organic compounds

Short intramolecular S···O interactions in S-substituted 2-mercaptoacetophenones

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The non-bonded S···O intramolecular interactions in the title compounds 2-(phenylthio)acetophenone {IUPAC: 2-[2-(phenylsulfanyl)phenyl]ethanone}, $C_{14}H_{12}OS$, and 2-(benzylthio)acetophenone {IUPAC: 2-[2-(benzylsulfanyl)phenyl]ethanone}, $C_{15}H_{14}OS$, are unusually short, indicating the contribution of heterocyclic oxathiole-type resonance structures to the overall bonding.

Comment

The crystal structure of 2-(phenylmethylthio)benzaldehyde, (I), was recently reported (Wong & Lee, 1995). In connection with the study of iminyl and thiophenoxyl radical cyclization reactions (Creed et al., 2001), we required the acetophenone derivatives (II) and (III) as starting materials. There is structural interest in related systems (Wong & Lee, 1995; Kucsman et al., 1984, 1986) because of the presence of a short S···O intramolecular distance which is suggestive of a weak interaction between the two heteroatoms. This can be represented by a contribution of the heterocyclic resonance form (Ia). Structural data on benzene derivatives containing ortho-disposed carbonyl and sulfur-containing substituents are rare; apart from aldehyde (I), the only relevant data available concern esters (IV)–(VII) and the diazo compound (VIII). We now report the crystal structures of two related acetophenone derivatives, namely 2-[2-(phenylsulfanyl)phenyl]ethanone, (II), and 2-[2-(benzylsulfanyl)phenyl]ethanone, (III).

In (I)–(III), the C=O group is aligned s-Z to the ortho substituent. The angle between the plane of the acetyl group and that of the aryl group to which it is attached is only 6.2 (4)° in (II), whereas it is 25.87 (16)° in (III); these compare with a corresponding angle of 4.4° in aldehyde (I). In (II), the phenyl rings are almost orthogonal to each other [88.29 (7)°], whereas

in (I) and (III) the corresponding angles are 78.3 and 62.21 (5)°, respectively. The two Ar—S bonds in (II) are significantly different. The shorter [1.7694 (18) Å] is associated with the ring bearing the acetyl group; that associated with the unsubstituted phenyl group [1.781 (2) Å] is longer because the group is twisted out of the plane of the rest of the molecule. Therefore, even in the diarylsulfide (II), the lone pair of the S atom interacts preferentially with the aryl ring carrying the acetyl group. These features would be expected if the cyclic resonance form, e.g. (Ia), contributes to the overall structure.
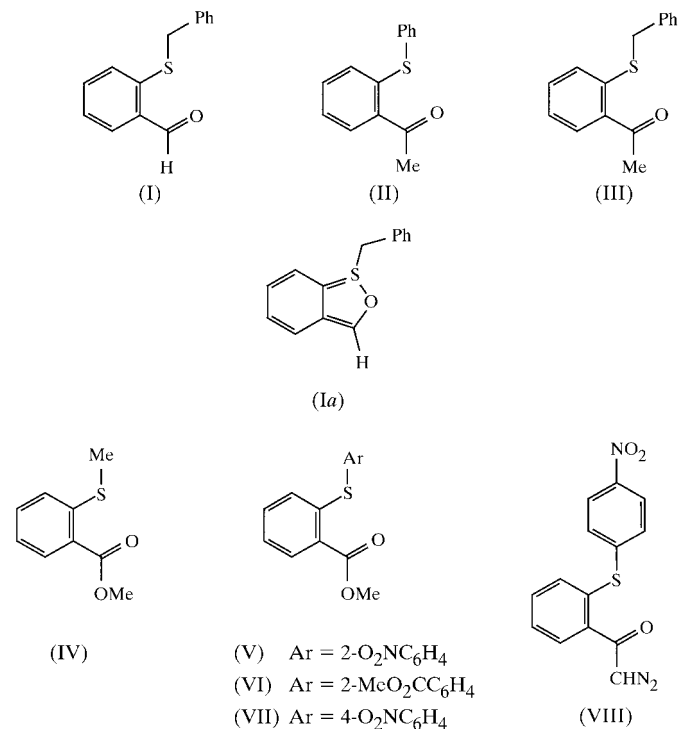
The non-bonded S···O distance in (I) was reported to be unusually short at 2.804 (2) Å, and this was interpreted as indicating a weak interaction. The related distances in (II) and (III) are even shorter, at 2.6578 (18) and 2.7125 (17) Å, respectively. These are of a similar order of magnitude to related distances in structures (IV)–(VIII). However, these interactions are substantially weaker than in the 6,6a-dithia-furophthenes, where S···O distances can be as short as 2.287 Å [for example, see Saethre & Hordvik (1975); Cambridge Structural Database (Allen & Kennard, 1993) refcode: MAPTFU10].

The geometries of the disubstituted aryl rings in (I)–(III) are substantially distorted. The bond between the two substituents is the longest in each case [1.408 (4), 1.414 (3) and 1.415 (3) Å in (I)–(III), respectively], which may, in part, be rationalized by a contribution of resonance structures of type (Ia). Similarly, the shortest bond, differing from the largest by over 6σ in all three structures, is C5—C6 [1.361 (4), 1.367 (3) and 1.375 (3) Å in (I)–(III), respectively]. In (I)–(III), the C3—C4 and C4—C5 bonds are shorter than average, whereas C2—C3 and C1—C6 are longer than average. Intra-ring bond

angles at the substituted sites in (II) and (III) are 118–119°, whereas the angles at C6 are around 122° in each case. The
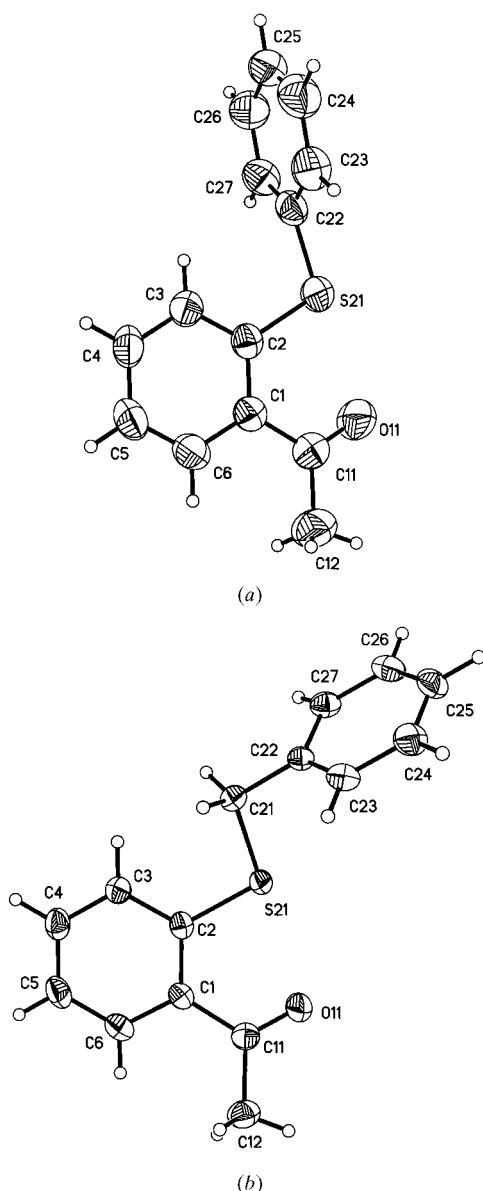
Figure 1
Views of (a) (II) and (b) (III) with the atom-numbering schemes. Displacement ellipsoids enclose 50% probability surfaces.

geometries of the S-phenyl group in (II) and the benzyl group in (III) are in contrast very regular.

Experimental

Compounds (II) and (III) were synthesized by displacement of halide by the appropriate thiol from the corresponding 2-halogenoacetophenone. Crystals of (II) were obtained directly from the reaction mixture and those of (III) were obtained by slow evaporation from an acetone solution.

Compound (II)

Crystal data

$C_{14}H_{12}OS$
$M_r = 228.30$
Monoclinic, $P2_1/c$
$a = 9.0151\ (7)$ Å
$b = 12.7805\ (14)$ Å
$c = 10.6400\ (12)$ Å
$\beta = 105.497\ (7)°$
$V = 1181.3\ (2)$ Å^3
$Z = 4$

$D_x = 1.284$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 48 reflections
$\theta = 20–22°$
$\mu = 2.22$ mm^{-1}
$T = 293\ (2)$ K
Block, colourless
$0.58 \times 0.47 \times 0.39$ mm

Data collection

Stoe Stadi-4 four-circle diffractometer
ω/θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$\quad T_{min} = 0.331, T_{max} = 0.420$
3137 measured reflections
2070 independent reflections
1754 reflections with $I > 2\sigma(I)$

$R_{int} = 0.033$
$\theta_{max} = 70.0°$
$h = -10 \rightarrow 10$
$k = -4 \rightarrow 15$
$l = -6 \rightarrow 12$
3 standard reflections
$\quad$ frequency: 60 min
$\quad$ intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.110$
$S = 1.07$
2070 reflections
147 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 0.297P]$
$\quad$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0107 (9)

Table 1
Selected geometric parameters (Å, °) for (II).

C1—C6	1.400 (3)	C2—S21	1.7694 (18)
C1—C2	1.414 (3)	C22—S21	1.781 (2)
C1—C11	1.484 (3)	C3—C4	1.381 (3)
C11—O11	1.213 (2)	C4—C5	1.376 (3)
C11—C12	1.498 (3)	C5—C6	1.367 (3)
C2—C3	1.389 (3)		
C6—C1—C2	118.13 (18)	C3—C2—S21	121.30 (15)
C6—C1—C11	119.97 (17)	C1—C2—S21	120.06 (14)
C2—C1—C11	121.90 (17)	C2—S21—C22	103.24 (9)
O11—C11—C1	120.64 (18)	C4—C3—C2	121.42 (19)
O11—C11—C12	119.6 (2)	C5—C4—C3	120.2 (2)
C1—C11—C12	119.76 (19)	C6—C5—C4	119.25 (19)
C3—C2—C1	118.64 (17)	C5—C6—C1	122.32 (19)

Compound (III)

Crystal data

$C_{15}H_{14}OS$
$M_r = 242.32$
Orthorhombic, $Pbca$
$a = 7.8838\ (18)$ Å
$b = 14.719\ (3)$ Å
$c = 21.277\ (4)$ Å
$V = 2469.1\ (9)$ Å^3
$Z = 8$
$D_x = 1.304$ Mg m^{-3}

Cu $K\alpha$ radiation
Cell parameters from 150 reflections
$\theta = 20–22°$
$\mu = 2.15$ mm^{-1}
$T = 150\ (2)$ K
Block, colourless
$0.54 \times 0.18 \times 0.12$ mm

organic compounds

Data collection

Stoe Stadi-4 four-circle diffrac-
tometer
ω/θ scans
Absorption correction: ψ scan
(North *et al.*, 1968)
$T_{min} = 0.429$, $T_{max} = 0.581$
2272 measured reflections
1790 independent reflections
1520 reflections with $I > 2\sigma(I)$

$R_{int} = 0.011$
$\theta_{max} = 59.9°$
$h = -8 \rightarrow 6$
$k = -15 \rightarrow 16$
$l = -23 \rightarrow 17$
3 standard reflections
    frequency: 60 min
    intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.087$
$S = 1.02$
1790 reflections
211 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 0.689P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0026 (2)

Table 2
Selected geometric parameters (Å, °) for (III).

C1—C6	1.393 (3)	C2—S21	1.7706 (19)
C1—C2	1.415 (3)	C3—C4	1.385 (3)
C1—C11	1.487 (3)	C4—C5	1.382 (3)
C11—O11	1.214 (2)	C5—C6	1.375 (3)
C11—C12	1.503 (3)	S21—C21	1.821 (2)
C2—C3	1.398 (3)		
C6—C1—C2	118.92 (18)	C3—C2—S21	121.27 (15)
C6—C1—C11	120.13 (18)	C1—C2—S21	120.27 (14)
C2—C1—C11	120.95 (17)	C4—C3—C2	120.90 (19)
O11—C11—C1	120.40 (18)	C5—C4—C3	120.6 (2)
O11—C11—C12	120.2 (2)	C6—C5—C4	119.0 (2)
C1—C11—C12	119.40 (19)	C5—C6—C1	122.0 (2)
C3—C2—C1	118.46 (17)	C2—S21—C21	102.62 (10)

For (II), the H atoms attached to C12 were located in a circular difference synthesis; the methyl group was thereafter treated as a rotating rigid group with $U_{iso}(H) = 1.5U_{eq}(C12)$ and C—H = 0.96 Å. Other H atoms were placed in calculated positions and allowed to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$ and C—H = 0.93 Å. For compound (III), all H atoms were refined; C—H = 0.90 (3)–1.00 (3) Å.

For both compounds, data collection: *DIF*4 (Stoe & Cie, 1990); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1990); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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