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Crystal and Molecular Structure of Thiophthalic Anhydride

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Abstract. Thiophthalic anhydride, $C_8H_4O_2S$, $M = 164.2$, is monoclinic, $P2_1/c$; $a = 8.565(5)$, $b = 5.695(4)$, $c = 19.002(9)$ Å, $\beta = 129.1(4)^\circ$. $D_c = 1.52$ g cm $^{-3}$, $U = 719.2$ Å 3 , $Z = 4$. $\mu(\text{Mo } K\alpha) = 10.4$ cm $^{-1}$. The structure was solved by Patterson and Fourier methods and refined by the full-matrix least-squares technique to $R = 5.7\%$ for 905 counter reflexions. Molecules show a small deviation from planarity, the S and O atoms being displaced about 0.07 and 0.04 Å respectively, above and below the plane of the C atoms of the five-membered ring. In the latter the average bond lengths C-S 1.801(5), C-C 1.480(6), C-O 1.197(7) Å indicate the absence of significant π -delocalization. The C-S-C angle is $92.6(2)^\circ$.

Introduction. Intensities were collected on a Siemens diffractometer by the θ - 2θ scan technique with Mo $K\alpha$ radiation for a maximum 2θ angle of 54° . All reflexions with $I < 3\sigma(I)$ were rejected, the remainder being corrected for Lorentz and polarization factors. 905 independent reflexions were used in the subsequent calculations. No correction for absorption (μR 0.06) was applied. The structure was solved by Patterson and Fourier methods. After anisotropic full-matrix least-squares refinement of all non-hydrogen atoms, a difference synthesis was calculated to locate the H atoms. Evaluated positions of these (C-H 1.08 Å) all occurred in regions of positive electron density. The final anisotropic refinement, in which the coordinates and tem-

perature factors of the H atoms were held constant, reduced $R = \sum ||F_o| - |F_c|| / \sum |F_c|$ to 0.057. Scattering factors were calculated according to Moore (1963). Table 1 gives final atomic parameters; the numbering of the atoms is shown in Fig. 1 with the bond lengths; angles are listed in Table 2; intermolecular contacts less than 3.75 Å are reported in Table 3; the equations of some molecular planes with the deviations of individual atoms are given in Table 4.

Table 2. Bond angles ($^\circ$) with estimated standard deviations in parentheses

In the third column the corresponding values of phthalimide are reported.

	X=S	X=N
C(1)-X-C(2)	92.6 (2)	112.2 (3)
X-C(1)-O(1)	123.1 (4)	125.4 (3)
X-C(1)-C(8)	109.8 (4)	106.2 (3)
O(1)-C(1)-C(8)	127.1 (5)	128.4 (3)
X-C(2)-O(2)	124.7 (4)	124.8 (3)
X-C(2)-C(3)	109.3 (4)	105.6 (3)
O(2)-C(2)-C(3)	126.0 (4)	130.0 (3)
C(2)-C(3)-C(4)	125.2 (5)	130.0 (3)
C(2)-C(3)-C(8)	114.7 (4)	108.2 (3)
C(4)-C(3)-C(8)	120.2 (5)	121.7 (3)
C(3)-C(4)-C(5)	118.3 (5)	116.6 (3)
C(4)-C(5)-C(6)	120.6 (4)	121.6 (3)
C(5)-C(6)-C(7)	121.1 (5)	121.4 (3)
C(6)-C(7)-C(8)	118.7 (6)	116.8 (3)
C(1)-C(8)-C(3)	113.4 (5)	107.8 (3)
C(1)-C(8)-C(7)	125.4 (5)	130.3 (3)
C(3)-C(8)-C(7)	121.2 (4)	121.9 (3)

Table 1. Fractional coordinates ($\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for H atoms) and anisotropic temperature factors ($\times 10^4$) with estimated standard deviations in parentheses

The thermal factors of H atoms are those of the C atoms to which they are bonded, before the anisotropic refinement. Anisotropic temperature factors in the form $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})]$.

	x	y	z	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
S	-218 (2)	-583 (3)	-1804 (1)	249 (3)	3 (7)	91 (2)	408 (5)	-26 (3)	38 (1)
O(1)	-1166 (5)	3136 (8)	-1300 (3)	267 (7)	275 (18)	115 (5)	404 (15)	41 (9)	63 (2)
O(2)	2567 (6)	-3955 (8)	-973 (2)	393 (8)	138 (18)	210 (5)	380 (15)	-67 (7)	70 (2)
C(1)	21 (6)	1574 (10)	-1048 (3)	183 (8)	9 (21)	99 (5)	315 (16)	12 (9)	43 (2)
C(2)	1972 (7)	-2168 (10)	-888 (3)	255 (8)	15 (21)	147 (5)	305 (19)	2 (9)	50 (2)
C(3)	2885 (6)	-921 (9)	-25 (3)	190 (7)	31 (17)	115 (4)	222 (15)	17 (8)	42 (1)
C(4)	4621 (6)	-1596 (10)	812 (3)	214 (7)	120 (21)	135 (5)	299 (16)	48 (9)	51 (2)
C(5)	5325 (7)	-187 (12)	1562 (3)	209 (8)	54 (23)	101 (5)	412 (22)	37 (10)	41 (2)
C(6)	4291 (7)	1831 (11)	1463 (3)	275 (9)	-59 (26)	148 (5)	378 (21)	-50 (11)	49 (2)
C(7)	2566 (7)	2487 (11)	635 (3)	239 (9)	21 (22)	129 (5)	304 (17)	-30 (9)	50 (2)
C(8)	1859 (6)	1105 (8)	-107 (3)	205 (7)	21 (17)	123 (4)	208 (15)	11 (8)	45 (2)
H(C4)	543	-318	88	3.857					
H(C5)	670	-67	223	4.414					
H(C6)	486	291	206	4.421					
H(C7)	177	407	56	3.969					

Table 3. Intermolecular distances (Å) less than 3.75 Å with their estimated standard deviations in parentheses

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z :

(I)	$x, 1+y, z$	(V)	$1-x, -y, -z$
(II)	$x, -1+y, z$	(VI)	$1-x, -1-y, -z$
(III)	$-x, -y, -z$	(VII)	$1+x, \frac{1}{2}-y, \frac{1}{2}+z$
(IV)	$-x, 1-y, -z$		

O(1)···O(2) ^I	3.294 (7)	C(1)···O(2) ^I	3.296 (8)
O(1)···C(2) ^I	3.512 (8)	C(1)···C(7) ^{III}	3.615 (9)
O(1)···C(4) ^{III}	3.721 (9)	C(2)···C(4) ^V	3.550 (9)
O(1)···C(5) ^{III}	3.677 (8)	C(2)···C(5) ^V	3.541 (10)
O(1)···C(7) ^{IV}	3.341 (9)	C(3)···C(3) ^V	3.715 (9)
O(2)···O(2) ^{VI}	3.608 (5)	C(3)···C(4) ^V	3.589 (9)
O(2)···C(4) ^{VI}	3.374 (8)	C(4)···C(7) ^{II}	3.717 (9)
O(2)···C(5) ^V	3.553 (9)	C(5)···O(1) ^{VII}	3.391 (6)
O(2)···C(6) ^V	3.568 (9)	C(6)···O(1) ^{VII}	3.513 (5)
O(2)···C(7) ^{II}	3.667 (8)	C(8)···C(8) ^{III}	3.677 (9)
O(2)···C(8) ^{II}	3.500 (7)		

Table 4. The equations of the mean planes: (I) S, O(1), O(2), C(1)–C(8); (II) C(3)–C(8); (III) C(1), C(2), C(3), C(8)

Equations are referred to the crystal axes and x, y, z are fractional coordinates.

(I)	$7.044x + 3.114y - 12.17z = 1.789$
(II)	$7.099x + 3.045y - 12.36z = 1.793$
(III)	$7.033x + 3.133y - 12.08z = 1.777$

Deviation from the mean planes in Å ($\times 10^3$)

	(I)	(II)	(III)
S	73	105	66
O(1)	-51	-58	-44
O(2)	-28	28	-36
C(1)	-8	-3	-3
C(2)	6	45	3
C(3)	-13	5	-6
C(4)	-19	-3	-8
C(5)	2	-1	23
C(6)	23	2	48
C(7)	20	1	40
C(8)	-5	-5	6

Discussion. In the crystal the molecule shows deviations from planarity. The six-membered ring is planar within 0.010 Å, but the five-membered one is puckered being planar only within 0.043 Å. The S and O atoms are displaced about 0.07 and 0.04 Å respectively, on opposite sides of the C(1), C(2), C(3), C(8) plane whose atoms are coplanar within 0.012 Å. This plane is slightly bent and twisted with respect to the benzene ring forming a dihedral angle of 1.2°.

The C–S length of 1.801 (5) Å is close to the value

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31124 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

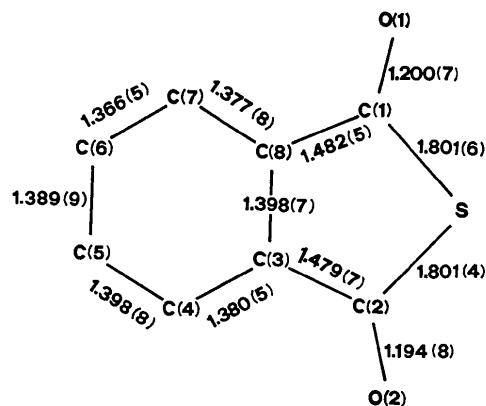


Fig. 1. Bond lengths (Å).

expected for a single bond $C(sp^2)$ –S(1.78 Å). The slight lengthening may be due to steric requirements in order to get a strain-free closure of the five-membered ring. The lack of π -character in the C–S bonds is consistent with the absence of conjugation in the heterocycle as indicated by the mean values of the C–O and C–C distances of 1.197(7) and 1.480(6) Å respectively, characteristic of a double bond $C=O$ and a single bond $C(sp^2)$ – $C(sp^2)$. The C–S–C angle of 92.6(2)° is in the range 88–93° usually found in five-membered rings containing S (Domiano & Musatti, 1974). It seems likely that the absence of π -delocalization over the whole molecule is related to its deviation from planarity. This is much more marked than in similar heterocyclic compounds (Hogg & Sutherland, 1974) where extensive conjugation occurs.

Finally it is interesting to compare bond angles between phthalimide (Von Eckart Matzat, 1972) and thiophthalic anhydride. It may be seen (Table 2) that because of the lengthening of the C–X distance passing from X=N to X=S and of the reduction of the C–X–C angle the molecule relaxes towards a more regular geometry, that is C atoms go towards a regular trigonal geometry. At present it is difficult to state how much molecules are distorted from planarity because of their intrinsic electronic and steric nature or because of crystal packing effects.

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References

- DOMIANO, P. & MUSATTI, A. (1974). *Cryst. Struct. Commun.* **3**, 335–338.
 HOGG, J. H. C. & SUTHERLAND, H. H. (1974). *Acta Cryst.* **B30**, 2058–2059.
 MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169–1175.
 VON ECKART MATZAT (1972). *Acta Cryst.* **B28**, 415–418.