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The effect of molecular planarity on crystal non-centrosymmetry in benzylidene–aniline derivatives

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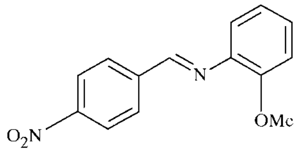
In the title compound, *N*-(2-methoxyphenyl)-4-nitrobenzylideneamine, $C_{14}H_{12}N_2O_3$, the two phenyl rings make a dihedral angle of 48.0 (2)° and the nitro group is at an angle of 6.5 (1)° with respect to its attached phenyl ring. In the crystal structure, molecules are related as centrosymmetric pairs through π–π interactions and are further connected through strong C—H···O hydrogen bonds [C···O 3.4259 (17) Å and C—H···O 167°], forming molecular stacks along [100]. These stacks associate further through longer C—H···O interactions, forming two-dimensional networks. In the *c* direction, there are only weak van der Waals interactions. The relationship between the molecular planarity and its centrosymmetry is also briefly described.

Comment

A number of benzylidene–aniline derivatives (BA) (Tetsuya *et al.*, 1990; Sun *et al.*, 1994; Qi *et al.*, 1996) have been shown to be potential crystalline compounds for second harmonic generation (SHG). For an SHG crystal, the molecule should have a relatively large dipole moment, but the crystal should not have a centre of symmetry. Since dipole–dipole interactions between molecules favours antiparallel packing, resulting in a centrosymmetric crystal, one should study the factors that can weaken the above tendency while not greatly reducing the molecular dipole. According to our preliminary study (Peng, 2001) on BA crystals, whose data were retrieved from the Cambridge Structural Database (2001; CSD), molecular planarity is an important factor. From the data presented in Table 1, a strong correlation can be noted, indicating that the more planar molecules have a greater possibility of crystallizing in a non-centrosymmetric space group.

During our systematic research on the crystal engineering of BA systems, we synthesized the title compound, (I), and describe its crystal structure here (Fig. 1 and Table 2). The two phenyl rings make a dihedral angle of 48.0 (2)° with one another and the nitro group is at an angle of 6.5 (2)° with respect to its attached aromatic ring. Because the –OCH_3 group is not sterically small and as it is positioned *ortho* to the central linkage, the title molecule is not especially planar, which may be a primary reason why it crystallized in a centrosymmetric space group.



(I)

In (I), the molecules are paired by strong π–π-stacking interactions (symmetry code: $-x$, $-y+2$, $-z$) (Fig. 2). The shortest distances between the ring planes and their centroids, respectively, are 3.46 (1) and 3.62 (1) Å. The packing potential energies (PPE), calculated using *OPEC* (Gavezzotti, 1983), for the whole crystal and the above molecular pair are −148.7 and −26.4 kJ mol^{-1}, respectively.

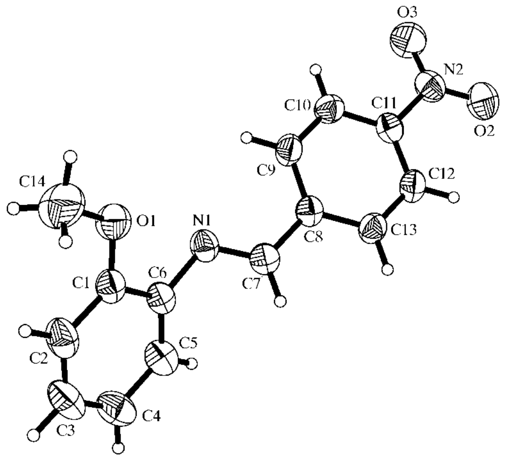


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

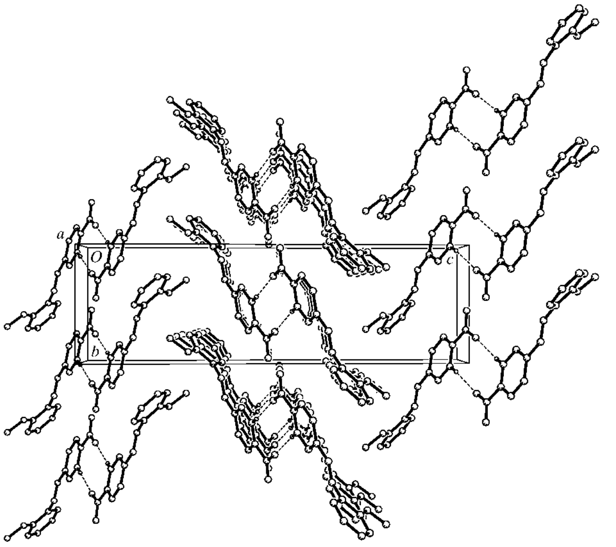


Figure 2
Packing diagram for (I) viewed down the *a* axis.

The molecular pairs are connected by strong C10—H10···O3 hydrogen bonds (Table 3) (Krishnamohan & Desiraju, 1994). The aforementioned interactions link the molecules stacked along [100] into chains. The chains are further connected through weak C9—H9···O2 hydrogen bonds, forming two-dimensional networks. In the third direction, [001], there are only relatively weak interactions, which may explain the plate-like crystal habit.

Experimental

4-Nitrophenylaldehyde (1.51 g, 10 mmol) and 2-methoxyphenylamine (1.13 g, 10 mmol) in ethanol (10 ml) were heated at 363 K with stirring for 30 min. After cooling to room temperature for 15 min, the product was separated and recrystallized from ethanol twice (m.p. 430 K). The yellow square-plate crystal used for analysis was grown from toluene. Spectroscopic analysis (IR): 1645, 1587, 1520, 864, 752, 727 cm^{-1}. Elemental analysis, found: C 58.97, H 4.98, N 10.66%; $C_{14}H_{12}N_2O_3$ requires: C 59.02, H 5.07, N 11.58%.

Crystal data

$C_{14}H_{12}N_2O_3$
$M_r = 256.26$
Monoclinic, $P2_1/c$
$a = 7.2703$ (6) Å
$b = 7.2963$ (8) Å
$c = 24.086$ (3) Å
$\beta = 94.517$ (8)°
$V = 1273.7$ (2) Å^3
$Z = 4$
$D_x = 1.336$ Mg m^{-3}
$D_m = 1.330$ Mg m^{-3}
D_m measured by flotation in a mixture of CCl_4 and cyclohexane
Mo $K\alpha$ radiation
Cell parameters from 22 reflections
$\theta = 4.2$–12.8°
$\mu = 0.10$ mm^{-1}
$T = 295$ (2) K
Square plate, yellow
0.50 × 0.48 × 0.46 mm

Data collection

Siemens *P*4 diffractometer
ω scans
2876 measured reflections
2372 independent reflections
1662 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\rm max} = 25.5°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 8$
$l = -29 \rightarrow 29$
3 standard reflections every 97 reflections intensity decay: 6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.108$
$S = 1.00$
2372 reflections
174 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.19$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.036 (3)

H atoms were placed in calculated positions and refined as riding (C—H = 0.93 and 0.96 Å).

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997*a*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1100). Services for accessing these data are described at the back of the journal.

Table 1
Comparison of dipole moment (*D*; Debye), planarity (PL; °) and space group (SG) in BA crystals.

CSD refcode	SG	*D*	PL
SIDQEB	$P2_12_12_1$	6.83	4.0
VOXPIH	$Pca2_1$	6.79	6.8
RIHJAT	$Pna2_1$	5.97	1.2
TSABAN	$Pca2_1$	6.88	33.4
NMBYAN22	Pc	6.62	4.7
NMBYAN	$P\overline{1}$	6.20	53.1
		6.70	32.5
CASTEV	$P2_1/n$	6.43	71.7
DUNVIR	$P2_1/n$	6.71	83.1
GARXIG	$P2/a$	8.29	65.9
GEXKUP	$C2/c$	7.63	57.8
LIJZUZ	$Pbca$	6.87	88.0
TEKMOL	$P2_1/n$	7.66	18.5
		7.49	47.5
SIRXOG01	$P2_1/c$	6.42	67.8
SIRXUM	$P\overline{1}$	6.91	65.3
		6.81	76.4
(I)	$P2_1/n$	7.02	48.0

Notes: the molecular dipole moments were calculated using the *AM*1 method in *MOPAC* (Version 6; Dewar *et al.*, 1985) using experimental geometry without further optimization. PL is defined as the dihedral angle between the two phenyl rings. Data are limited to those BA molecules whose *D* value is close to that of the title molecule.

Table 2
Selected geometric parameters (Å, °).

N1—C7	1.2661 (18)	C7—C8	1.463 (2)
N1—C6	1.4136 (18)		
C7—N1—C6	118.54 (13)	C1—C6—N1	118.31 (13)
C5—C6—N1	122.30 (14)	N1—C7—C8	122.40 (14)
C14—O1—C1—C2	1.9 (2)	C6—N1—C7—C8	175.13 (12)
C6—C1—C2—C3	0.4 (2)	N1—C7—C8—C9	−1.5 (2)
C7—N1—C6—C1	137.14 (15)	O2—N2—C11—C12	−6.3 (2)

Table 3
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10···O3$^{\rm i}$	0.93	2.51	3.4259 (17)	167
C12—H12···O2$^{\rm ii}$	0.93	2.67	3.4376 (19)	141
C9—H9···O2$^{\rm iii}$	0.93	2.90	3.5977 (19)	133
C12—H12···N1$^{\rm iv}$	0.93	2.90	3.5861 (17)	132

Symmetry codes: (i) $-1-x, 2-y, -z$; (ii) $-x, 3-y, -z$; (iii) $x, y-1, z$; (iv) $x, 1+y, z$.

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