

The Crystal and Molecular Structures of Thiobenzophenone *S*-Oxide and Thiobenzophenone

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Abstract

The crystal and molecular structures of thiobenzophenone *S*-oxide, C₁₃H₁₀OS (TBPSO), and thiobenzophenone, C₁₃H₁₀S (TBP), were determined from diffractometer data. The unit cell of TBPSO is orthorhombic, space group *P*2₁2₁2₁; *a* = 5.903 (3), *b* = 13.497 (4), *c* = 13.661 (4) Å, *V* = 1088.3 Å³, *Z* = 4, *D*_c = 1.31 Mg m⁻³. The unit cell of TBP is monoclinic, space group *P*2₁/*n*; *a* = 14.042 (2), *b* = 5.863 (2), *c* = 13.403 (3) Å, β = 106.40 (2)°, *V* = 1058.5 Å³, *D*_c = 1.24 Mg m⁻³. Least-squares refinements gave for TBPSO *R* = 0.066 for 560 observed reflections and for TBP *R* = 0.044 for 1367 observed reflections. The torsion angles of the phenyl rings out of the plane through the bridging atoms are 48 (1.5) and 25 (1.5)° in TBPSO and 43 (0.4) and 32 (0.4)° in TBP.

Introduction

The photolytic conversion of thiobenzophenone *S*-oxides into the corresponding benzophenones *via* the thermally unstable three-membered oxathiiranes has been reported (Carlsen, Harrit & Holm, 1976). Possible intermediates in the further thermal (Snyder, 1974) or photolytic (Pedersen, Holm & Carlsen, 1978) conversion of oxathiiranes into benzophenones are the thermally highly unstable benzophenone *O*-sulfides, which decompose at temperatures above 110 K. The assumption that benzophenone *O*-sulfides are intermediates in the decomposition of oxathiiranes is partly due to an experimental and theoretical study of the electronic absorption spectra of the benzophenone *O*-sulfides (Carlsen, Holm & Snyder, 1979). The theoretical procedure (CNDO/S-CI) was tested by calculating the electronic absorption spectra of a series of *para*-substituted thiobenzaldehyde *S*-oxides, the aryl group being *exo* to the oxygen atom, as model

compounds. It was possible to reproduce the experimentally observed absorption spectra of the model compounds to within 60 Å by assuming a 45° twist between the C=Š–Ö plane and the plane of the aryl group.

Unambiguous evidence for the conformation of the phenyl ring in sulfoxes was, however, lacking. Crystal structures had been determined earlier for two mono-aryl cases, where the phenyl ring was found twisted out of the CSO plane by 60–80° (Hummelink, 1974*a*, *b*, 1975, 1976). Unfortunately, in both compounds the *ortho* positions of the ring are occupied by methyl groups, thereby masking any stereoelectronic influences which may be present. On the other hand, in benzophenone the two phenyl rings are twisted relative to C=O by *ca* 30° (Vul & Lobanova, 1967; Fleischer, Sung & Hawkinson, 1968). With this background, we now report the crystal and molecular structures of thiobenzophenone *S*-oxide (TBPSO) and thiobenzophenone (TBP).

Experimental

Thiobenzophenone was prepared as described by Houben & Weyl (1955). Suitable crystals were obtained directly from the recrystallization procedure (hexane) of the crude, dried reaction product. The crystals were dried *in vacuo*. Thiobenzophenone *S*-oxide was prepared by peracid oxidation of purified thiobenzophenone (Zwanenburg, Thijs & Strating, 1967). Crystals were prepared by slow evaporation from a saturated solution of TBPSO in pentane at 243 K. The crystals were dried *in vacuo*.

TBP is unstable under atmospheric conditions so the crystal chosen for data collection was mounted in a sealed capillary with nitrogen. No special precautions were made for TBPSO, but the crystal gradually decomposed during the data collection. For both compounds, the unit-cell dimensions and the reflection

Table 1. *Crystal data*

TBPSO, C₁₃H₁₀OS, FW = 214.29, space group *P*2₁2₁2₁,
 $a = 5.903$ (3), $b = 13.497$ (4), $c = 13.661$ (4) Å,
 $V = 1088.26$ Å³, $Z = 4$, $T = 295$ K, $\mu(\text{Mo } K\alpha) = 0.220$ mm⁻¹,
 $D_c = 1.306$, $D_m(\text{floatation}) = 1.28$ Mg m⁻³,
 size of the crystal $0.13 \times 0.13 \times 0.50$ mm.

TBP, C₁₃H₁₀S, FW = 198.29, space group *P*2₁/*n*,
 $a = 14.042$ (2), $b = 5.863$ (2), $c = 13.403$ (3) Å,
 $\beta = 106.40$ (2)°,
 $V = 1058.47$ Å³, $Z = 4$, $T = 295$ K, $\mu(\text{Mo } K\alpha) = 0.217$ mm⁻¹,
 $D_c = 1.244$ Mg m⁻³
 size of the crystal $0.20 \times 0.20 \times 0.70$ mm.

intensities were measured with a four-circle diffractometer. Graphite-monochromatized Mo *K* α radiation was used ($\lambda = 0.71073$ Å). The crystal data are given in Table 1. For TBPSO, 2872 reflections ($k > 0$, $l > 0$) in the interval $0.07 < (\sin \theta)/\lambda < 0.66$ Å⁻¹ and, for TBP, 4328 reflections in the interval $0.07 < (\sin \theta)/\lambda < 0.70$ Å⁻¹ were obtained by the ω -scan technique. Averaging symmetry-equivalent reflections gave 1532 and 3070 unique reflections for TBPSO and TBP respectively. Agreement among equivalent reflections was (TBPSO) $R = 0.07$, (TBP) $R = 0.024$. The set of reflections from TBPSO was corrected for crystal decomposition with two standard reflections. Only the data having $I > 2\sigma(I)$ (TBPSO, 560; TBP, 1367) were corrected for Lp effects and used in the subsequent calculations. No corrections were made for absorption, extinction or anomalous dispersion.

Solution and refinement

Both structures were solved by direct methods. The structures were refined by full-matrix least-squares calculations.

TBPSO

All observations were given unit weight. O, S and all C atoms were refined with anisotropic thermal parameters. All H atoms were fixed with a benzene-type bond 1.00 Å in length and with isotropic thermal parameters, $U = 0.05$ Å². In the final least-squares refinement the maximum shift/error was 0.03 and $R = 0.066$.

TBP

During the final stages of refinement, a weight function was applied: $w^{-1} = 0.60 - 0.056F + 0.017F^2 + 0.30(\sin \theta)/\lambda$ (Nielsen, 1977). S and C atoms were refined with anisotropic thermal parameters, while the H atoms were given the isotropic thermal parameters equivalent to those of the atoms to which they are

bonded. The maximum shift/error for non-hydrogen atoms in the final least-squares refinement was 0.06 and $R = 0.044$.

The final fractional atomic coordinates for both compounds are given in Tables 2 and 3.*

The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The structure analysis was performed with the *SHELX* system of programs (Sheldrick, 1976). The illustrations were made with the *ORTEP* II program (Johnson, 1965). For other calculations, locally written programs were used.

Results and discussion

The two molecules are shown in Figs. 1 and 2 with the numbering of the atoms and the angles, projected onto

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34252 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates ($\times 10^4$) for the non-hydrogen atoms*

E.s.d.'s are in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
TBPSO			
C(1)	8654 (22)	2056 (8)	3117 (9)
C(2)	10493 (22)	1804 (10)	3718 (11)
C(3)	11973 (21)	2546 (14)	4055 (10)
C(4)	11619 (29)	3511 (11)	3791 (12)
C(5)	9952 (28)	3762 (11)	3173 (12)
C(6)	8402 (21)	3035 (11)	2855 (9)
C(1')	6377 (22)	1256 (8)	1718 (9)
C(2')	4320 (20)	849 (10)	1417 (11)
C(3')	3863 (24)	790 (11)	444 (10)
C(4')	5297 (33)	1102 (12)	-268 (9)
C(5')	7370 (30)	1486 (11)	18 (10)
C(6')	7775 (23)	1574 (9)	1004 (10)
C(7)	6933 (18)	1293 (9)	2751 (9)
S	6037 (6)	600 (3)	3631 (3)
O	4496 (15)	-189 (7)	3310 (7)
TBP			
C(1)	2108 (2)	2342 (5)	5503 (2)
C(2)	2615 (2)	4273 (5)	5980 (2)
C(3)	2184 (3)	5711 (6)	6537 (3)
C(4)	1272 (3)	5248 (7)	6657 (3)
C(5)	769 (3)	3333 (7)	6212 (3)
C(6)	1177 (2)	1904 (6)	5629 (2)
C(1')	1889 (2)	16 (5)	3870 (2)
C(2')	2022 (2)	-2109 (5)	3441 (3)
C(3')	1457 (3)	-2687 (6)	2461 (3)
C(4')	760 (3)	-1215 (7)	1878 (3)
C(5')	615 (2)	871 (6)	2291 (3)
C(6')	1162 (2)	1447 (6)	3281 (2)
C(7)	2540 (2)	769 (4)	4879 (2)
S	3708 (0.5)	22 (2)	5282 (0.6)

the least-squares planes of the bridging atoms. According to the classification suggested by Heijden, Griffith, Chandler & Robertson (1975), the basic conformations of both TBPSO and TBP are twisted and the torsion angles of the two phenyl rings S—C(7)—C(1)—C(2) and S—C(7)—C(1')—C(2') within the same molecule have the same sign. The structure of TBP has a center of symmetry so both the (+ +) and the (— —) combinations appear in the crystal. In the noncentrosymmetric structure of TBPSO only one combination is present. Bond lengths are listed in Table 4.

Table 3. Fractional atomic coordinates ($\times 10^3$) and thermal parameters ($\times 10^2$) for H atoms

E.s.d.'s are in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ²)
TBPSO				
H(2)	1075 (4)	110 (2)	390 (2)	5
H(3)	1327 (4)	237 (2)	449 (2)	5
H(4)	1263 (4)	404 (2)	406 (2)	5
H(5)	981 (4)	446 (2)	294 (2)	5
H(6)	710 (4)	324 (2)	243 (2)	5
H(2')	320 (4)	61 (2)	191 (2)	5
H(3')	238 (4)	49 (2)	24 (2)	5
H(4')	487 (4)	106 (2)	-97 (2)	5
H(5')	852 (4)	169 (2)	-47 (2)	5
H(6')	923 (4)	189 (2)	121 (2)	5
TBP				
H(2)	326 (2)	453 (5)	589 (2)	5.2
H(3)	253 (2)	687 (5)	683 (2)	6.4
H(4)	98 (2)	625 (6)	704 (2)	7.2
H(5)	15 (2)	303 (6)	629 (2)	7.3
H(6)	83 (2)	60 (5)	530 (2)	5.7
H(2')	254 (2)	-303 (5)	387 (2)	5.3
H(3')	157 (2)	-406 (6)	220 (2)	6.6
H(4')	38 (2)	-160 (5)	118 (2)	6.2
H(5')	17 (2)	189 (5)	189 (2)	5.8
H(6')	108 (2)	286 (5)	358 (2)	4.8

Table 4. Bond lengths (Å) in TBPSO and TBP

E.s.d.'s are in parentheses.

	TBPSO	TBP
O—S	1.47 (1)	
S—C(7)	1.61 (2)	1.636 (9)
C(7)—C(1)	1.53 (2)	1.485 (7)
C(7)—C(1')	1.45 (2)	1.469 (13)
C(1)—C(2)	1.40 (2)	1.392 (6)
C(2)—C(3)	1.41 (2)	1.377 (7)
C(3)—C(4)	1.37 (2)	1.362 (7)
C(4)—C(5)	1.34 (2)	1.370 (7)
C(5)—C(6)	1.41 (2)	1.376 (8)
C(6)—C(1)	1.38 (2)	1.388 (5)
C(1')—C(2')	1.40 (2)	1.406 (5)
C(2')—C(3')	1.36 (2)	1.371 (12)
C(3')—C(4')	1.36 (2)	1.372 (10)
C(4')—C(5')	1.39 (2)	1.381 (6)
C(5')—C(6')	1.37 (2)	1.375 (12)
C(6')—C(1')	1.35 (2)	1.384 (9)

TBPSO

The S—O bond length, 1.47 Å, is slightly longer than the usual S—O double bond, 1.43 Å; the S—C(7) double bond, 1.61 Å, is shorter than the normal 1.71 Å. The C(7)—C(1) bond is 1.53 Å, the same as a normal single bond attached to an aromatic ring, while the C(7)—C(1') bond, 1.45 Å, is remarkably shorter. From these results, we conclude that the conjugation through the system of double bonds O—S—C(7) continues towards C(1'), in agreement with the evidence that the torsion angle S—C(7)—C(1')—C(2') (25°), is smaller than the torsion angle S—C(7)—C(1)—C(2) (48°). The dihedral angle between the two phenyl rings is 67°. The distance O—H(2') is 2.32 Å.

TBP

The S—C(7) double bond in TBP is not significantly different from that in TBPSO, but the C(7)—C(1) and C(7)—C(1') bonds are of the same length, 1.48 and 1.47 Å. They are shortened by the presence of both the S—C double bond and the phenyl ring. The difference

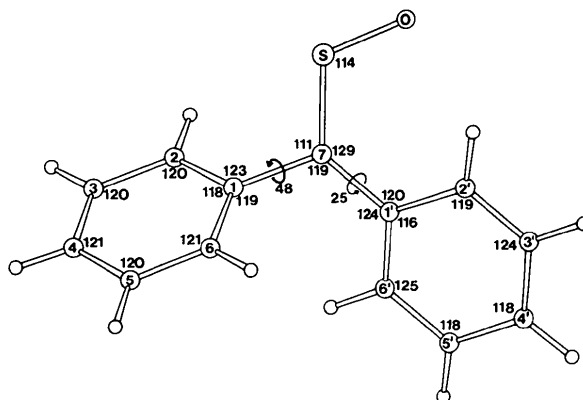


Fig. 1. TBPSO. Projection onto the bridging plane. The angles are in degrees. The e.s.d.'s for the angles, including the dihedral angles, are about 1.5°.

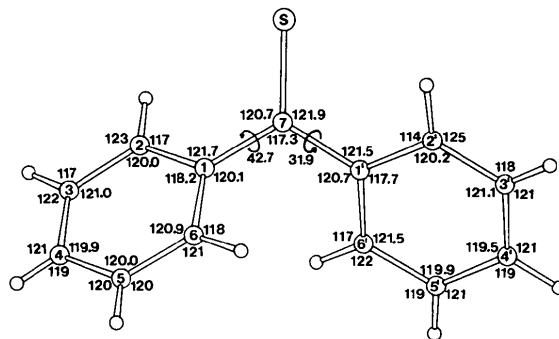


Fig. 2. TBP. Projection onto the bridging plane. The angles are in degrees. The e.s.d.'s for angles not involving H are about 0.3°, for angles involving H about 2°, and for the dihedral angles about 0.4°.

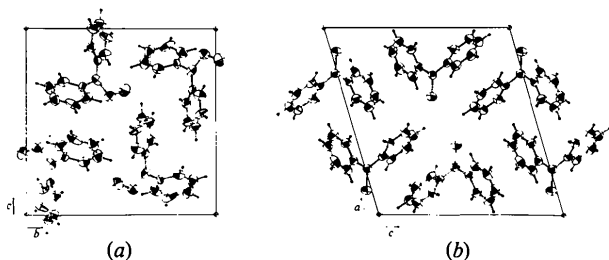


Fig. 3. (a) $\overline{\text{TBPSO}}$ viewed along the a axis; (b) $\overline{\text{TBP}}$ viewed along the b axis.

between the torsion angles $\text{S}-\text{C}(7)-\text{C}(1)-\text{C}(2)$ (42.7°) and $\text{S}-\text{C}(7)-\text{C}(1')-\text{C}(2')$ (31.9°) must be the result of the crystallographic packing. The dihedral angle between the two phenyl rings is 68.6° .

The crystal packing for both molecules is shown in Fig. 3.

The excellent agreement between the experimental results given above and the theoretical predictions concerning the twist angle of the phenyl ring in TBPSO demonstrates the applicability of the CNDO/S-CI procedure to the thiocarbonyl S -oxide system, justifying its further use on the unknown carbonyl O -sulfide system.

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The Crystal Structure of a New Antitumour Agent: 2,2,4,4,6,6,8,8-Octapyrrolidinylcyclotetra(phosphazene), $\text{N}_4\text{P}_4(\text{NC}_4\text{H}_8)_8$

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Abstract

2,2,4,4,6,6,8,8-Octapyrrolidinylcyclotetra(phosphazene), $\text{C}_{32}\text{H}_{64}\text{N}_{12}\text{P}_4$, $\text{N}_4\text{P}_4(\text{NC}_4\text{H}_8)_8$, $M_r = 740$, crystallizes in the tetragonal system, space group $P4_2/c$, with the unit-cell parameters $a = 14.218$ (2), $c = 9.675$ (2) Å, $V = 1956$ Å³, $Z = 2$, $d_m = 1.25$ (2), $d_x = 1.257$

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Mg m^{-3} . The unit cell contains two discrete molecules. The data were collected using an automatic X-ray diffractometer (Cu $K\alpha$ radiation). The structure analysis followed by anisotropic least-squares refinement reduced the R value to 0.058. The saddle-shaped eight-membered (N–P)₄ ring has $\bar{4}$ symmetry. Within the ring the two valence angles P–N–P and N–P–N are different [118.8 (4) and 131.7 (4) $^\circ$]. The two short endocyclic bond lengths are equal [1.575 (6) and 1.574 (6) Å]. The $p_\pi-d_\pi$ electron delocalization