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2-(4-Chloroanilino)- and 2-(4-methoxyanilino)-1,2-diphenylethanone

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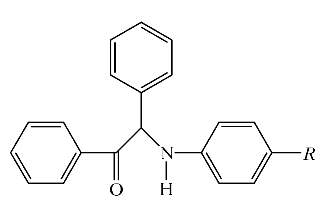
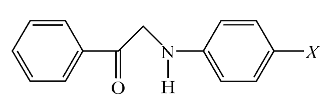
The title compounds, $C_{20}H_{16}ClNO$ and $C_{21}H_{19}NO_2$, adopt *syn* orientations of the C=O and N—H bonds but, like their analogues, form no strong intermolecular hydrogen bonds.

Comment

Few 1-arylanilinoethanone derivatives have been structurally studied so far, although some of them are important in synthesis (Saraogi *et al.*, 2003), while others possess interesting charge-transfer properties (Abdulla *et al.*, 1985). These compounds also display rather unusual supramolecular arrangements (see below). The present low-temperature study of compounds (I) and (II) follows on from our structural determinations of the parent compound 2-anilino-1,2-diphenylethanone, (III) (Au & Tafeenko, 1987), its methyl derivative 1,2-diphenyl-2-(*p*-toluidino)ethanone, (IV) (Au & Tafeenko, 1986), and 1,2-bis(2-furyl)-2-(*p*-toluidino)ethanone, (V) (Au & Tafeenko, 1988).



R = Cl (I), OMe (II), H (III), Me (IV)



X = Br (VI), NO_2 (VII)

The structures of (I) and (II) both contain one molecule per asymmetric unit. Crystals of (I) and (IV) are isostructural, the Cl atom of van der Waals radius 1.76 Å (Rowland & Taylor, 1996) replacing the methyl group of effective radius 2.0 Å. In (I), the C3—C1—C2—N—C15 backbone adopts an all-*trans* conformation and is planar within ±0.1 Å (Fig. 1). The terminal benzene rings, *A* and *B*, are nearly coplanar, whereas the central ring, *C*, is nearly normal to them [interplanar angles: 6.1 (1)° for *A*/*B*, 81.7 (1)° for *A*/*C* and 86.1 (1)° for *B*/*C*]. Very similar conformations have been observed previously in (III), (IV) and (V), as well as in analogues without substituents in the 2-position, such as (VI) (Saraogi *et al.*, 2003) or (VII) (Abdulla *et al.*, 1985). Such a conformation brings the C1=O1 and N—H1 bonds into a *syn* orientation, and apparently favours the formation of a centrosymmetric dimer of molecules, linked *via* a pair of strong N—H···O hydrogen bonds. A dimer of topology $R_2^2(10)$ according to the graph-set nomenclature (Etter, 1990) is present in the structure (Fig. 2), but the molecules are so widely separated that only weak N—H···O interactions can exist. The N···O1′ distance [3.479 (2) Å] is much longer and the corrected H1···O1′ distance [2.59 (2) Å] is only marginally shorter than the corresponding sums of van der Waals radii, 3.22 and 2.68 Å (Rowland & Taylor, 1996).

Two molecules of (I), related *via* the inversion ($2 - x$, $-y$, $1 - z$), have their $PhCOCNHC_6H_4Cl$ systems stacked face-to-face, the C=O bond of each molecule overlapping with the *B* ring of another. Notwithstanding the tight interplanar separation of 3.33 Å, there is no evidence of intermolecular charge transfer, such as occurs in the intensely coloured crystal of (VII). The formation of continuous stacks is rendered impossible by the perpendicular phenyl ring *C*.

Compound (II) (Fig. 1) has a more twisted conformation of the backbone (see Fig. 3, and the torsion angles in Tables 1 and

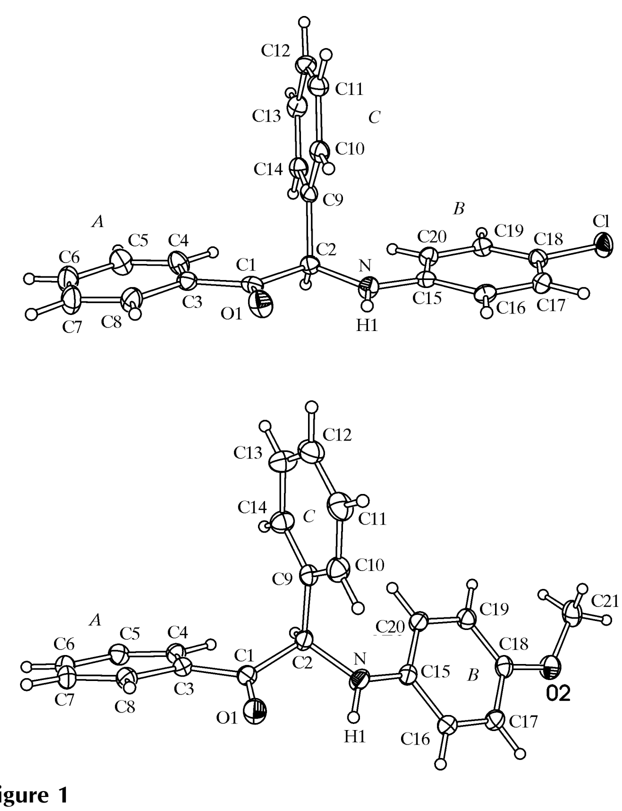


Figure 1
The molecular structures of (I) (top) and (II) (bottom). Displacement ellipsoids are drawn at the 50% probability level.

3), and the inter-ring angles are 64.0 (1)° for *A*/*B*, 85.0 (1)° for *A*/*C* and 77.3 (1)° for *B*/*C*. Nevertheless, the C═O and N—H bonds remain in a *syn* orientation. Unlike (I), the structure contains no dimers. The N—H bond points roughly toward the $p\pi$ orbital of atom C6 of an adjacent molecule, related *via* an inversion at ($-x$, $1 - y$, $-z$), the corrected H···C distance being 2.90 (2) Å.

Thus, a prominent feature of both structures is the absence of strong intermolecular hydrogen bonds. The intramolecular H1···O1 contacts (Tables 2 and 4) have awkward angular geometry, quite atypical for unconstrained hydrogen bonds, although these interactions probably help to stabilize the *syn* conformations of the molecules. Compounds (IV), (VI) and (VII) form 'distant dimers', as in (I), with N···O distances of 3.57, 3.41 and 3.60 Å, respectively. The structures of (III) and (V), in broad resemblance of (II), contain no dimers at all, but show intermolecular N—H···C(aryl) contacts, in both cases with the *ortho* atom of the 'anilinic' benzene ring (ring *B* in Fig. 1). The H···C distances of 2.97 Å in (III) and 3.05 Å in (V) are unexceptional.

Thus, none of the structurally characterized 1-arylanilino-ethanones forms strong intermolecular hydrogen bonds. If the terminal benzene rings (*A* and *B*) are coplanar with the molecular backbone, as in (I), their steric repulsion can prevent closer approach of the polar groups to one another. Thus, in (I), the intradimer distances H8···H16′ and H16···H8′ (Fig. 2) are 2.14 Å, *i.e.* they constitute close van der Waals contacts. However, in principle, the rings could adopt a less hindering orientation.

The N atom has planar–trigonal geometry in (I) but is significantly pyramidal in (II), the refined position of atom H1 deviating from the C2/N/C15 plane by 0.038 (18) and 0.354 (15) Å, respectively. It is noteworthy that the N atom is also nearly planar in (IV), (VI) and (VII) but strongly pyramidal in (III) and (V). In other words, planar geometry always accompanies 'distant dimers', whereas pyramidalization accompanies N—H···C(aryl) contacts. Thus, even these apparently weak intermolecular interactions can influence the molecular geometry.

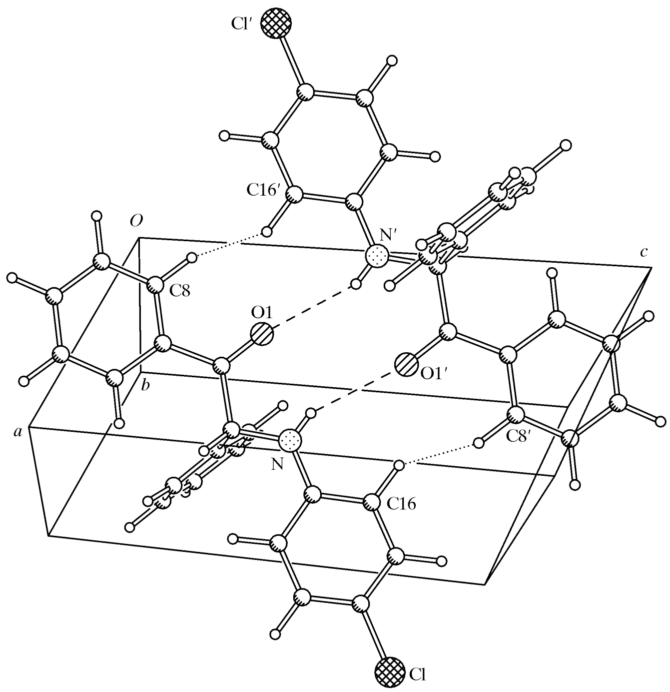


Figure 2
'Distant' dimers in the structure of (I). Primed atoms are generated by an inversion at ($1 - x$, $-y$, $1 - z$).

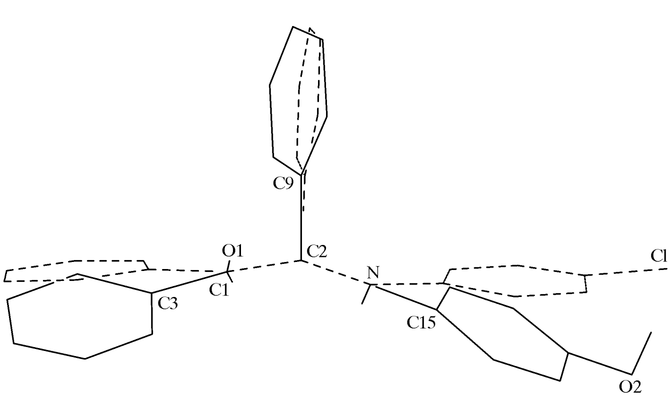


Figure 3
A comparison of the conformations of (I) (dashed lines) and (II) (solid lines).

Experimental

Compounds (I) and (II) were prepared by refluxing benzoin (28 mmol) with *p*-chloroaniline or *p*-methoxyaniline (28 mmol), respectively, in dimethylformamide (1 ml) for 4 h. Crystals of X-ray quality were grown from ethanol [m.p. 435–436 K for (I) and 373–374 K for (II)]. IR (cm^{-1}): ν(C═O) 1670 (I), 1673 (II); ν(N—H) 3391 (I), 3400 (II); ν(C—Cl) 752 (I).

Compound (I)

Crystal data

$C_{20}H_{16}ClNO$
$M_r = 321.79$
Triclinic, $P\overline{1}$
$a = 5.7748$ (8) Å
$b = 11.485$ (2) Å
$c = 13.086$ (2) Å
$\alpha = 113.47$ (1)°
$\beta = 100.39$ (1)°
$\gamma = 97.29$ (1)°
$V = 763.8$ (2) Å^3
$Z = 2$
$D_x = 1.399$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.25$ mm^{-1}
$T = 120$ (2) K
Thin plate, colourless
0.52 × 0.12 × 0.04 mm

Data collection

Bruker PROTEUMM APEX CCD area-detector diffractometer
ω scans
8385 measured reflections
3452 independent reflections
2860 reflections with $I > 2\sigma(I)$
$R_{int} = 0.099$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.101$
$S = 1.06$
3452 reflections
212 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0218P)^2 + 0.0976P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

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

O1—C1	1.2237 (16)	C1—C3	1.487 (2)
N—C15	1.3718 (19)	C1—C2	1.5375 (19)
N—C2	1.4423 (18)		
C15—N—C2	122.94 (11)	C2—N—H1	117.8 (14)
C15—N—H1	119.2 (14)		
C3—C1—C2—N	−165.81 (12)	O1—C1—C2—N	15.53 (18)
C1—C2—N—C15	178.20 (12)		

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N—H1···O1	0.817 (17)	2.238 (19)	2.6259 (17)	109.5 (16)
N—H1···O1^{i}	0.817 (17)	2.756 (18)	3.4791 (15)	148.6 (17)

Symmetry code: (i) $-x+1, -y, -z+1$.

Compound (II)

Crystal data

$C_{21}H_{19}NO_2$
M_r = 317.37
Monoclinic, $P2_1/n$
a = 5.8230 (8) Å
b = 10.069 (1) Å
c = 27.316 (3) Å
β = 91.75 (1)°
V = 1600.8 (3) Å^3
Z = 4
D_x = 1.317 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 120 (2) K
Block, light yellow
0.32 × 0.22 × 0.18 mm

Data collection

Bruker SMART CCD 6K area-detector diffractometer
ω scans
21531 measured reflections
4666 independent reflections
3800 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 30.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.119
S = 1.02
4666 reflections
223 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0577P)^2 + 0.5575P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

The amine H atoms were refined freely in isotropic approximation; the methyl group in (II) was refined as a rigid body (C—H = 0.98 Å) with a single refined U_{iso}(H) value. All other H atoms were treated as riding on their carrier C atoms (Csp^2—H = 0.95 Å and Csp^3—H = 1.00 Å), with U_{iso}(H) values of $1.2U_{eq}$(C). The discussion of intermolecular contacts refers to idealized H-atom positions, corresponding to the 'neutron' bond lengths (N—H = 1.01 Å and C—H = 1.08 Å).

Table 3
Selected geometric parameters (Å, °) for (II).

N—C15	1.3900 (13)	C1—C3	1.4898 (14)
N—C2	1.4472 (13)	C1—C2	1.5348 (14)
O1—C1	1.2174 (13)		
C15—N—C2	121.91 (9)	C2—N—H1	115.0 (10)
C15—N—H1	117.7 (10)		
C3—C1—C2—N	−147.78 (9)	O1—C1—C2—N	33.86 (13)
C1—C2—N—C15	154.74 (10)		

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N—H1···O1	0.878 (15)	2.300 (15)	2.6875 (12)	106.7 (12)
N—H1···C6^{i}	0.878 (15)	3.021 (16)	3.8499 (16)	158.1 (13)

Symmetry code: (i) $-x, -y+1, -z$.

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* [Version 6.45A (Bruker, 2003) for (I) and Version 6.02A (Bruker, 2001) for (II)]; data reduction: *SAINT* [Version 6.45A for (I) and Version 6.02A for (II)]; program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3012). Services for accessing these data are described at the back of the journal.

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