

Zhi-Yong Xing, Hui-Min Liu,  
Li Wu and Wen-Qin Zhang\*Department of Chemistry, College of Sciences,  
Tianjin University, Tianjin 300072, People's  
Republic of China

Correspondence e-mail: wqzhang@tju.edu.cn

## Key indicators

Single-crystal X-ray study  
 $T = 294$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.045  
 $wR$  factor = 0.124  
Data-to-parameter ratio = 15.9For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

## 2-Amino-2'-chloro-5-methylbenzophenone

The title compound,  $\text{C}_{14}\text{H}_{12}\text{ClNO}$ , was synthesized by the photo-Fries reaction of 2-chloro-*N*-(4-methylphenyl)benzamide in acetonitrile. The crystal structure contains intramolecular  $\text{N}-\text{H}\cdots\text{O}$  and intermolecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds.

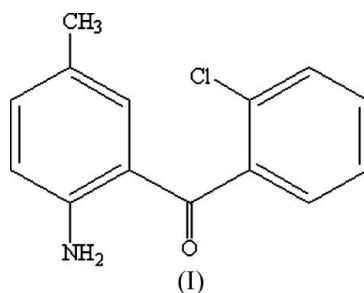
Received 10 October 2005

Accepted 17 October 2005

Online 22 October 2005

## Comment

The derivatives of benzophenone have been widely studied because of their extensive application in varied areas, such as medicine (Mahendra *et al.*, 2004; Wiesner *et al.*, 2003), materials (Wang & Lee, 2003) and photochemistry (Koshima *et al.*, 2003; Wrzyszczyński *et al.*, 2003). They are mainly produced by Fridel–Crafts acylation. Some amine- or hydroxy-substituted derivatives are also prepared by the photo-Fries rearrangement (Mayouf, 2005; Sriraghavan, 2003). Recently, our group has focused on the effect of halogen on the photo-Fries rearrangement of related benzophenone derivatives. We present here the crystal structure of the photo-Fries product of *N*-(4-methylphenyl)-2-chlorobenzamide, *viz.* the title compound, (I).



The molecular structure of (I) is non-planar (Fig. 1). The dihedral angle between the two benzene rings is  $96.2(2)^\circ$ , and the dihedral angles of the 2-chlorophenyl and 4-methylphenyl planes with the  $\text{C}7/\text{C}8/\text{C}9/\text{N}1/\text{O}1$  plane [mean deviation of  $0.0028(2)$  Å] are  $94.7(3)$  and  $1.8(2)^\circ$ , respectively. The  $\text{C}9-\text{C}8-\text{C}7-\text{O}1$  and  $\text{O}1-\text{C}7-\text{C}6-\text{C}5$  torsion angles are  $1.0(3)$  and  $92.4(2)^\circ$ , respectively. The above results indicate that the carbonyl is almost coplanar with the 4-methylphenyl plane and nearly perpendicular to the 2-chlorophenyl plane.

As shown in Fig. 2, the carbonyl O atom acts as a double hydrogen-bond receptor, involved in not only an intramolecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bond with one amine H atom to form a six-membered ring, but also an intermolecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bond with another amine H atom of an adjacent molecule (Table 2). The molecules are linked into an infinite chain structure through the intermolecular hydrogen bonds.

## Experimental

The title compound was prepared by the photolysis of *N*-(4-methylphenyl)-2-chlorobenzamide (MPCB) in acetonitrile. A solution of MPCB (245 mg) in acetonitrile (100 ml) was irradiated under a 254 nm low-pressure mercury lamp for 7 h and then concentrated. The product was isolated by column chromatography (cyclohexane/dichloromethane, 7: 1 v/v). Single crystals of (I) suitable for X-ray analysis were obtained from a cyclohexane/dichloromethane (1:1) solution.

### Crystal data

$C_{14}H_{12}ClNO$   
 $M_r = 245.70$   
 Monoclinic,  $P2_1/c$   
 $a = 10.3419$  (19) Å  
 $b = 10.892$  (2) Å  
 $c = 11.592$  (2) Å  
 $\beta = 102.982$  (3)°  
 $V = 1272.4$  (4) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.283$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 2400 reflections  
 $\theta = 3.0$ – $25.6$ °  
 $\mu = 0.28$  mm<sup>-1</sup>  
 $T = 294$  (2) K  
 Block, light yellow  
 $0.28 \times 0.22 \times 0.14$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.908$ ,  $T_{\max} = 0.961$   
 7003 measured reflections

2595 independent reflections  
 1758 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.027$   
 $\theta_{\text{max}} = 26.4$ °  
 $h = -12 \rightarrow 12$   
 $k = -12 \rightarrow 13$   
 $l = -6 \rightarrow 14$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.124$   
 $S = 1.03$   
 2595 reflections  
 163 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.056P)^2 + 0.3319P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.20$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.34$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Cl1—C1	1.740 (2)	N1—C9	1.346 (3)
O1—C7	1.239 (2)		
C5—C6—C7—O1	−92.4 (2)	O1—C7—C8—C9	−1.0 (3)

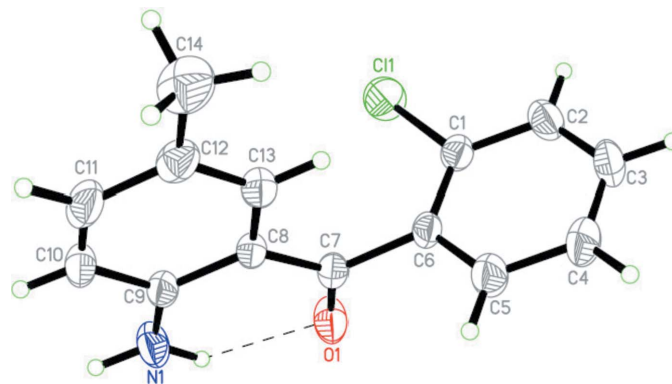
**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1B $\cdots$ O1	0.89 (3)	2.03 (3)	2.691 (3)	131 (2)
N1—H1A $\cdots$ O1 <sup>i</sup>	0.92 (3)	2.20 (3)	3.121 (3)	172 (2)

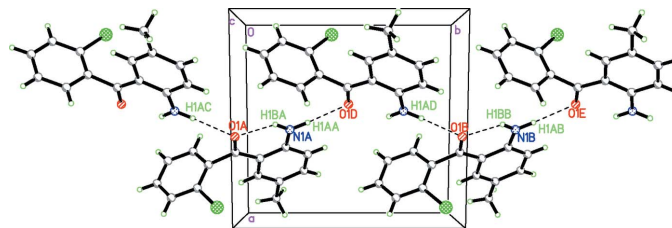
Symmetry code: (i)  $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$ .

All H atoms were initially located in a difference Fourier map. The C—H atoms were then constrained to an ideal geometry, with  $C_{\text{methyl}}-H$  distances of 0.96 Å,  $C_{\text{aromatic}}-H$  distances of 0.93 Å, and



**Figure 1**

The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 35% probability level. The intramolecular hydrogen bond is shown as a dashed line.



**Figure 2**

Packing view of (I), showing the inter- and intramolecular hydrogen bonds as dashed lines.

$U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C_{\text{aromatic}})$  or  $1.5U_{\text{eq}}(C_{\text{methyl}})$ . The amine H atoms were refined with the restraint  $N-H = 0.89$  (3) Å.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

## References

- Bruker (1997). SMART, SAINT and SHELXTL. Bruker AXS Inc., Madison, Wisconsin, USA.
- Koshima, H., Matsusaka, W. & Yu, H. (2003). *J. Photochem. Photobiol. A Chem.* **156**, 83–90.
- Mahendra, M., Doreswamy, B., Sridhar, M., Prasad, J., Khanum, S., Shashikanth, S. & Venu, T. (2004). *Struct. Chem.* **15**, 211–214.
- Mayouf, M. M. (2005). *J. Photochem. Photobiol. A Chem.* **172**, 258–268.
- Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Sriraghavan, K. (2003). *Tetrahedron*, **59**, 1791–1796.
- Wang, S. P. & Lee, W. T. (2003). *J. Chromatogr. A*, **987**, 269–275.
- Wiesner, J., Fucik, K., Kettler, K., Sakowski, J., Ortman, R., Jomaa, H. & Schlitzer, M. (2003). *Bioorg. Med. Chem. Lett.* **13**, 1539–1541.
- Wrzyszczyński, A., Bartoszewicz, J., Hug, G. L., Marciniak, B. & Paczkowski, J. (2003). *J. Photochem. Photobiol. A Chem.* **155**, 253–259.