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4-Biphenylyl Phenyl Thioketone (I), $C_{19}H_{14}S$, and 1-Naphthyl Phenyl Thioketone (II), $C_{17}H_{12}S$

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Abstract. (I): $M_r = 274\cdot39$, orthorhombic, *Pbca*, $a = 7\cdot443$ (1), $b = 32\cdot691$ (3), $c = 11\cdot828$ (2) Å, $V = 2877\cdot98$ Å^3, $Z = 8$, $D_m = 1\cdot216$ (flotation in KI), $D_x = 1\cdot266$ g cm^{-3}, μ(Cu $K\alpha$, $\lambda = 1\cdot5418$ Å) $= 17\cdot55$ cm^{-1}, $F(000) = 1152\cdot0$, $T = 293$ K, $R = 6\cdot8\%$, 1378 significant reflections. (II): $M_r = 248\cdot35$, orthorhombic, $P2_12_12_1$, $a = 5\cdot873$ (3), $b = 13\cdot677$ (3), $c = 15\cdot668$ (5) Å, $V = 1260\cdot14$ Å^3, $Z = 4$, $D_m = 1\cdot297$ (flotation in KI), $D_x = 1\cdot308$ g cm^{-3}, μ(Cu $K\alpha$, $\lambda = 1\cdot5418$ Å) $= 19\cdot55$ cm^{-1}, $F(000) = 520\cdot0$, $T = 293$ K, $R = 6\cdot9\%$, 751 significant reflections. Crystals of (I) and (II) undergo photo-oxidation in the crystalline state. In (I) the dihedral angle between the phenyl rings of the biphenyl moiety is 46 (1)°. The C=S bond length is $1\cdot611$ (5) Å in (I) and $1\cdot630$ (9) Å in (II). The correlation between molecular packing and reactivity is discussed.

Introduction. Aromatic thioketones are known to undergo oxidation readily in solution to the corresponding *S*-oxides and/or ketones. In general, the reactions of organic compounds are more selective when performed in the solid state rather than in isotropic solvents. Among a large number of diaryl thioketones investigated only a few exhibited photoreactivity in the crystalline state (Arjunan, Ramamurthy & Venkatesan, 1984*a*). This shows that the nature of the molecular packing is an important factor controlling the reactivity in the crystalline state. To correlate the reactivity with the packing mode, we have carried out X-ray structure studies of both stable and reactive thioketones. In our previous paper (Arjunan, Ramamurthy & Venkatesan, 1984*b*) we report the crystal structures of two stable thioketones [4,4′-dimethoxy(thiobenzophenone) and 4,4′-bis(dimethylamino)thiobenzophenone] and allude to reasons for their stability in the crystalline state. Here, the X-ray structures of the two reactive thioketones (I) and (II) are reported.

Experimental. (I) and (II) prepared from the corresponding ketones by standard procedures (Scheeren, Ooms & Nivard, 1973). Single crystals of (I) and (II) obtained from benzene and methanol respectively by slow evaporation in nitrogen atmosphere. During data collection crystals kept in capillary tubes. Crystals approximately $0\cdot38 \times 0\cdot43 \times 0\cdot13$ mm (I) and $0\cdot05 \times 0\cdot13 \times 0\cdot18$ mm (II). Lattice parameters refined using 17 reflections for (I) and 13 for (II). Nonius CAD-4 diffractometer, graphite-monochromated Cu $K\alpha$ radiation, $\theta \leq 60°$, scan speed 1° min^{-1}, $\omega/2\theta$ mode. For (I), three standard reflections (262, 322 and 264) showed intensity variation of 4%; 2221 reflections collected, 1378 significant $[|F_o| \geq 3\sigma(|F_o|)]$. For (II), two standard reflections (032, 133) monitored after every fifty reflections showed an intensity variation of ~3%; 1188 reflections collected, 751 significant $[|F_o| \geq 3\sigma(|F_o|)]$. Data not corrected for absorption. Structures solved by direct methods (*MULTAN*80; Main *et al.*, 1980). For (II), the best *E* map gave a fragment consisting of 11 atoms; after Karle recycling (Karle, 1968) all the remaining non-hydrogen atoms were identified. Full-matrix least-squares program *SHELX*76 (Sheldrick, 1976) used for refinement. Positional and anisotropic thermal parameters of all non-hydrogen atoms and positional and isotropic thermal parameters of H atoms refined. $\sum w(|F_o| - |F_c|)^2$ minimized; $w = 2\cdot09/[\sigma(|F_o|)^2 + 0\cdot002|F_o|^2]$ for (I) and $w = 1\cdot78/[\sigma(|F_o|)^2 + 0\cdot003|F_o|^2]$ for (II). At the end of the last cycle of refinement $R = 0\cdot068$, $R_w = 0\cdot073$, $S = 1\cdot83$ for (I) and $R = 0\cdot069$, $R_w = 0\cdot072$, $S = 1\cdot45$ for (II). Δ/σ for non-hydrogen atoms for both (I) and (II) about $0\cdot02$. Final difference maps for both structures featureless. No corrections for secondary extinction. Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974). Illustrations with *ORTEP*II (Johnson, 1976).

Discussion. Final atomic parameters are given in Tables 1 and 2.* The numbering schemes with bond lengths and angles for non-hydrogen atoms for (I) and (II) are shown in Figs. 1 and 2 respectively.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond lengths and angles involving H atoms for (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38953 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final positional parameters and equivalent isotropic thermal parameters for non-hydrogen atoms of compound* (I), *with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}(Å^2 × 10^2)
S	0·42380 (25)	0·16925 (4)	0·23594 (13)	8·64 (0·06)
C(1)	0·3758 (6)	0·1741 (1)	0·4606 (4)	5·40 (0·17)
C(2)	0·2454 (7)	0·1698 (1)	0·5421 (4)	6·72 (0·20)
C(3)	0·2374 (9)	0·1939 (2)	0·6372 (5)	8·41 (0·25)
C(4)	0·3633 (11)	0·2232 (2)	0·6522 (5)	9 ·08 (0·28)
C(5)	0·4929 (12)	0·2285 (2)	0·5718 (7)	10·60 (0·32)
C(6)	0·5048 (8)	0·2042 (2)	0·4764 (5)	8·13 (0·24)
C(7)	0·2526 (6)	0·0837 (1)	0·2751 (3)	4·89 (0·15)
C(8)	0·2178 (6)	0·0427 (1)	0·2792 (3)	4·82 (0·16)
C(9)	0·2932 (6)	−0·0493 (1)	0·2875 (4)	5·15 (0·17)
C(10)	0·2718 (7)	−0·0908 (1)	0·2896 (4)	6·29 (0·19)
C(11)	0·1947 (7)	−0·1093 (1)	0·3821 (5)	6·71 (0·20)
C(12)	0·1395 (7)	−0·0858 (1)	0·4740 (4)	5·72 (0·18)
C(13)	0·1611 (6)	−0·0443 (1)	0·4724 (4)	4·84 (0·16)
C(14)	0·2378 (6)	−0·0252 (1)	0·3781 (3)	4·32 (0·14)
C(15)	0·2650 (6)	0·0198 (1)	0·3746 (3)	4·04 (0·14)
C(16)	0·3404 (6)	0·0410 (1)	0·4661 (3)	4·34 (0·15)
C(17)	0·3691 (6)	0·0823 (1)	0·4623 (3)	4·49 (0·15)
C(18)	0·3311 (6)	0·1047 (1)	0·3652 (4)	4·63 (0·15)
C(19)	0·3739 (6)	0·1486 (1)	0·3556 (4)	5·41 (0·17)

Table 2. *Final positional parameters and equivalent isotropic thermal parameters for non-hydrogen atoms of compound* (II), *with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}(Å^2 × 10^2)
S	0·1593 (6)	0·1519 (2)	0·9977 (2)	6·83 (0·10)
C(1)	−0·1019 (17)	0·0410 (7)	0·8938 (5)	4·25 (0·28)
C(2)	−0·2797 (19)	0·1039 (7)	0·8877 (7)	5·21 (0·32)
C(3)	−0·4393 (20)	0·1017 (8)	0·8214 (7)	6·64 (0·37)
C(4)	−0·4127 (18)	0·0301 (8)	0·7603 (7)	5·57 (0·33)
C(5)	−0·2305 (17)	−0·0358 (6)	0·7606 (6)	4·15 (0·27)
C(6)	−0·2101 (23)	−0·1055 (8)	0·6972 (6)	6·40 (0·37)
C(7)	−0·0350 (22)	−0·1673 (7)	0·6958 (6)	5·95 (0·35)
C(8)	0·1384 (18)	−0·1618 (7)	0·7589 (6)	5·42 (0·32)
C(9)	0·1136 (18)	−0·0944 (6)	0·8220 (5)	4·51 (0·30)
C(10)	−0·0649 (16)	−0·0302 (6)	0·8269 (5)	3·71 (0·27)
C(11)	0·1024 (14)	−0·0429 (7)	1·0178 (5)	3·36 (0·25)
C(12)	0·2966 (20)	−0·0517 (6)	1·0657 (6)	5·50 (0·32)
C(13)	0·3359 (21)	−0·1353 (7)	1·1144 (6)	5·73 (0·34)
C(14)	0·1798 (22)	−0·2082 (7)	1·1164 (6)	5·73 (0·40)
C(15)	−0·0217 (19)	−0·1990 (7)	1·0718 (6)	5·42 (0·32)
C(16)	−0·0569 (19)	−0·1165 (6)	1·0214 (5)	4·55 (0·30)
C(17)	0·0555 (17)	0·0467 (6)	0·9682 (5)	4·44 (0·28)

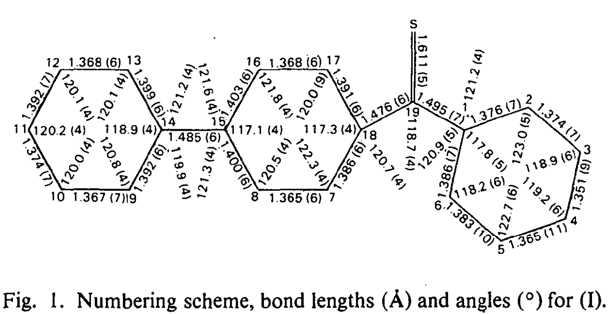

Fig. 1. Numbering scheme, bond lengths (Å) and angles (°) for (I). E.s.d.'s are in parentheses. [C(17)–C(18)–C(19) 122·1 (4), C(18)–C(19)–S 121·6 (3), C(1)–C(19)–S 119·6 (3)°.]

In compound (I), the S–C(19) bond length of 1·611 (5) Å is shorter than the normal bond length of 1·71 Å (*International Tables for X-ray Crystallography,* 1968). For 4,4'-disubstituted biphenyl derivatives (Brock, Mei-Shiow Kuo & Levy, 1978) the twist angle between the phenyl rings is close to the expected mean gas-phase value of 42° (Almenningen & Bastiansen, 1958). In (I), the dihedral angle between the phenyl rings is slightly higher: C(13)–C(14)–C(15)–C(16) is 46 (1)°. The conformational angles C(6)–C(1)–C(19)–S and C(7)–C(18)–C(19)–S are −38 (1) and −30 (1)°, respectively.

Molecule (II) is non-planar, the dihedral angles C(2)–C(1)–C(17)–S and C(12)–C(11)–C(17)–S being −48 (1) and −27 (1)°, respectively. Here too the S–C(17) double bond of 1·630 (9) Å is shorter than the normal double-bond length (1·71 Å). The differences in the aromatic C–C distances are not significant.

The packing arrangements of molecules in the unit cells for compounds (I) and (II) are depicted in Figs. 3 and 4. (I) and (II) are photoreactive in the crystalline state. Gatterman & Schulze (1896) have reported that thiobenzophenone is also photoreactive in the crystalline state and the X-ray structure has been reported (Rindorf & Carlsen, 1979). In all three reactive crystals (I), (II) and thiobenzophenone, the thiocarbonyl chromophores (C=S) are stacked opposite to each other, the S···S distances between the closest S atoms varying from 3·7 to 3·9 Å with a channel along the shortest crystallographic axis in each case. As a typical example, the channel cross-sectional area of reactive (II) and of unreactive 4,4'-bis(dimethylamino)thiobenzophenone crystals are shown in Fig. 5 (the channel boundaries were delimited by drawing circles centered on the atom positions with their corresponding van der Waals radii). The channel cross-sectional area for the

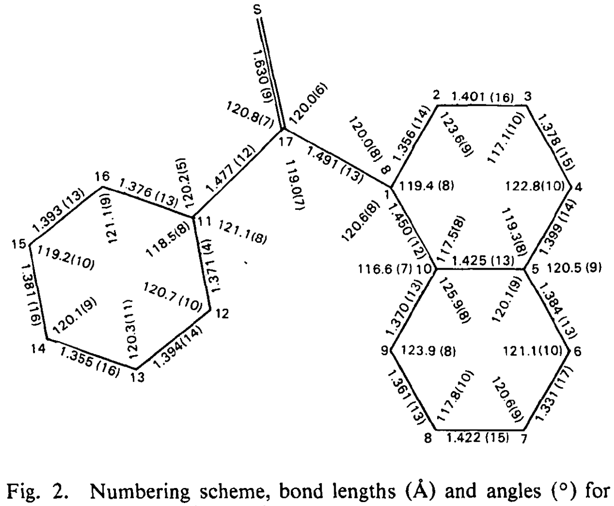

Fig. 2. Numbering scheme, bond lengths (Å) and angles (°) for (II). E.s.d.'s are in parentheses.

reactive crystal is 8·3 Å^2 and for the unreactive crystal as small as about 2·3 Å^2. Therefore, the reactive nature of these crystals can be explained by the ability of the oxygen molecule to diffuse into the crystal along this channel and oxidize the thione chromophore (C=S). It is noteworthy that in the unreactive crystals of 4,4′-dimethoxy(thiobenzophenone) and 4,4′-bis(dimethylamino)thiobenzophenone, there is no such arrangement of thiocarbonyl chromophores to facilitate the diffusion of the oxygen molecule to effect the oxidation.

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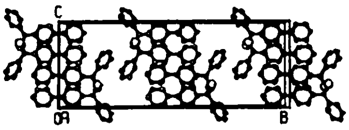

Fig. 3. view down **a** of the crystal packing for (I).

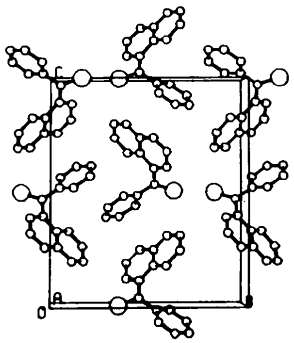

Fig. 4. View down **a** of the crystal packing for (II).

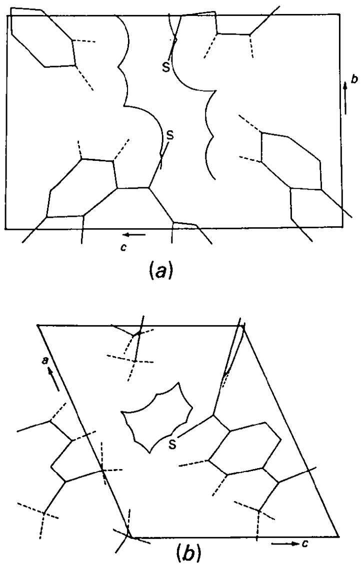

Fig. 5. Projection of the crystal packing on a plane perpendicular to the channel axis. (*a*) Compound (II). (*b*) 4,4′-bis(dimethylamino)thiobenzophenone.

References

Almenningen, A. & Bastiansen, O. (1958). *K. Nor. Vidensk. Selsk. Skr.* **4**, 1–16.

Arjunan, P., Ramamurthy, V. & Venkatesan, K. (1984*a*). *J. Org. Chem.* In the press.

Arjunan, P., Ramamurthy, V. & Venkatesan, K. (1984*b*). *Acta Cryst.* C**40**, 552–555.

Brock, C. P., Mei-Shiow Kuo & Levy, H. A. (1978). *Acta Cryst.* B**34**, 981–985.

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

International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed. Birmingham: Kynoch Press.

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

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

Karle, J. (1968). *Acta Cryst.* B**24**, 182–186.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray DiffractionData.* Univs. of York, England, and Louvain, Belgium.

Rindorf, G. & Carlsen, L. (1979). *Acta Cryst.* B**35**, 1179–1182.

Scheeren, J. W., Ooms, P. H. J. & Nivard, R. J. F. (1973). *Synthesis*, pp. 149–151.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.