Table 3. P—O bond lengths (Å) in some simple phosphate monoester dianions $ROPO_3^{2-}$

R	Cation	P—OR	Others	Reference
Ethyl	K^+	1·56 (2)	1·54 (2), 1·48 (2), 1·55 (2)	McDonald & Cruickshank (1971)
Methyl	NH_4^+	1·597 (6)	1·500 (7), 1·525 (7), 1·495 (6)	Garbassi, Giarda & Fagherazzi (1972)
Propargyl	$C_6H_{11}NH_3^+$	1·626 (4)	1·510 (4), 1·503 (4), 1·501 (5)	Jones et al. (1984)
Phenyl	K^+	1·64 (2)	1·53 (2), 1·51 (2), 1·53 (2)	Caughlan & Mazhar-ul-Haque (1967)
4-Nitrophenyl	$C_6H_{11}NH_3^+$	1·664 (5)	1·498 (4), 1·498 (5), 1·495 (5)	This work

from (2), since the metaphosphate fragment is likely to be trigonal at P. [Similar coupled bond-length/angle changes have been noted previously in PO_4^{3-} tetrahedra (Murray-Rust, Bürgi & Dunitz (1978, and references therein).] The fact that the three P—O⁻ bond lengths are equal is presumably the result of a symmetrical pattern of hydrogen bonding, though the lengths of the shorter P—O bonds of (1) are expected to be less sensitive to environment than those of alkyl phosphate dianions. Details of the hydrogen-bonding network, which links hydrophilic residues in bands parallel to b, are given in Table 4 (deposited) and Fig. 2.

References

CAUGHLAN, C. N. & MAZHAR-UL-HAQUE (1967). Inorg. Chem. 6, 1998–2002.
CLEGG, W. (1981). Acta Cryst. A37, 22–28.
GARBASSI, F., GIARDA, L. & FAGHERAZZI, G. (1972). Acta Cryst. B28, 1665–1670.
JONES, P. G. & KIRBY, A. J. (1979). J. Chem. Soc. Chem. Commun. pp. 288–289.
JONES, P. G., SHELDRICK, G. M., KIRBY, A. J. & ABELL, K. W. Y. (1984). Acta Cryst. C40, 547–549.
MCDONALD, W. S. & CRUICKSHANK, D. W. J. (1971). Acta Cryst. B27, 1315–1319.
MURRAY-RUST, P., BÜRGI, H. B. & DUNITZ, J. D. (1978). Acta Cryst. B34, 1793–1803.
SHELDRICK, G. M (1978). SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data. Univ. of Göttingen.

Gas–Crystal Photoreaction: the Structures of 4,4′-Dimethoxy(thiobenzophenone) (I), C15H14O2S, and 4,4′-Bis(dimethylamino)thiobenzophenone (II), C17H20N2S

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Abstract. (I): $M_r = 258·34$, triclinic, $P\bar{1}$, $a = 9·810$ (3), $b = 9·635$ (3), $c = 15·015$ (4) Å, $\alpha = 79·11$ (2), $\beta = 102·38$ (3), $\gamma = 107·76$ (3)°, $V = 1308·5$ Å³, $Z = 4$, $D_m = 1·318$ (3) (by flotation in KI solution), $D_x = 1·311$ g cm⁻³, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 20·05$ cm⁻¹, $F(000) = 544$, $T = 293$ K, $R = 0·074$ for 2663 reflections. (II): $M_r = 284·43$, monoclinic, $P2_1/c$, $a = 17·029$ (5), $b = 6·706$ (5), $c = 14·629$ (4), $\beta = 113·55$ (2)°, $V = 1531·4$ Å³, $Z = 4$, $D_m = 1·230$ (5) (by flotation in KI solution), $D_x = 1·234$ g cm⁻³, Mo $K\alpha$, $\lambda = 0·7107$ Å, $\mu = 1·63$ cm⁻¹, $F(000) = 608$, $T = 293$ K, $R = 0·062$ for 855 reflections. The orientation of the C=S chromophores in the crystal lattice and their reactivity in the crystalline state are discussed. The C=S bonds are much shorter than the normal bond length [1·605 (4) (I), 1·665 (8) Å (II) cf. 1·71 Å].

Introduction. The basic difference between solution and solid-state reactivity is that, while the former is crucially dependent on the electronic properties of the reactants, reactivity in crystals depends to a large extent on the packing factors. Thioketones in general are readily oxidized in solution to the corresponding S oxides and/or ketones (Ramnath, Ramesh & Ramamurthy, 1983) and the rate and product distribution of oxidation are controlled by their inherent electronic and steric properties. However, among a large number of diaryl thioketones investigated for their reactivity in the crystalline state only a few underwent photo-oxidation (Arjunan, Ramamurthy & Venkatesan, 1984). It is therefore of interest to examine the molecular packing of these compounds and explore the factors that control their reactivity in the crystalline media. X-ray results

on 4,4'-dimethoxy(thiobenzophenone) (I) and 4,4'-bis(dimethylamino)thiobenzophenone (II) (which do not undergo oxidation in the crystalline state) are reported below.

Experimental. (I) and (II) prepared from corresponding ketones by standard procedures (Scheeren, Ooms & Nivard, 1973). Single crystals of (I) obtained from benzene by slow evaporation in nitrogen atmosphere; crystals approximately $0.7 \times 0.33 \times 0.18$ mm; preliminary Weissenberg photographs indicated triclinic symmetry with four molecules in unit cell; lattice parameters refined using 16 reflections collected on an Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Cu $K\alpha$, $\omega/2\theta$ mode, scan speed $1°$ min^{-1}, $\theta_{max} = 60°$; 2 standard reflections (422 and 007), observed intensity variation $\sim 2\%$; 4202 reflections collected, 2663 significant, $|F_o| \geq 3\sigma(|F_o|)$. Single crystals of (II) obtained from toluene by slow evaporation in nitrogen atmosphere; crystals approximately $0.2 \times 0.1 \times 0.33$ mm; preliminary Weissenberg photograph indicated monoclinic symmetry, space group $P2_1/c$; data collected on Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$, $\theta_{max} = 20°$, scan speed of $1°$ min^{-1}, $\omega/2\theta$ mode; 12 reflections used in least-square refine-

Table 1. *Final positional parameters for nonhydrogen atoms* ($\times 10^4$) *with equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^2$) *for* (I) *(e.s.d.'s are given in parentheses)*

$$U_{eq} = \tfrac{1}{3}\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	U_{eq}
S(1)	4839 (2)	−3024 (2)	7251 (1)	10·46 (7)
O(1)	8670 (4)	3376 (3)	5467 (2)	7·58 (13)
O(2)	8665 (3)	−2794 (3)	11433 (3)	7·18 (13)
C(1)	6250 (4)	−1837 (4)	7674 (3)	5·71 (17)
C(2)	6931 (4)	−474 (4)	7094 (3)	5·21 (16)
C(3)	6665 (5)	−426 (5)	6140 (3)	6·28 (18)
C(4)	7222 (5)	831 (5)	5587 (3)	6·68 (20)
C(5)	8050 (4)	2081 (5)	5961 (3)	5·89 (18)
C(6)	8292 (4)	2051 (4)	6913 (3)	5·79 (17)
C(7)	7750 (4)	798 (4)	7451 (3)	5·29 (16)
C(8)	8432 (7)	3480 (6)	4489 (4)	10·12 (28)
C(9)	6877 (4)	−2079 (4)	8671 (3)	5·01 (16)
C(10)	5969 (4)	−2739 (4)	9318 (3)	5·73 (17)
C(11)	6524 (4)	−2999 (4)	10242 (3)	5·81 (18)
C(12)	8005 (5)	−2611 (4)	10542 (3)	5·45 (17)
C(13)	8931 (4)	−1965 (4)	9906 (3)	5·62 (17)
C(14)	8354 (4)	−1698 (4)	8990 (2)	5·42 (17)
C(15)	7778 (6)	−3418 (6)	12114 (3)	8·62 (24)
S(1')	10231 (2)	3059 (2)	12742 (1)	11·24 (8)
O(1')	6386 (4)	2689 (3)	8548 (2)	7·17 (13)
O(2')	6127 (4)	−3135 (4)	14595 (2)	8·68 (15)
C(1')	8810 (5)	1867 (5)	12314 (3)	6·63 (20)
C(2')	8153 (4)	2115 (4)	11321 (2)	5·58 (17)
C(3')	8349 (5)	3519 (4)	10842 (3)	6·60 (19)
C(4')	7794 (5)	3764 (4)	9917 (3)	6·59 (19)
C(5')	7013 (4)	2585 (3)	9453 (2)	5·69 (18)
C(6')	6835 (4)	1159 (3)	9914 (2)	5·42 (16)
C(7')	7386 (4)	936 (3)	10834 (2)	5·60 (17)
C(8')	6576 (7)	4100 (5)	8052 (3)	9·34 (26)
C(9')	8131 (4)	512 (5)	12902 (3)	5·74 (17)
C(10')	8965 (5)	−170 (5)	13598 (3)	7·01 (20)
C(11')	8353 (6)	−1380 (6)	14175 (3)	7·47 (22)
C(12')	6867 (5)	−1929 (4)	14069 (3)	6·29 (19)
C(13')	6020 (4)	−1238 (5)	13383 (3)	5·82 (17)
C(14')	6625 (4)	−80 (5)	12803 (3)	5·53 (17)
C(15')	6921 (7)	−3868 (6)	15318 (4)	11·53 (32)

Table 2. *Final positional parameters for nonhydrogen atoms* ($\times 10^4$) *with equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^2$) *for* (II) *(e.s.d.'s are given in parentheses)*

$$U_{eq} = \tfrac{1}{3}\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	U_{eq}
S	3090 (2)	236 (4)	4482 (2)	7·28 (12)
N(1)	4103 (4)	8422 (13)	2583 (6)	6·4 (4)
N(2)	−676 (5)	−1338 (12)	809 (6)	6·2 (4)
C(1)	2990 (5)	3264 (14)	3204 (6)	4·7 (4)
C(2)	3608 (6)	4378 (17)	3930 (8)	6·1 (5)
C(3)	3990 (6)	6043 (17)	3772 (8)	5·5 (5)
C(4)	3757 (5)	6714 (14)	2764 (7)	4·8 (4)
C(5)	3145 (5)	5605 (15)	1992 (8)	4·7 (4)
C(6)	2785 (6)	3940 (16)	2233 (8)	5·2 (5)
C(7)	1766 (6)	757 (16)	2698 (6)	4·9 (5)
C(8)	1592 (7)	−1272 (17)	2512 (8)	5·9 (6)
C(9)	806 (6)	−1987 (16)	1888 (7)	5·3 (5)
C(10)	135 (6)	−624 (16)	1409 (6)	4·9 (5)
C(11)	311 (6)	1422 (16)	1569 (6)	4·8 (5)
C(12)	1120 (7)	2098 (18)	2180 (7)	5·7 (5)
C(13)	4738 (6)	9569 (16)	3352 (7)	8·0 (5)
C(14)	3832 (6)	9245 (15)	1574 (8)	7·6 (5)
C(15)	−830 (6)	−3410 (15)	581 (7)	7·2 (5)
C(16)	−1370 (6)	10 (16)	315 (7)	7·3 (4)
C(17)	2602 (5)	1459 (14)	3413 (6)	4·8 (4)

ment of cell parameters; 2 standard reflections ($31\bar{2}$ and $41\bar{3}$) monitored after every 50 reflections, intensity variation $\sim 4\%$; 1737 reflections collected, 855 significant, $|F_o| \geq 3\sigma(|F_o|)$; data not corrected for absorption. Both structures solved by direct methods using MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); the distribution of normalized structure factors of (I) was centric and hence the space group $P\bar{1}$ was chosen for structure solution and refinement; full-matrix least-squares program SHELX76 (Sheldrick, 1976) used for refinement. The positional and anisotropic thermal parameters of all non-hydrogen atoms (S,O,N,C) were refined. Hydrogen atoms were refined with their positional and isotropic parameters only. However, in compound (I) the isotropic temperature factors of the methyl hydrogens showed a tendency to increase from one cycle to another and hence these positional and thermal parameters were not allowed to vary during the final stages of refinement. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(|F_o|)$. At the end of the last cycle of refinement, for (I) $R = 0.074$ ($R_w = 0.084$; $S = 2.44$), and for (II) $R = 0.062$ ($R_w = 0.065$; $S = 1.47$), $R_w = \Sigma(w)^{1/2}||F_o| - |F_c||/\Sigma(w)^{1/2}|F_o|$. Δ/σ for non-hydrogen atoms for both (I) and (II) was about 0·02. The final difference map was featureless. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The illustrations were made with ORTEPII (Johnson 1976).*

* Lists of structure factors, anisotropic thermal parameters H-atom coordinates and bond lengths and angles involving hydrogen have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39054 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The final atomic coordinates are given in Tables 1 and 2. A perspective view and the numbering scheme (with bond lengths and angles for non-hydrogen atoms) for (I) and (II) are shown in Figs. 1 to 4.

In (I), the average S—C(1) double bond, 1·605 (4) Å, is shorter than the normal bond length (1·71 Å) (*International Tables for X-ray Crystallography*, 1968). The difference between the torsion angles S(1)—C(1)—C(2)—C(3) (−20·9°) and S(1)—C(1)—C(9)—C(10) (−35·8°) in molecule 1 and S(1')—C(1')—C(2')—C(3') (−24·8°) and S(1')—C(1')—C(9')—C(10') (−34·6°) in molecule 2 are probably the result of the crystallographic packing. As may be seen from the torsion angles C—C—O—Me, the terminal methyl groups are almost in the plane of the phenyl rings. The slight asymmetry in the length and angle distribution within the phenyl rings may arise because of the substituents (Domenicano, Vaciago & Coulson, 1975). Some of the important torsion angles are given in Table 3.

In (II), the S=C(17) bond, 1·665 (8) Å, is longer than that in (I), but shorter than the normal bond length (1·71 Å). Also, the N(1)—C(4) and N(2)—C(10) distances [1·361 (13) and 1·392 (11)] are significantly shorter than the normal N—C single-bond distance of 1·48 Å. This indicates that there is considerable double-bond character associated with the N—C bond. As in the case of (I), here too the torsion angles C(2)—C(1)—C(17)—S (−19·4°) and C(8)—C(7)—C(17)—S (−40·6°) differ significantly.

The arrangements of molecules in the unit cells for (I) and (II) are depicted in Figs. 5 and 6. As we have mentioned earlier, these two thioketones [(I) and (II)] are photostable in the solid state. Gatterman & Schulze (1896) reported that thiobenzophenone undergoes oxidation in the crystalline state to give the corresponding ketone. We have observed that a few other thioketones also undergo photooxidation (Arjunan, Ramamurthy & Venkatesan, 1984) in the crystalline state. The X-ray structure of thiobenzophenone (Rindorf & Carlsen, 1979) has already been reported and it is noteworthy that the thiocarbonyl (C=S) chromophores are stacked opposite to each other, the S···S distance being 3·9 Å with a channel along the shortest crystallographic axis. But in the case of unreactive thioketones (I) and (II), such an arrangement of thiocarbonyl groups, which would facilitate diffusion of the oxygen molecule, is not observed. The non-reactivity of these two compounds in their crystalline state may be attributed to this feature of the molecular packing.
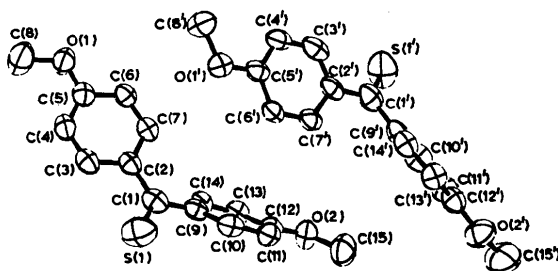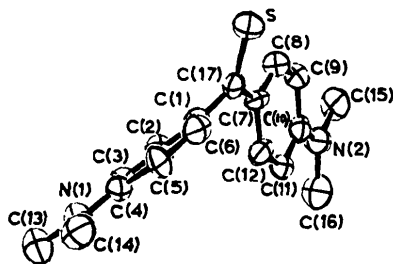
Fig. 1. A perspective view of molecules (I).

Fig. 2. A perspective view of molecule (II).

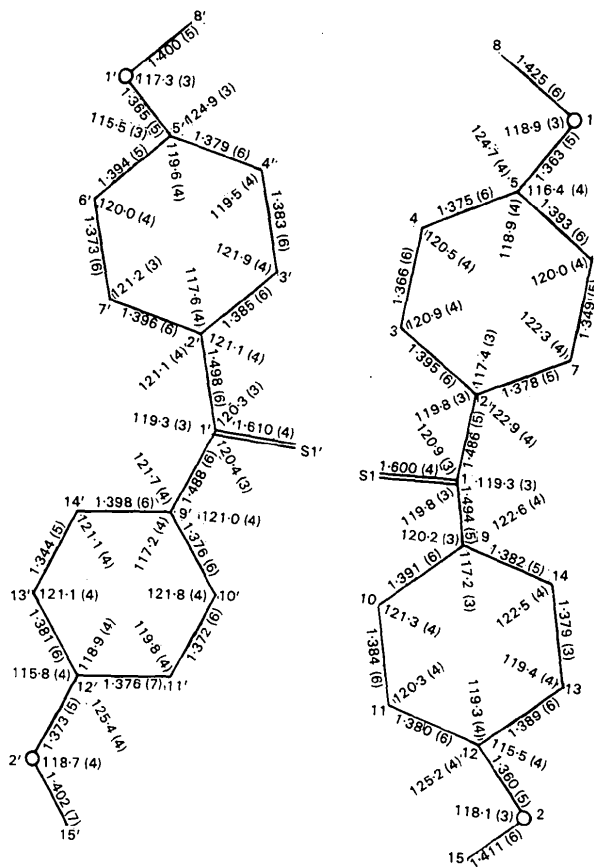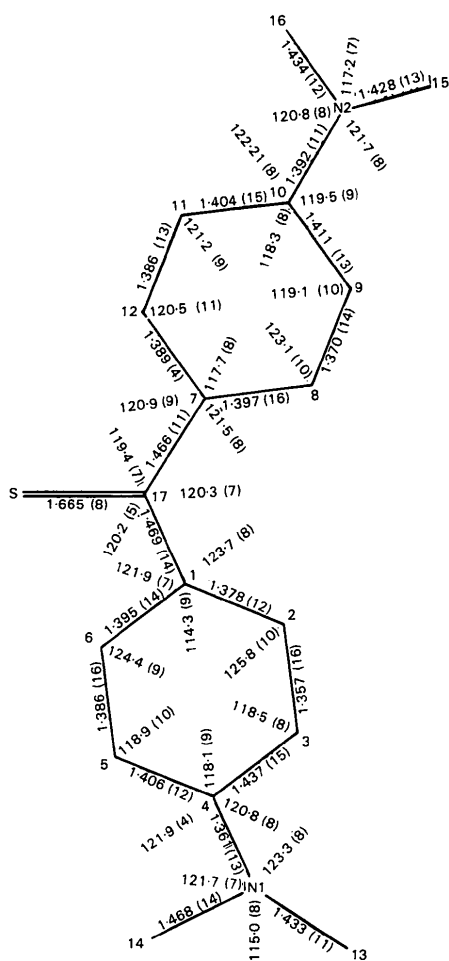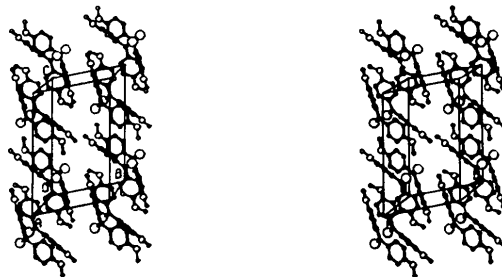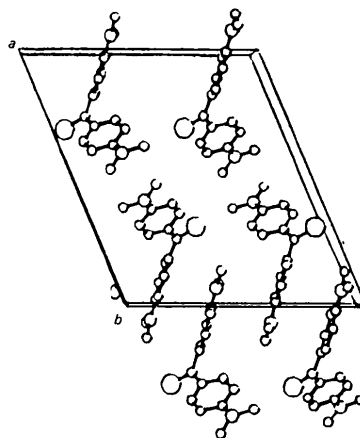Fig. 3. Bond lengths (Å) and angles (°) of nonhydrogen atoms with atom-numbering scheme for (I). E.s.d.'s are given in parentheses.

Table 3. *Torsion angles* (°) *with e.s.d.'s in parentheses*

(I)

C(8)–O(1)–C(5)–C(4)	1·5 (7)
C(15)–O(2)–C(12)–C(11)	−0·6 (7)
S(1)–C(1)–C(2)–C(3)	−20·9 (6)
S(1)–C(1)–C(9)–C(10)	−35·8 (5)
C(8')–O(1')–C(5')–C(4')	1·3 (6)
C(15')–O(2')–C(12')–C(11')	1·6 (7)
S(1')–C(1')–C(2')–C(3')	−24·8 (6)
S(1')–C(1')–C(9')–C(10')	−34·6 (6)

(II)

C(2)–C(1)–C(17)–S	−19·4 (12)
C(8)–C(7)–C(17)–S	−40·6 (12)
C(13)–N(1)–C(4)–C(3)	3·6 (14)
C(14)–N(1)–C(4)–C(5)	2·4 (14)
C(15)–N(2)–C(10)–C(9)	−6·5 (14)
C(16)–N(2)–C(10)–C(11)	0·8 (14)

Fig. 5. Stereoscopic view of the crystal packing for (I) looking down the *a* axis.

Fig. 6. View of the crystal packing for (II) looking down the *b* axis.

Fig. 4. Bond lengths (Å) and angles (°) of nonhydrogen atoms with atom-numbering scheme for (II). E.s.d.'s are given in parentheses.

References

ARJUNAN, P., RAMAMURTHY, V. & VENKATESAN, K. (1984). *J. Org. Chem.* In the press.

DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* B31, 221–234.

GATTERMAN, L. & SCHULZE, H. (1896). *Ber. Dtsch. Chem. Ges.* 29, 2944–2945.

International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

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

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.

RAMNATH, N., RAMESH, V. & RAMAMURTHY, V. (1983). *J. Org. Chem.* 48, 214–222.

RINDORF, G. & CARLSEN, L. (1979). *Acta Cryst.* B35, 1179–1182.

SCHEEREN, J. W., OOMS, P. H. J. & NIVARD, R. J. F. (1973). *Synthesis*, pp. 149–151.

SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.