Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4-Acetyl-*N*-methylaniline

Tsonko Kolev,[a] Michael Spiteller,[b] William S. Sheldrick[c] and Heike Mayer-Figge[c]*

[a]Institute of Organic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. build. 9, 1113 Sofia, Bulgaria, [b]Institut für Umweltforschung, Universität Dortmund, Otto-Hahn-Strasse 6, 44221 Dortmund, Germany, and [c]Lehrstuhl für Analytische Chemie, Ruhr-Universität Bochum, Universitätsstrasse 150, 44780 Bochum, Germany

Correspondence e-mail:
william.sheldrick@rub.de

Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.004 Å
R factor = 0.063
wR factor = 0.141
Data-to-parameter ratio = 14.2

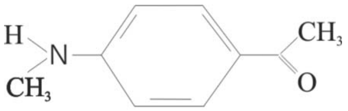
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 11 January 2006
Accepted 12 January 2006

Molecules of the title compound, $C_9H_{11}NO$, are connected into infinite chains by intermolecular N—H···O hydrogen bonds of length 2.893 (3) Å between the *N*-methylamino and carbonyl functions.

Comment

The non-linear optical properties of organic molecules are of great current interest, with a view to expanding the application of such materials in non-linear optics (NLO). It is known, for instance, that 'push–pull' systems, such as 4-acetylanilines, show high NLO and electro-optical (EO) effects (Chemla & Zyss, 1987). The electron non-linearity of this compound is based on the presence of a strongly delocalized π-electron system, with donor (–$NHCH_3$) and acceptor ($COCH_3$) groups at opposite ends of the molecule (Nalwa *et al.*, 1997; Wolff & Wortmann, 1999). One of the most important tasks of molecular engineering is the efficiency–transparency trade-off. Conjugated and polar molecules possessing the CT characteristics needed for large hyperpolarizability exhibit an almost inevitable loss of transparency. The aim of our research is to investigate new promising materials for non-linear optical and electro-optical applications, having a large non-linear figure of merit for frequency conversion, a high laser damage threshold and a fast optical response time. In the course of these studies on some 'push–pull' substituted 4-acetylanilines, the crystal structure of the title compound, 4-acetyl-*N*-methylaniline, (I), has been determined.



(I)

4-Acetyl-*N*-methylaniline is a typical one-dimensional (dipole) non-ionic system having a good transparency–efficiency trade-off (Nalwa *et al.*, 1997; Chemla & Zyss, 1987). The aromatic ring of (I) exhibits a quinoid-like structure, with C2—C3 = 1.376 (4) Å and C5—C6 = 1.379 (4) Å, while the remaining four aromatic bonds (C1—C2, C1—C6, C3—C4 and C4—C5) all lie in the narrow range 1.384 (4)–1.407 (3) Å. The short C1—N1 distance of 1.367 (3) Å is indicative of partial double-bond character, as is the C4—C41 distance of 1.473 (4) Å. This extension of the conjugated system leads to a lengthening of the C41—O4 carbonyl double-bond length to 1.231 (3) Å, a fact that is also reflected in the observed relatively low frequency of its ν(C═O) vibration at 1650 cm^{-1}. Interplanar angles of 6.20 (4) and 9.62 (2)° are observed for

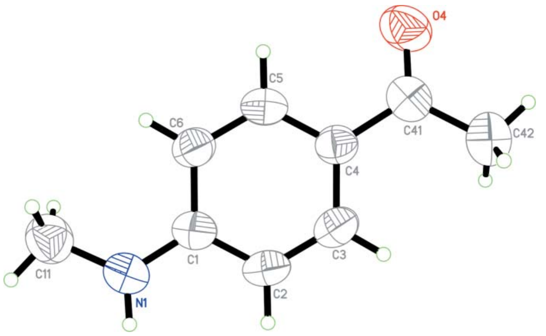


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

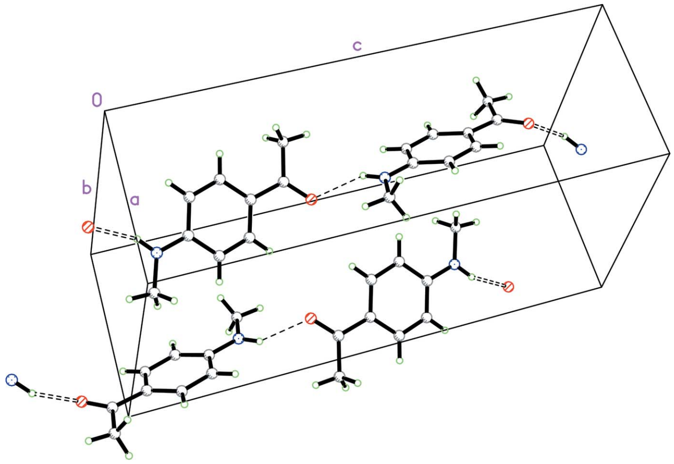


Figure 2
The crystal structure of (I), showing the hydrogen-bonded (dashed lines) chains in the [001] direction].

the methylamine (C1/N1/C11) and acetyl functions (C4/C41/C42/O4) relative to the plane of the aromatic ring. Molecules of (I) are connected through N—H$\cdots$O hydrogen bonds (Table 1) into chains running parallel to [001]. We have calculated the theoretical electronic spectrum of (I) on the *ab initio* RHF 6–311++G** and DFT B3LYP 6–311++G**levels (Kolev & Stamboliyska, 2006). This spectrum, together with theoretical vibrational frequencies, λ_{max} from the experimental (UV–vis) positive solvatochromy and the value of the first hyperpolarizability (β), confirms our assumption that (I) should demonstrate good NLO performance.

Experimental

4-Acetyl-*N*-methylaniline was obtained as a yellow powder (m.p. 377–378 K) according to the literature method of Korytnyk *et al.* (1978) and recrystallized three times, firstly from water–ethanol (1:2 *v*/*v*) and then twice from 96% ethanol. Prismatic single crystals, suitable for X-ray analysis, were grown from a methanol solution at room temperature over a period of three weeks. IR (KBr pellet), cm^{-1}: 3321 [*s*, ν(NH)], 3094, 3062, 3021 [*w*, ν(CH benzene)], 2983, 2933, 2904, 2888, 2857, 2823 [*w*, ν(CH methyl)], 1653 [ν(C=O)], 1589, 1560, 1532, 1449 (radial vibrations, benzene ring), 1279 [ν(Ph—C(O)CH$_3$)], 1160, 1115, 1082 [δ (in-plane benzene)], 994, 959, 828, 815 [δ (out-of-plane benzene)].

Crystal data

$C_9H_{11}NO$
M_r = 149.19
Monoclinic, $P2_1/c$
a = 6.286 (4) Å
b = 7.6675 (16) Å
c = 17.358 (5) Å
β = 97.33 (4)°
V = 829.8 (6) Å^3
Z = 4
D_x = 1.194 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 18 reflections
θ = 7.3–16.0°
μ = 0.08 mm^{-1}
T = 294 (2) K
Prism, light yellow
0.54 × 0.52 × 0.35 mm

Data collection

Siemens P4 four-circle diffractometer
Profile-fitted ω scans
Absorption correction: ψ scan (*XPREP* in *SHELXTL*; Sheldrick, 1995)
T_{min} = 0.937, T_{max} = 0.981
2178 measured reflections
1462 independent reflections
733 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 25.0°
$h = -1 \rightarrow 7$
$k = -1 \rightarrow 9$
$l = -20 \rightarrow 20$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.141
S = 0.99
1462 reflections
103 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.016
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.010 (3)

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O4^{i}	0.86	2.13	2.893 (3)	148

Symmetry code: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$.

H atoms were constrained to idealized positions and refined using a riding model, with C—H = 0.93 Å for aromatic H and 0.98 Å for methyl groups, and N1—H1 = 0.88 Å for the amide nitrogen. Displacement parameters were set at U_{iso}(H) = 1.2U_{eq}(C) for the benzene H atoms, 1.5U_{eq}(C) for the methyl H atoms and 1.2U_{eq}(N1) for the amide H atom. The methyl groups were allowed to rotate but not to tip.

Data collection: *R3m/V* (Siemens, 1989); cell refinement: *R3m/V*; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

TK and MS thank the DAAD for a grant within the priority programme ‘Stability Pact South-Eastern Europe’, the Alexander von Humboldt Foundation and the Bulgarian National Fund for Research (grant No. X-1213).

References

Chemla, D. & Zyss, J. (1987). Editors. *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vol. 1, pp. 23187. New York: Academic Press.
Kolev, T. & Stamboliyska, B. (2006). *Spectrochim. Acta* . Submitted.
Korytnyk, W., Angelino, N., Dave, C. & Caballes, L. (1978). *J. Med. Chem.* **21**, 507–513.

Acta Cryst. (2006). E**62**, o774–o776 Kolev *et al.* • $C_9H_{11}NO$ **o775**

Nalwa, H. S., Watanabe, T. & Miyata, S. (1997). *Nonlinear Optics of Organic Molecules and Polymers,* edited by H. S. Nalwa & S. Miyata, pp. 89–329. Boca Raton: CRC Press.

Sheldrick, G. M. (1995). *SHELXTL*. Release 5.03 for Siemens *R*3 crystallographic research system. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Siemens (1989). *R3m/V Crystallographic-Systems User's Guide* (Version 3.2) and *XDISK*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Wolff, J. J. & Wortmann, R. (1999). *Adv. Phys. Org. Chem.* **32**, 121–127.

o776 Kolev *et al.* • $C_9H_{11}NO$ *Acta Cryst.* (2006). E**62**, o774–o776