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N-[(*E*)-(2,4-Dinitrophenyl)methylene]aniline

Maciej Barys* and Zbigniew Ciunik

Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie St., Wrocław 50-383, Poland

Correspondence e-mail:
barys@wcheto.chem.uni.wroc.pl

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The title compound, $C_{13}H_9N_3O_4$, was obtained from the condensation reaction of 2,4-dinitrobenzaldehyde and aniline. It crystallizes with two independent molecules in the asymmetric unit. In the aniline moiety, the C═N and C—N bond lengths are normal. The crystal packing reveals short contacts [3.374 (2)–3.632 (3) Å] between the benzene rings of neighbouring molecules, suggesting the existence of π–π stacking effects.

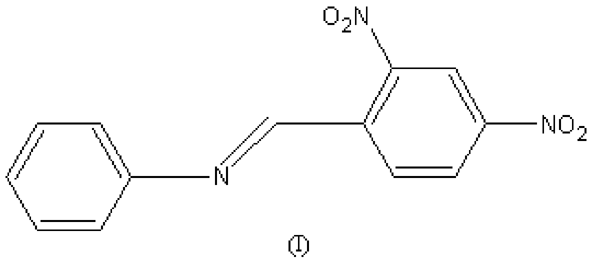
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.043
wR factor = 0.086
Data-to-parameter ratio = 13.9

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

Comment

Benzylideneanilines constitute an important class of Schiff bases that have been widely used in coordination, medical and biological chemistry over the last 25 years (Metzler *et al.*, 1980; Tarafder *et al.*, 2002). They possess significant anticancer and anti-inflammatory activity, and may also serve as reagents for stereoselective organic synthesis. Recently, the thermochromism (Pistolis *et al.*, 1996), photochromism (Jalali-Heravi, 2000) and non-linear optical properties of these compounds have found applications in modern technologies (Sekikawa *et al.*, 1997). In the design of solid materials, one of the key steps is to understand how the constituent molecules are packed, what kinds of interactions play a role in crystal packing and how they interplay with each other (Desiraju, 1989). To make a contribution in this direction, we present a crystal structure of the title compound, (I), obtained as a reaction product of aniline and 2,4-dinitrobenzaldehyde in hot methanol.



(I)

The asymmetric unit of (I) contains two independent molecules (Fig. 1), having the same bond lengths and angles within experimental error (Table 1). The average C14═N14 bond length of 1.270 (2) Å is close to the sum of the covalent radii of doubly-bonded C and N atoms (Hollemann & Wiberg, 1995). This C═N bond length is longer than that in free benzylideneaniline [1.237 (3) Å; Bürgi & Dunitz, 1970] and shorter than that found in coordinated benzylideneaniline [1.285 (10) Å; Little & Doedens, 1973]. The average (for two molecules) N14—C6 bond distance of 1.424 (2) Å is marginally shorter than the corresponding bond length of 1.460 (3) Å in free benzylideneaniline and close to that in the coordinated ligand of 1.428 (10) Å. The torsion angles C6*A*—C14*A*—

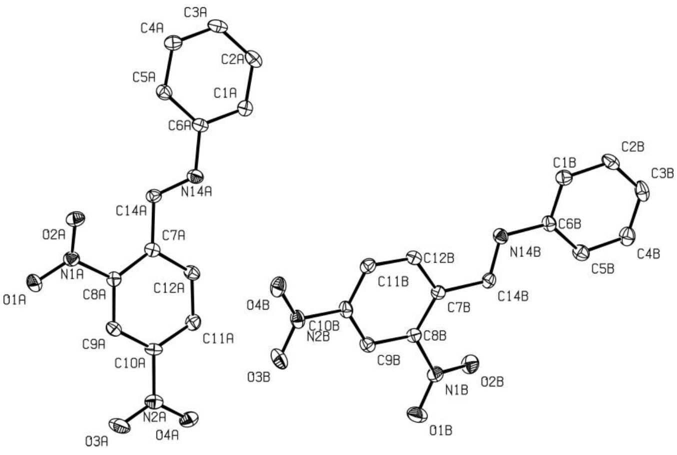


Figure 1
The two independent molecules of (I), shown with 50% probabilty displacement elipsoids. H atoms have been omitted for clarity.

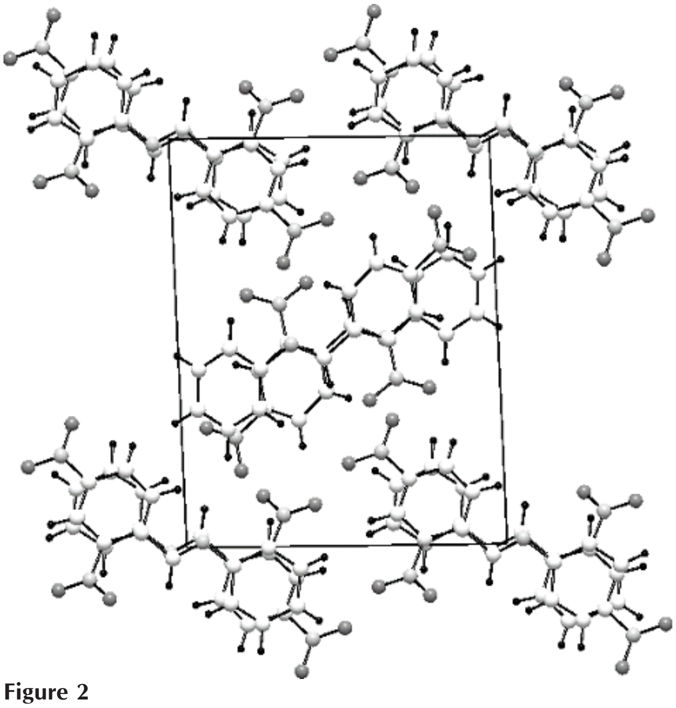


Figure 2
A packing diagram, viewed along the *a* axis.

N14*A*—C7*A* [175.30 (13)°] and C6*B*—C14*B*—N14*B*—C7*B* [176.96 (13)°] differ slightly for the two crystallographically independent molecules.

In the crystal structure, a partially overlapped arrangement of nearly parallel aromatic rings is observed for neighbouring independent molecules (Fig. 2). For molecule *A*, the dihedral angle and the centroid-to-centroid distance between the C1*A*–C6*A* and $\mathrm{C7}A^{\mathrm{i}}$–$\mathrm{C12}A^{\mathrm{i}}$ benzene rings are 8.65 (3) and 3.789 (2) Å, respectively [symmetry code: (i) $-x, 1-y, 1-z$]. The distances between the mean planes of the C1*A*–C6*A* and $\mathrm{C7}A^{\mathrm{i}}$–$\mathrm{C12}A^{\mathrm{i}}$ rings, and C7*A*–C12*A* and $\mathrm{C1}A^{\mathrm{i}}$–$\mathrm{C6}A^{\mathrm{i}}$ rings are 3.632 (3) and 3.494 (2) Å, respectively. For molecule *B*, the dihedral angle and the centroid-to-centroid distance between the C1*B*–C6*B* and $\mathrm{C7}B^{\mathrm{ii}}$–$\mathrm{C12}B^{\mathrm{ii}}$ benzene rings are 3.64 (2) and 3.737 (2) Å, respectively [symmetry code: (ii) $2-x, 2-y, -z$]. The distances between the mean planes of C1*B*–C6*B* and $\mathrm{C7}B^{\mathrm{ii}}$–$\mathrm{C12}B^{\mathrm{ii}}$, and C7*B*–C12*B* and $\mathrm{C1}B^{\mathrm{ii}}$–$\mathrm{C6}B^{\mathrm{ii}}$ rings are 3.469 (2) and 3.374 (2) Å, respectively. These findings suggest the existence of π–π stacking between the aromatic rings (Janiak, 2000) in the crystal structure of (I).

Experimental

Commercially available reagents, *viz*. aniline and 2,4-dinitrobenzaldehyde, were used without further purification. Aniline (0.5 ml) was added to a solution of 2,4-dinitrobenzaldehyde (0.005 mol) in hot methanol (40 ml). The reaction mixture was refluxed for 4 h. The title compound spontaneously crystallized from the warm methanol. The crystals were filtered off, washed in methanol and dried in an air (m.p. 410–411 K). Calculated: C 57.56, H 3.32, N 15.49%; found: C 57.50, H 3.34, N 15.22%.

Crystal data

$\mathrm{C_{13}H_9N_3O_4}$
$M_r = 271.23$
Triclinic, $P\overline{1}$
$a = 7.5001$ (8) Å
$b = 11.9920$ (13) Å
$c = 14.1110$ (14) Å
$\alpha = 90.867$ (10)°
$\beta = 93.531$ (7)°
$\gamma = 107.084$ (8)°
$V = 1210.1$ (2) Å^3

$Z = 4$
$D_x = 1.489$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3726 reflections
$\theta = 3.1$–36.6°
$\mu = 0.11$ mm^{-1}
$T = 100$ (2) K
Plate, brown
0.3 × 0.2 × 0.1 mm

Data collection

Kuma KM-4-CCD κ-geometry diffractometer
ω scans
Absorption correction: none
14484 measured reflections
6029 independent reflections

3926 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.052$
$\theta_{\mathrm{max}} = 28.5$°
$h = -9 \rightarrow 9$
$k = -16 \rightarrow 15$
$l = -16 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.086$
$S = 1.05$
6029 reflections
433 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\mathrm{max}} = 0.045$
$\Delta\rho_{\mathrm{max}} = 0.22$ e Å^{-3}
$\Delta\rho_{\mathrm{min}} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C7*A*—C14*A*	1.490 (2)	C7*B*—C14*B*	1.488 (2)
N14*A*—C14*A*	1.2690 (19)	N14*B*—C14*B*	1.271 (2)
N14*A*—C6*A*	1.4260 (19)	N14*B*—C6*B*	1.4211 (19)
C7*A*—C8*A*—N1*A*—O2*A*	−19.7 (2)	C7*B*—C8*B*—N1*B*—O2*B*	−16.8 (2)
C6*A*—N14*A*—C14*A*—C7*A*	175.34 (12)	C6*B*—N14*B*—C14*B*—C7*B*	176.98 (13)

After their location in a difference Fourier map, H atoms were placed in calculated positions and allowed to ride on their parent atoms, with C—H = 0.93 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2001); data reduction: *CrysAlis RED*; 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: *SHELXL97*.

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