Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

4-Methoxy-2-methyl-*N*-phenylaniline

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Received 28 April 2005
Accepted 18 May 2005
Online 28 May 2005

Key indicators

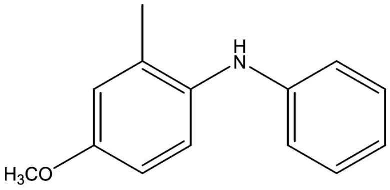
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.034
wR factor = 0.097
Data-to-parameter ratio = 9.8

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

The title compound, $C_{14}H_{15}NO$, is a key intermediate in the synthesis of the corresponding fluoran dye, which is used in thermal- or pressure-sensitive recording systems and light-resistant anthracene-type fluorescent colourants. The two aromatic rings are almost perpendicular to one another. The supramolecular aggregation is mainly due to the presence of π–π stacking interactions and intermolecular N—H···O hydrogen bonds.

Comment

Diphenylamines are well known for their anti-inflammatory properties but they can also act as precurors for fluoran dyes, which are used as thermal- or pressure-sensitive recording systems and light-resistant anthracene-type fluorescent colourants. The molecular and crystal structures of several diphenylamines are available in the Cambridge Structural Database (CSD, Version 5.25; Allen, 2002). An X-ray study of the title compound, (I), was undertaken in order to determine its crystal structure and to study its structure–activity relationships further.



(I)

The molecular structure of (I) is shown in Fig. 1 and some selected geometric parameters are given in Table 1. The bond distances and angles in (I) are consistent with values found in some other diphenylamines in the CSD and in *N*-phenyl-2-

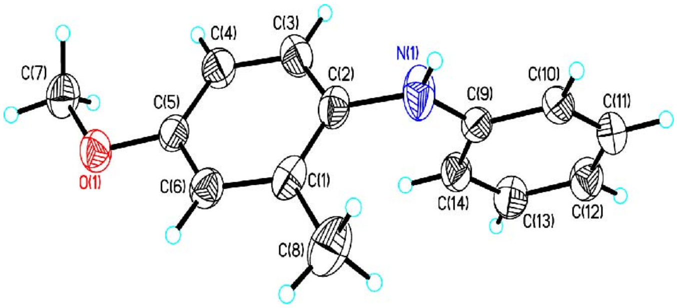


Figure 1
The molecular structure of (I), showing the atom-labelling scheme and 40% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

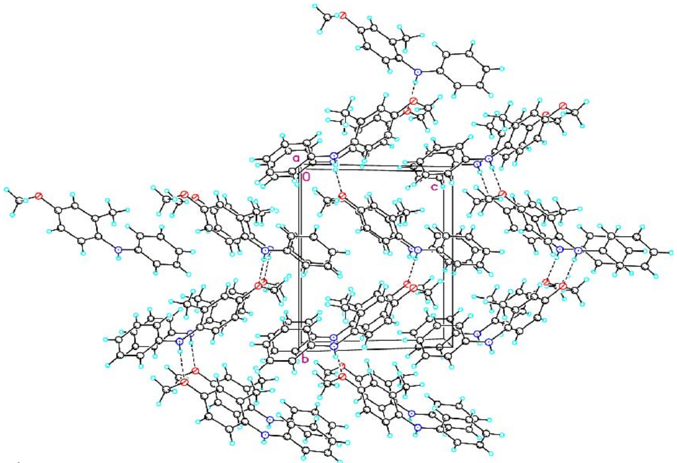


Figure 2
A packing diagram for (I), viewed along the *c* axis. Dashed lines indicate hydrogen bonds.

pyridine (Mefetah *et al.*, 1997). The N1—C9 [1.380 (2) Å] and N1—C2 [1.424 (2) Å] bonds are shorter than the standard N—C bond length of 1.47 Å (Mak *et al.*, 2002). This is similar to what has been found in some β-enaminoesters (Zhang, Jin, Shang *et al.*, 2004; Zhang, Jin, Liu & Guo, 2004). This difference is considered to be the result of π–π conjugation between the N atom and the aromatic rings. The dihedral angle between the two aromatic rings formed by atoms C1–C6 and C9–C14 is 75.3°, indicating that the rings are almost perpendicular to one another (Fig. 1). The twist is most likely due to a van der Waals repulsion effect between the methyl group attached to atom C1 and the C9–C14 aromatic ring.

As is shown in Fig. 2, the molecules of (I) are stacked in layers held together by a π–π stacking interaction, with a centroid-to-centroid distance of 5.050 Å and an intermolecular N—H···O hydrogen bond (Table 2), which links the molecules to form a zigzag chain along the *c* axis.

Experimental

o-Nitrotoluene (0.25 mol), sulfuric acid (98%, 0.63 mol), water (7.2 mol), methanol (11.9 mol) and Pt/C (0.11 g, 3%) were added to a flask fitted with a stirrer and a hydrogen pipe and reacted for 5 h at 323 K. 4-Methoxy-2-methylaniline was obtained in 75% yield. This product (10 mmol), phenol (50 mmol), cyclohexanone (1 mmol) and Pt/C (0.054 g, 5%) were added to a 500 ml autoclave and the mixture was heated to 473 K and stirred under a nitrogen atmosphere for 3 h. The precipitated solid product, (I) (10 mmol), was recrystallized from ethanol (yield 99%, m.p. 345–347 K).

Crystal data

$C_{14}H_{15}NO$
$M_r = 213.27$
Monoclinic, $P2_1$
$a = 6.3265\ (13)$ Å
$b = 11.047\ (2)$ Å
$c = 9.0030\ (18)$ Å
$\beta = 109.14\ (3)^\circ$
$V = 594.4\ (2)$ Å^3
$Z = 2$
$D_x = 1.192$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5203 reflections
$\theta = 2.4$–27.4°
$\mu = 0.08$ mm^{-1}
$T = 293\ (2)$ K
Plate, colourless
0.79 × 0.71 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer
Oscillation scans
Absorption correction: multi-scan (*ABSCOR*: Higashi, 1995)
$T_{\min} = 0.943$, $T_{\max} = 0.986$
5203 measured reflections
1424 independent reflections
1248 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\max} = 27.4^\circ$
$h = -8 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.097$
$S = 1.01$
1424 reflections
146 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0661P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.11$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997*a*)
Extinction coefficient: 0.19 (2)

Table 1
Selected geometric parameters (Å, °).

O1—C5	1.380 (2)	N1—C9	1.380 (2)
O1—C7	1.424 (2)	N1—C2	1.424 (2)
C5—O1—C7	117.64 (15)	N1—C9—C10	119.81 (16)
C2—N1—H1*A*	118.13	C9—N1—H1*A*	118.13
C3—C2—N1	120.3 (2)	C9—N1—C2	123.80 (15)
N1—C9—C14	121.87 (15)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1$^{\rm i}$	0.86	2.28	3.134 (2)	171

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

H atoms were placed in idealized positions and allowed to ride on their respective parent atoms, with C—H distances in the range 0.93–0.96 Å and an N—H distance of 0.86 Å, and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(C,N). In the absence of significant anomalous dispersion effects, Friedel pairs were averaged.

Data collection: *RAPID-AUTO* (Rigaku, 2003); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

We are grateful to the Center for Physiochemical Analysis Measurement Institute of Chemistry, the Chinese Academy of Sciences. We also acknowledge Professor Hong-Wei Ma for his helpful measurement and discussion during the preparation of this paper.

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