C(13)—C(14)	118.9 (2)
C(3)—C(4)—C(5)	117.0 (2)	C(13)—C(14)—C(15)	119.3 (3)
C(4)—C(5)—C(6)	121.5 (3)	C(14)—C(15)—C(16)	121.2 (3)
C(5)—C(6)—C(7)	121.4 (3)	C(11)—C(16)—C(15)	121.6 (2)
C(6)—C(7)—C(8)	117.0 (2)	C(12)—N(2)—O(21)	117.4 (2)
C(3)—C(8)—C(7)	121.7 (2)	C(12)—N(2)—O(22)	119.6 (2)
C(3)—C(8)—C(9)	108.6 (2)	O(21)—N(2)—O(22)	123.1 (2)
C(7)—C(8)—C(9)	129.6 (2)		
S...O(21)	2.501 (2)	C(11)—S...O(21)	76.1 (1)
N(1)—S...O(21)	175.7 (1)	S...O(21)—N(2)	105.2 (2)

The six-membered ring of the phthalimido group is planar with deviations within 0.006 (3) Å. The five-membered ring is distorted with significant out-of-plane deformation of the C(9)=O(9) carbonyl groups [0.011 (3), 0.060 (3) Å for C(9) and O(9), respectively]. The deviation of S from this plane is 0.026 (2) Å. The dihedral angle between the six- and five-membered rings of the phthalimido group is 1.4 (3)°. The dimensions of the phthalimido group are consistent with those in other *N*- or *S*-phthalimides (Andreotti, Bocelli & Sgarabotto, 1977; Mazhar-ul-Haque & Behforouz, 1979). The S—N(1) distance (1.694 Å) is shorter than the normal S—N single-bond length (1.74 Å), but is usual in this type of case where many S—N single bonds have been found between 1.63 and 1.68 Å because of the contribution of  $\pi$  character to the S—N bond.

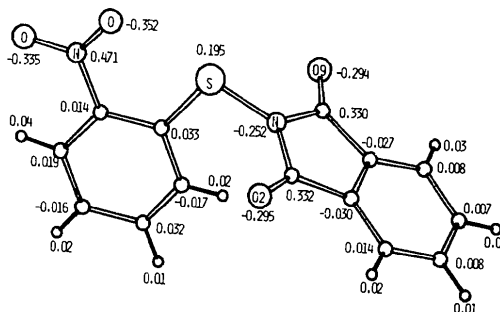
The dimensions of the *o*-nitrophenyl group have normal values. C(11)—C(12) (1.400 Å) is longer than the C—C length of  $sp^2$ — $sp^2$  type. The phenyl ring is planar with deviations within 0.008 (4) Å. Deviations of S, N(2), O(21) and O(22) from this plane are -0.072 (3), 0.038 (4), -0.026 (4) and 0.141 (4) Å, respectively. The dihedral angle between the nitro and phenyl groups is 4.7 (3)°. Associated with this planarity a very short intramolecular distance (2.501 Å) is found between S and O(2) atoms. The sum of the van der Waals radii for S and O is 3.25 Å and the S—O single-bond length is 1.70 Å. This short distance and the lack of any tendency of the nitro group to rotate out of the plane of the benzene ring are indicative not only of a strong resonance stabilization of the molecule but also of a strong non-bonding attractive interaction between S and O. The N—S...O arrangement is almost linear (175.7°). The same situation was reported in the preceding paper (Iwasaki, 1986).

There are other weaker intramolecular non-bonding interactions between S and O of the phthalimido group. S...O(2) and S...O(9) are 3.084 (2) and 3.075 (2) Å, respectively.

Fig. 2 shows the net charge at each atom calculated by the CNDO/2 method based on the determined structure. The values of the charges on S and O(21), +0.195 and -0.352 respectively, suggest an attractive electrostatic interaction between S and O(21). The same trend is shown in the final difference map, which shows a negative region about S and a positive region about O. Besides the S—C(11) and S—N(1) bonding electrons, two residual peaks, each at 0.95 Å from S, are observed and form a distorted tetrahedral arrangement around S.

The total energies were calculated by the CNDO/2 method as a function of the torsion angle  $\varphi$ , C(11)—C(12)—N(2)—O(21) (Fig. 3). In these calculations a model structure was employed with fixed bond lengths for N—O (1.220 Å) and fixed angles for C—N—O (118°) for the planar nitro group and the observed dimensions for the other parts of the molecule. The

minimum value is obtained for  $\varphi = -10^\circ$ , with a total energy of -5778.6957 Hartree. The difference between maximum and minimum energies is 0.0584 Hartree, which corresponds to 154.4 kJ mol<sup>-1</sup>. For the X-ray-determined structure with a torsion angle of -3.8 (3)°, the total energy is -5778.7413 Hartree, which is more stable than the minimum value of the model structure.



A stereoscopic view of the crystal structure is shown in Fig. 4. The nitrophenyl groups stack along **b**. The angle between the nitrophenyl plane and **b** is  $86.2(2)^\circ$  and that between the phthalimido plane and **c** is  $59.6(2)^\circ$ . The mean distance between the nitrophenyl plane at  $(x, y, z)$  and that at  $(1-x, 2-y, 1-z)$  is  $3.471(5)$  Å. The packing contacts are of van der Waals type.

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*Acta Cryst.* (1986). **C42**, 127–128

**1,4-Butanediyl bis(*p*-chlorobenzoate) (BDDP) and 1,6-hexanediyl bis(*p*-chlorobenzoate) (HDDP): further refinement in space group  $P\bar{1}$ .** By G. BOCELLI, *Centro di Studio per la Strutturistica Diffraattometrica del CNR, Via M. D'Azeglio 85, 43100 Parma, Italy*, M. F. GRENIER-LOUSTALOT, *Institut Universitaire de Recherche Scientifique, Avenue Philippon, 64100 Pau, France* and R. E. MARSH, *Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, USA*

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**Abstract.** The crystal structures of the title compounds, recently reported in space group  $P1$ , have been more satisfactorily refined in the centrosymmetric space group  $P\bar{1}$  based on the data obtained from a new crystal for BDDP and the original data for HDDP. Whereas the original data for BDDP showed, for the  $0kl$  reflections, significantly larger values of  $F_o$  than  $F_c$ , the new  $F_o$  values are smaller than before and in good agreement with the  $F_c$ 's. The final parameters lead to more satisfactory geometries for both compounds.

Recently we described (Bocelli & Grenier-Loustalot, 1984*a,b*) the crystal structures of  $C_{18}H_{16}Cl_2O_4$  (BDDP) and  $C_{20}H_{22}Cl_2O_4$  (HDDP) in the noncentrosymmetric space group  $P1$  [BDDP:  $a = 7.609(2)$ ,  $b = 10.318(1)$ ,  $c = 5.924(3)$  Å,  $\alpha = 96.31(2)$ ,  $\beta = 98.35(3)$ ,  $\gamma = 111.05(2)^\circ$ ,  $Z = 1$ ; HDDP:  $a = 10.483(2)$ ,  $b = 7.760(2)$ ,  $c = 6.746(2)$  Å,  $\alpha = 107.77(2)$ ,  $\beta = 98.32(2)$ ,  $\gamma = 70.43(3)^\circ$ ,

$Z = 1$ ]. Both structures were very nearly centrosymmetric, and we have now carried out more successful refinements in  $P\bar{1}$ .

**BDDP:** The earlier blocked-matrix refinement in  $P1$  resulted in somewhat unusual geometry with, for example, the aromatic C–C distances ranging from  $1.316(9)$  to  $1.494(7)$  Å. Moreover, the observed intensities for the  $0kl$  reflections were significantly larger than the calculated ones ( $\sum |F_o| = 487.5$ ,  $\sum |F_c| = 322.7$ ). Since the original crystal has gone, we are unable to check this phenomenon on Weissenberg photographs. Accordingly, we have collected intensity data from a new crystal.

The new crystal was prismatic, about  $0.08 \times 0.12 \times 0.19$  mm in size. Data were collected using the same experimental procedures as described earlier (Bocelli & Grenier-Loustalot, 1984*a*). Cell dimensions were:  $a = 7.612(2)$ ,  $b = 10.357(3)$ ,  $c = 5.926(2)$  Å,  $\alpha = 96.28(3)$ ,