

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. University of Cambridge, England.

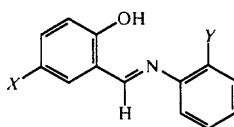
Ping, L., Lucken, E. A. C. & Bernardinelli, G. (1990). *J. Am. Chem. Soc.* **112**, 8754–8764.

Rigaku Corporation (1985). *Rigaku/AFC Diffractometer Control Software*. Rigaku Corporation, Tokyo, Japan.

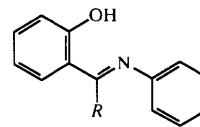
Ripmeester, J. A. (1983). *J. Incl. Phenom.* **1**, 87–91.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Zaborowski, E. & Vega, S. (1993). *Mol. Phys.* **78**, 703–732.



- (1) X=Y=H
 (4) X=Cl, Y=H
 (5) X=H, Y=Cl



- (2) R=Me
 (3) R=Ph

While the crystal structure of the parent salicylideneaniline, (1), is severely disordered, precluding detailed comparison with (2) and (3), data for the chloro derivatives (4) (Bregman, Leiserowitz & Schmidt, 1964) and (5) (Bregman, Leiserowitz & Osaki, 1964) are adequate for this purpose. All of the compounds (1)–(5) have an *E* (or *anti*) configuration at the C=N moiety in order to accommodate hydrogen bonding with the *ortho*-hydroxy function (Figs. 1 and 2). The overall conformation of this family of compounds appears to be governed by steric factors in the neighbourhood of the imine function. Thus compound (4), in which Y = H, is planar to within 1°, whereas in (5) (Y = Cl), the angle between the two phenyl rings is 51.5°, and in

Acta Cryst. (1998). **C54**, 1360–1362

Methyl- and Phenyl-Substituted Salicylideneanilines

RINO LEARDINI,^a GRAHAM MCDUGALD,^b HAMISH MCNAB,^b DANIELE NANNI^a AND SIMON PARSONS^b

^aDipartimento di Chimica Organica 'A. Mangini', Università di Bologna, Viale Risorgimento 4, I-40136, Bologna, Italy, and ^bDepartment of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland. E-mail: s.parsons@ed.ac.uk

(Received 4 February 1998; accepted 20 March 1998)

Abstract

The angles between the phenol and anil ring systems attached to the imine functions of 2-hydroxyacetophenone anil [IUPAC name: 2-(1-phenyliminoethyl)-phenol; C₁₄H₁₃NO] and 2-hydroxybenzophenone anil {IUPAC name: 2-[phenyl(phenylimino)methyl]phenol; C₁₉H₁₅NO} are 101.6 (1) and 103.2 (1)°, respectively. These are larger than in the corresponding salicylideneanilines derived from aldehydes because of steric repulsions arising from the substitution of H by Me or Ph. Bond lengths and angles are, however, broadly similar in the aldehyde- and ketone-derived systems.

Comment

Although there are several reports of crystal structures of salicylaldehyde anils, including the parent member of the series, (1) (Destro *et al.*, 1978), none is available for derivatives of the corresponding ketones. Here we rectify this omission in the literature and report the crystal structures of two anil derivatives of acetophenone and benzophenone, (2) and (3), respectively.

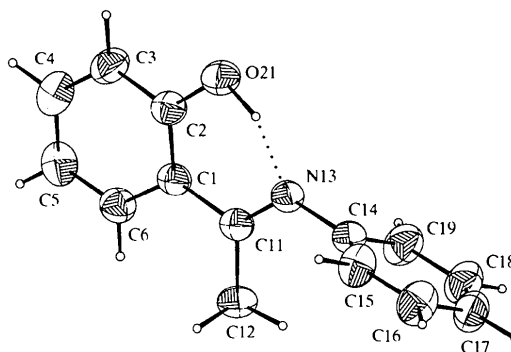


Fig. 1. A view of (2) with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces. Hydrogen-bonding parameters are O21...N13 2.554 (3) and H21...N13 1.63 (3) Å.

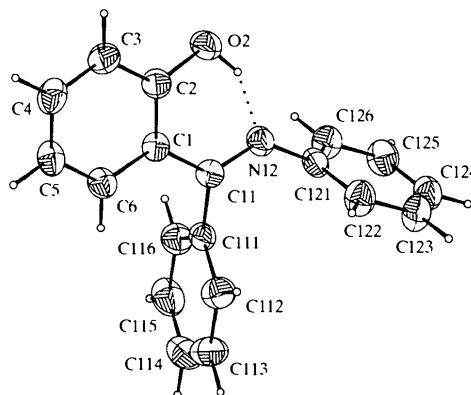


Fig. 2. A view of (3) with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces. Hydrogen-bonding parameters are O2...N12 2.550 (2) and H2...N12 1.70 (2) Å.

the ketone derivatives (2) and (3), these parameters are 101.6 (1) and 103.2 (1)°, respectively.

While bond lengths within the C=N—Ar moieties of compounds (2)–(5) are similar, the Ar—C bond length in the Ar—C=N unit ranges from 1.438 (7) Å in (4) to 1.475 (2) Å in (3). Surprisingly, perhaps, these fragments are identical in (2) and (3), this similarity extending to the bonds in the methyl and phenyl substituents. This is clearly a consequence of the phenyl ring in (3) being twisted out of plane by 90.4°, precluding $p\pi$ – $p\pi$ interactions along C11—C111. The substituted phenol ring (C1—C6) is prone to distortion from ideal D_{6h} symmetry in all structures, and in the case of C1—C2, this may be related to the formation of the six-membered hydrogen-bonded ring and to push–pull conjugation between the O atom and the imine function.

The substituent at C11 in compounds (2) and (3) appears to reduce the angle C1—C11=N [average 118.2 (2)°] with respect to corresponding parameters in compounds (4) and (5) (121.2°). This is likely to be a steric effect; consistent with this view, C12—C11—N13 in (2) and C111—C11—N12 in (3) are significantly greater than 120° [both 123.4 (2)°].

There appear to be no especially significant intermolecular contacts in either structure. In (2), the molecules pack *via* a classic herring-bone motif, while in (3), molecules pair-up *via* two symmetry-related C3—H···O2 contacts (H···O = 2.46 Å) disposed about a crystallographic twofold axis.

Experimental

Compounds (2) (Cazaux & Tisnés, 1976) and (3) (Graebe & Keller, 1899) were prepared by condensation of aniline with the appropriate ketone at 453 K [as described by Graebe & Keller (1899)]. Crystals were grown by evaporation of alcoholic solutions.

Compound (2)

Crystal data

C₁₄H₁₃NO
 $M_r = 211.26$
 Orthorhombic
Pbca
 $a = 5.5431$ (5) Å
 $b = 8.9090$ (6) Å
 $c = 45.893$ (4) Å
 $V = 2266.4$ (3) Å³
 $Z = 8$
 $D_x = 1.24$ Mg m⁻³
 D_m not measured

Data collection

Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)

Cu $K\alpha$ radiation
 $\lambda = 1.5418$ Å
 Cell parameters from 103 reflections
 $\theta = 20$ – 22°
 $\mu = 0.62$ mm⁻¹
 $T = 220$ K
 Plate developed in (001)
 $0.70 \times 0.62 \times 0.04$ mm
 Colourless

2003 independent reflections
 1288 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.02$
 $\theta_{\text{max}} = 70.07^\circ$

ω – θ scans

Absorption correction:

ψ scans (North *et al.*, 1968)

$T_{\text{min}} = 0.604$, $T_{\text{max}} = 0.965$
 3454 measured reflections

Refinement

Refinement on F

$R = 0.060$

$wR = 0.074$

$S = 1.089$

1288 reflections

150 parameters

H atom attached to O21

refined freely; H atoms

attached to C iteratively

re-idealized

Chebyshev polynomial

(Carruthers & Watkin,

1979)

Table 1. Selected geometric parameters (Å, °) for (2)

C1—C2	1.409 (3)	C4—C5	1.383 (5)
C1—C6	1.409 (4)	C5—C6	1.373 (4)
C1—C11	1.471 (4)	C11—C12	1.498 (4)
C2—C3	1.389 (4)	C11—N13	1.291 (3)
C2—O21	1.349 (3)	N13—C14	1.421 (3)
C3—C4	1.375 (4)		
C2—C1—C6	117.2 (2)	C4—C5—C6	120.0 (3)
C2—C1—C11	121.7 (2)	C1—C6—C5	121.7 (3)
C6—C1—C11	121.1 (2)	C1—C11—C12	118.6 (2)
C1—C2—C3	120.5 (3)	C1—C11—N13	118.0 (2)
C1—C2—O21	121.4 (2)	C12—C11—N13	123.4 (2)
C3—C2—O21	118.1 (2)	C11—N13—C14	121.2 (2)
C2—C3—C4	120.6 (3)	N13—C14—C15	119.7 (2)
C3—C4—C5	120.1 (3)	N13—C14—C19	121.1 (3)

Compound (3)

Crystal data

C₁₉H₁₅NO
 $M_r = 273.33$
 Monoclinic
C2/c
 $a = 18.339$ (3) Å
 $b = 9.642$ (1) Å
 $c = 16.323$ (2) Å
 $\beta = 90.26$ (2)°
 $V = 2886.3$ (7) Å³
 $Z = 8$
 $D_x = 1.26$ Mg m⁻³
 D_m not measured

Data collection

Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)
 ω – θ scans with learnt-profile (Clegg, 1981)
 Absorption correction: none
 2810 measured reflections
 2451 independent reflections

$h = -2 \rightarrow 6$

$k = -10 \rightarrow 10$

$l = -45 \rightarrow 55$

3 standard reflections

frequency: 60 min

intensity decay: none

$(\Delta/\sigma)_{\text{max}} = 0.04$

$\Delta\rho_{\text{max}} = 0.21$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.25$ e Å⁻³

Extinction correction:

Larson (1969)

Extinction coefficient:

102 (17)

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Refinement

Refinement on *F**R* = 0.044*wR* = 0.048*S* = 1.126

1978 reflections

195 parameters

H atom attached to O22

refined freely; H atoms
attached to C iteratively
re-idealized

Chebychev polynomial

(Carruthers & Watkin,
1979) $(\Delta/\sigma)_{\max} = 0.007$ $\Delta\rho_{\max} = 0.19 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -0.14 \text{ e } \text{Å}^{-3}$

Extinction correction:

Larson (1969)

Extinction coefficient:

143 (9)

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)Table 2. Selected geometric parameters (Å , $^\circ$) for (3)

C1—C2	1.409 (2)	C3—C4	1.374 (2)
C1—C6	1.402 (2)	C4—C5	1.384 (2)
C1—C11	1.475 (2)	C5—C6	1.375 (2)
O2—C2	1.350 (2)	C11—N12	1.285 (2)
O2—H2	0.96 (2)	C11—C111	1.495 (2)
C2—C3	1.394 (2)	N12—C121	1.429 (2)
C2—C1—C6	118.0 (1)	C3—C4—C5	120.8 (1)
C2—C1—C11	121.0 (1)	C4—C5—C6	119.6 (1)
C6—C1—C11	120.9 (1)	C1—C6—C5	121.4 (1)
C1—C2—O2	121.9 (1)	C1—C11—N12	118.3 (1)
C1—C2—C3	120.0 (1)	C1—C11—C111	118.3 (1)
O2—C2—C3	118.1 (1)	N12—C11—C111	123.4 (1)
C2—C3—C4	120.2 (1)	C11—N12—C121	123.0 (1)

Crystals of (2) formed as large plates developed in (001) which fragmented into very small shards when cut. The crystal used for data collection was thus rather large by normal standards. A 1.2 mm collimator was used for data collection. Values of R_{int} for data with $I < 2\sigma(I)$ were very high (1.04 and 4.49) for both crystal structures. Given this very poor internal agreement, these data were omitted from the refinement. The range of transmission coefficients determined experimentally for compound (2) is at some variance with that anticipated on the basis of the dimensions of the crystal. This is attributed to the difficulty in measuring the thickness of a very thin plate.

For both compounds, data collection: *DIF4* (Stoe & Cie, 1990a); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1990b); program(s) used to solve structures: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structures: *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1996); molecular graphics: *CAMERON* (Watkin, Prout & Pearce, 1996); software used to prepare material for publication: *CRYSTALS*.

We thank EPSRC for provision of a four-circle diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1237). Services for accessing these data are described at the back of the journal.

References

- Bregman, J., Leiserowitz, L. & Osaki, K. (1964). *J. Chem. Soc.* pp. 2086–2101.
 Bregman, J., Leiserowitz, L. & Schmidt, G. M. J. (1964). *J. Chem. Soc.* pp. 2068–2085.
 Carruthers, J. R. & Watkin, D. J. (1979). *Acta Cryst.* A35, 698–699.
 Cazaux, L. & Tisné, P. (1976). *J. Heterocycl. Chem.* 13, 665–668.
 Clegg, W. (1981). *Acta Cryst.* A37, 22–28.

- Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* 19, 105–108.
 Destro, R., Gavezzotti, A. & Simoneita, M. (1978). *Acta Cryst.* B34, 2867–2869.
 Graebe, C. & Keller, F. (1899). *Ber. Dtsch. Chem. Ges.* 32, 1683–1688.
 Larson, A. C. (1969). *Crystallographic Computing*, edited by F. R. Ahmed, pp. 291–294. Copenhagen: Munksgaard. (Equation 22 in this paper was used with *V* replaced by the cell volume.)
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.
 Sheldrick, G. M. (1997). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
 Stoe & Cie (1990a). *DIF4. Diffractometer Control Program*. Version 7.09/DOS. Stoe & Cie, Darmstadt, Germany.
 Stoe & Cie (1990b). *REDU4. Data Reduction Program*. Version 7.03/DOS. Stoe & Cie, Darmstadt, Germany.
 Watkin, D. J., Prout, C. K., Carruthers, J. R. & Betteridge, P. W. (1996). *CRYSTALS*. Issue 10. Chemical Crystallography Laboratory, University of Oxford, England.
 Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.

Acta Cryst. (1998). C54, 1362–1364

2,3-Benzoquino[15]crown-5

AKIHIKO TSUDA,^a TATSUYA KAWAMOTO^b AND TAKUMI OSHIMA^a

^aDepartment of Applied Chemistry, Faculty of Engineering, Osaka University, 1-16 Machikaneyama, Toyonaka, Osaka 560, Japan, and ^bDepartment of Chemistry, Graduate School of Science, Osaka University, 1-16 Machikaneyama, Toyonaka, Osaka 560, Japan. E-mail: oshima@ch.wani.osaka-u.ac.jp

(Received 16 October 1997; accepted 16 February 1998)

Abstract

The X-ray structure analysis of the title compound, 2,5,8,11,14-pentaoxabicyclo[13.4.0]nonadeca-15(1),17-diene-16,19-dione, C₁₄H₁₈O₇, reveals that the fused quinone causes a significant deformation of the crown ring from the expected rectangular form, because of the serious steric repulsion between the two carbonyl groups and the two adjacent OCH₂CH₂ units. One of these units deviates significantly from the mean plane of the quinone, while the other bends inward, remaining coplanar with the quinone. Such a constrained and folded structure is reflected in the abnormal *sp*² bond angles (110 and 130°) of one of the bridgehead quinonoid C atoms.

Comment

The crystal structures of crown ethers have received constant attention in view of the cation-binding abilities