Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4-Methoxy-*N*-(4-nitrobenzyl)aniline

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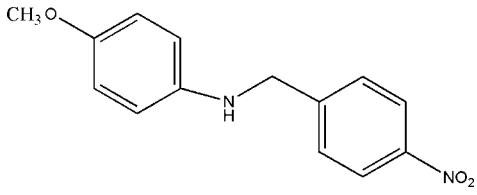
Received 17 February 2012; accepted 25 February 2012

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.048; wR factor = 0.130; data-to-parameter ratio = 14.1.

In the title compound, $C_{14}H_{14}N_2O_3$, the nitro group is nearly coplanar with the benzene ring to which it is bonded [dihedral angle = 1.70 (2)°], and this ring is *para*-substituted by the aminomethylene group. The dihedral angle between the benzene rings is 57.8 (1)°. The crystal structure is stabilized by N—H···O and C—H···O hydrogen bonds and weak C—H···π interactions are also observed.

Related literature

For related structures, see: Iwasaki *et al.* (1988). For the biological properties of aldimines, see: Rjosk & Neumann (1971); Hillesheim *et al.* (1995). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{14}H_{14}N_2O_3$
M_r = 258.27
Monoclinic, $P2_1/n$
a = 7.4993 (3) Å
b = 17.1516 (7) Å
c = 10.0048 (5) Å
β = 96.861 (4)°
V = 1277.65 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 293 K
0.3 × 0.2 × 0.1 mm

Data collection

Oxford Diffraction Xcalibur Sapphire3 diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2010)
T_{min} = 0.955, T_{max} = 1.000
11435 measured reflections
2511 independent reflections
1692 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.130
S = 1.05
2511 reflections
178 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

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

*Cg*1 and *Cg*2 are the centroids of the nitrophenyl (C1–C6) and methoxyphenyl (C9–C14) rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
N8—H8···O1^{i}	0.89 (2)	2.42 (3)	3.231 (2)	152.8 (19)
C16—H16*B*···O2^{ii}	0.96	2.47	3.372 (3)	155
C3—H3···*Cg*2^{iii}	0.93	2.77	3.560 (2)	143
C6—H6···*Cg*2^{iv}	0.93	2.87	3.524 (2)	129
C16—H16*A*···*Cg*1^{v}	0.96	2.96	3.830 (2)	151

Symmetry codes: (i) $-x, -y, -z+1$; (ii) $x+2, y, z+1$; (iii) $-x, -y+1, -z$; (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (v) $x+1, y, z+1$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2009).

RK acknowledges the Department of Science & Technology for the single-crystal X-ray diffractometer sanctioned as a National Facility under project No. SR/S2/CMP-47/2003. He is also thankful to the University of Jammu (India) for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2415).

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supplementary materials

Acta Cryst. (2012). E**68**, o988 [doi:10.1107/S160053681200846X]

4-Methoxy-*N*-(4-nitrobenzyl)aniline

Kamini Kapoor, Vivek K. Gupta, Indresh Kumar, Nisar A. Mir and Rajni Kant

Comment

In continuation of our project on the preparation of various aldimines from *p*-anisidine and aromatic aldehydes in refluxing methanol, the title compound has been prepared using the reductive amination method. In undergoing further applications of aldimines in various cycloaddition reactions (Rjosk & Neumann, 1971; Hillesheim *et al.*, 1995), we observed that aldimines undergo a reductive amination with $NaBH_4$ in presence of catalytic amounts of AcOH in MeOH, to afford 4-methoxy-*N*-(4-nitrobenzyl)aniline as one of the products. We further tried to prepare this compound under similar conditions in a separate flask, and the title compound was obtained in high yield (> 90%) through reductive amination of *p*-nitrobenzaldehyde with *p*-anisidine.

The bond lengths in the molecule are within normal ranges (Allen *et al.*, 1987) and comparable with those found in related molecules (Iwasaki *et al.*, 1988). The nitro group is nearly coplanar to the benzene ring to which it is bonded, the dihedral angle being 1.70 (2)°. The 4-methoxy phenyl group is *trans* to the 4-nitro phenyl group about the C7—N8 bond. The torsion angle C1—C7—N8—C9 is 178.22 (17)°. Hydrogen H8 on atom N8 forms an intermolecular hydrogen bond with the nitro O atom O1 of a neighbouring centrosymmetrically related molecule. This interaction links the molecules into N—H···O hydrogen bonded dimers. Dimers are connected *via* C—H···O hydrogen bonds and form chains along the *c*-axis of the unit cell (Table 1, Fig. 2). On the other hand, C—H···π interactions (*Cg*1 is the centroid of the nitro-phenyl ring and *Cg*2 is the centroid of the methoxy-phenyl ring, Table 1) play important role in stabilizing the crystal structure.

Experimental

To a stirred solution of *p*-nitro-benzaldehyde (0.5 g, 3.3 mmol) in MeOH (10 ml) was added *p*-anisidine (0.41 g, 3.3 mmol) at room temperature and the mixture was refluxed for 4 h. The resulting reaction mixture was cooled to 273 K, which resulted in the precipitation of the corresponding aldimine intermediate. Few drops of AcOH were added, followed by $NaBH_4$ (0.09 g, 2.5 mmol), at the same temperature. The combined reaction mixture was stirred additionally for 2 h and quenched with sat. $NaHCO_3$ solution, extracted with EtOAc (2×15 ml), and concentrated under reduced pressure. The resulting crude amine compound was crystallized in hexane/EtOAc (2:1), to afford the title compound with 92% yield. ^{1}H-NMR: 3.68 (*s*, 3H), 4.38 (*s*, 2H), 6.40 (*d*, 2H), 6.72 (*d*, 2H), 7.65 (*d*, 2H), 8.10 (*d*, 2H).

Refinement

Hydrogen atom H8 was found in a difference map and refined isotropically. All other H atoms were positioned geometrically and were treated as riding on their parent C atoms, with C—H distances of 0.93–0.97 Å and with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2010); data reduction: *CrysAlis RED* (Oxford Diffraction, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick,

2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2009).

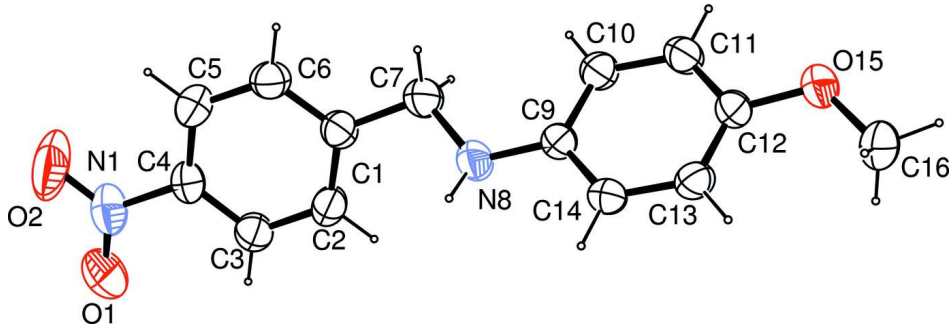

Figure 1

ORTEP view of the molecule with thermal ellipsoids drawn at the 40% probability level. H atoms are shown as small spheres of arbitrary radii.

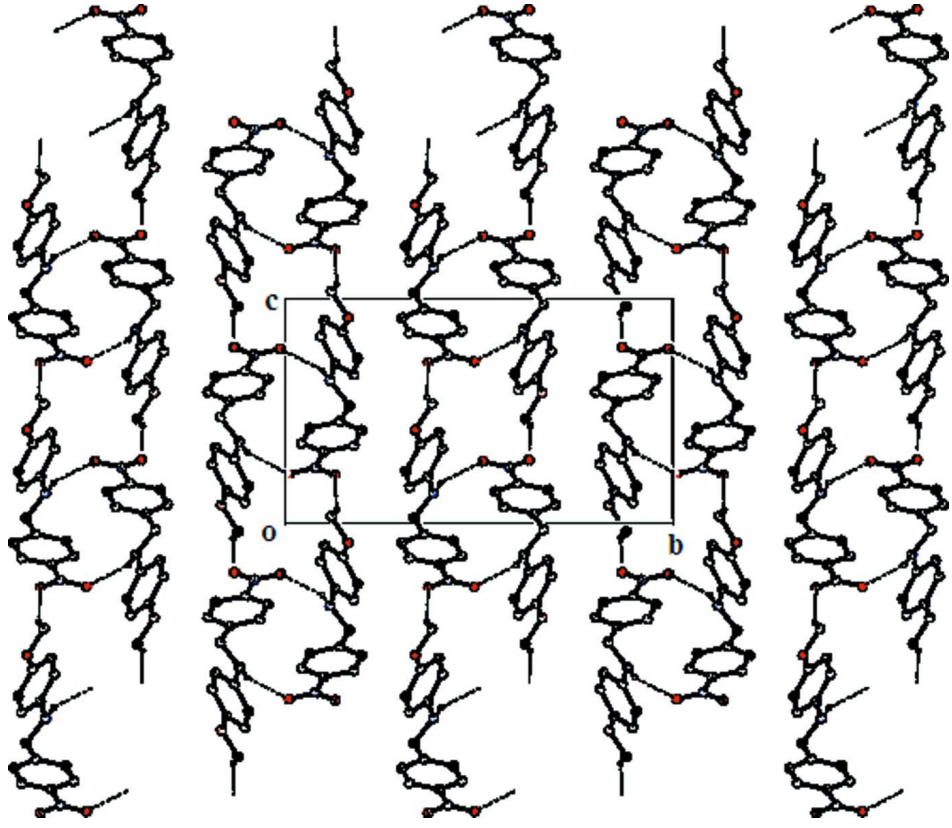

Figure 2

The packing arrangement of molecules viewed down the *a* axis. The broken lines show the intermolecular N—H···O and C—H···O hydrogen bonds.

4-Methoxy-*N*-(4-nitrobenzyl)aniline

Crystal data

$C_{14}H_{14}N_2O_3$
$M_r = 258.27$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 7.4993$ (3) Å
$b = 17.1516$ (7) Å
$c = 10.0048$ (5) Å
$\beta = 96.861$ (4)°
$V = 1277.65$ (10) Å^3
$Z = 4$
$F(000) = 544$
$D_x = 1.343$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4747 reflections
$\theta = 3.6$–29.0°
$\mu = 0.10$ mm^{-1}
$T = 293$ K
Block, red
0.3 × 0.2 × 0.1 mm

Data collection

Oxford Diffraction Xcalibur Sapphire3 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 16.1049 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2010)
$T_{min} = 0.955$, $T_{max} = 1.000$
11435 measured reflections
2511 independent reflections
1692 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 26.0°$, $\theta_{min} = 3.6°$
$h = -9 \rightarrow 9$
$k = -21 \rightarrow 21$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.130$
$S = 1.05$
2511 reflections
178 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 0.2077P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0116 (18)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.2703 (2)	0.01096 (11)	0.2223 (2)	0.0948 (6)
O2	−0.3470 (3)	0.12998 (13)	0.2161 (3)	0.1390 (10)
N1	−0.2400 (2)	0.07908 (13)	0.24933 (19)	0.0695 (5)
C1	0.2618 (2)	0.14226 (11)	0.45527 (19)	0.0499 (5)
C2	0.2220 (3)	0.06469 (12)	0.4248 (2)	0.0581 (5)
H2	0.3072	0.0265	0.4505	0.070*
C3	0.0581 (3)	0.04336 (11)	0.3571 (2)	0.0550 (5)
H3	0.0320	−0.0086	0.3367	0.066*
C4	−0.0654 (2)	0.10088 (11)	0.32049 (18)	0.0491 (5)
C5	−0.0304 (3)	0.17839 (12)	0.3476 (2)	0.0563 (5)
H5	−0.1155	0.2165	0.3210	0.068*

C6	0.1338 (3)	0.19793 (11)	0.4152 (2)	0.0547 (5)
H6	0.1593	0.2501	0.4344	0.066*
C7	0.4411 (3)	0.16668 (12)	0.5260 (2)	0.0636 (6)
H7A	0.5284	0.1668	0.4619	0.076*
H7B	0.4319	0.2195	0.5592	0.076*
N8	0.5039 (2)	0.11659 (10)	0.63639 (18)	0.0597 (5)
C9	0.6719 (2)	0.13024 (10)	0.71064 (19)	0.0464 (5)
C10	0.7998 (2)	0.17809 (11)	0.66267 (19)	0.0511 (5)
H10	0.7719	0.2042	0.5814	0.061*
C11	0.9671 (3)	0.18720 (11)	0.73402 (19)	0.0531 (5)
H11	1.0507	0.2194	0.7000	0.064*
C12	1.0133 (2)	0.14945 (10)	0.85483 (19)	0.0485 (5)
C13	0.8871 (3)	0.10262 (10)	0.90428 (19)	0.0510 (5)
H13	0.9152	0.0772	0.9863	0.061*
C14	0.7188 (2)	0.09308 (10)	0.83278 (19)	0.0505 (5)
H14	0.6354	0.0610	0.8674	0.061*
O15	1.18447 (17)	0.16348 (8)	0.91664 (14)	0.0652 (4)
C16	1.2455 (3)	0.12020 (13)	1.0336 (2)	0.0724 (7)
H16A	1.1723	0.1321	1.1034	0.109*
H16B	1.3681	0.1337	1.0633	0.109*
H16C	1.2375	0.0655	1.0135	0.109*
H8	0.421 (3)	0.0966 (13)	0.683 (2)	0.072 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0735 (11)	0.0908 (13)	0.1143 (15)	−0.0263 (10)	−0.0125 (10)	−0.0124 (11)
O2	0.0739 (12)	0.1245 (17)	0.199 (3)	0.0363 (13)	−0.0627 (14)	−0.0507 (16)
N1	0.0484 (10)	0.0889 (14)	0.0686 (12)	0.0022 (11)	−0.0032 (9)	−0.0163 (11)
C1	0.0495 (11)	0.0541 (11)	0.0451 (11)	−0.0046 (9)	0.0008 (8)	0.0047 (8)
C2	0.0502 (11)	0.0527 (11)	0.0680 (14)	0.0079 (9)	−0.0063 (9)	0.0017 (10)
C3	0.0534 (11)	0.0500 (11)	0.0604 (13)	−0.0011 (9)	0.0020 (9)	−0.0047 (9)
C4	0.0407 (10)	0.0625 (12)	0.0435 (11)	0.0003 (9)	0.0030 (8)	−0.0043 (9)
C5	0.0539 (12)	0.0570 (12)	0.0570 (12)	0.0117 (10)	0.0021 (9)	0.0001 (10)
C6	0.0603 (12)	0.0471 (11)	0.0557 (12)	−0.0016 (9)	0.0029 (9)	0.0009 (9)
C7	0.0614 (13)	0.0599 (12)	0.0648 (14)	−0.0114 (10)	−0.0119 (10)	0.0118 (10)
N8	0.0488 (10)	0.0669 (11)	0.0601 (11)	−0.0124 (9)	−0.0074 (8)	0.0165 (9)
C9	0.0459 (10)	0.0408 (9)	0.0505 (11)	−0.0027 (8)	−0.0026 (8)	0.0000 (8)
C10	0.0549 (11)	0.0525 (11)	0.0442 (11)	−0.0055 (9)	−0.0011 (9)	0.0067 (9)
C11	0.0520 (11)	0.0520 (11)	0.0545 (12)	−0.0124 (9)	0.0033 (9)	0.0048 (9)
C12	0.0470 (10)	0.0426 (10)	0.0533 (12)	−0.0028 (8)	−0.0044 (9)	−0.0038 (8)
C13	0.0582 (12)	0.0454 (10)	0.0473 (11)	−0.0010 (9)	−0.0020 (9)	0.0067 (8)
C14	0.0503 (11)	0.0457 (10)	0.0544 (12)	−0.0075 (9)	0.0017 (9)	0.0081 (9)
O15	0.0553 (8)	0.0660 (9)	0.0688 (10)	−0.0128 (7)	−0.0150 (7)	0.0086 (7)
C16	0.0653 (13)	0.0741 (14)	0.0711 (15)	−0.0024 (12)	−0.0196 (11)	0.0062 (12)

Geometric parameters (Å, º)

O1—N1	1.214 (2)	N8—C9	1.404 (2)
O2—N1	1.206 (2)	N8—H8	0.89 (2)

N1—C4	1.462 (2)	C9—C14	1.386 (2)
C1—C6	1.379 (3)	C9—C10	1.390 (3)
C1—C2	1.389 (3)	C10—C11	1.377 (2)
C1—C7	1.502 (2)	C10—H10	0.9300
C2—C3	1.380 (3)	C11—C12	1.378 (3)
C2—H2	0.9300	C11—H11	0.9300
C3—C4	1.373 (3)	C12—C13	1.378 (3)
C3—H3	0.9300	C12—O15	1.378 (2)
C4—C5	1.376 (3)	C13—C14	1.384 (2)
C5—C6	1.373 (3)	C13—H13	0.9300
C5—H5	0.9300	C14—H14	0.9300
C6—H6	0.9300	O15—C16	1.415 (2)
C7—N8	1.433 (2)	C16—H16A	0.9600
C7—H7A	0.9700	C16—H16B	0.9600
C7—H7B	0.9700	C16—H16C	0.9600

O2—N1—O1	122.31 (19)	C9—N8—H8	115.1 (14)
O2—N1—C4	118.5 (2)	C7—N8—H8	116.8 (14)
O1—N1—C4	119.17 (19)	C14—C9—C10	117.59 (16)
C6—C1—C2	118.38 (17)	C14—C9—N8	120.47 (16)
C6—C1—C7	119.78 (18)	C10—C9—N8	121.88 (17)
C2—C1—C7	121.81 (17)	C11—C10—C9	120.77 (17)
C3—C2—C1	121.14 (18)	C11—C10—H10	119.6
C3—C2—H2	119.4	C9—C10—H10	119.6
C1—C2—H2	119.4	C10—C11—C12	121.28 (17)
C4—C3—C2	118.24 (18)	C10—C11—H11	119.4
C4—C3—H3	120.9	C12—C11—H11	119.4
C2—C3—H3	120.9	C13—C12—O15	125.72 (17)
C3—C4—C5	122.36 (17)	C13—C12—C11	118.53 (16)
C3—C4—N1	118.84 (18)	O15—C12—C11	115.75 (16)
C5—C4—N1	118.80 (18)	C12—C13—C14	120.43 (17)
C6—C5—C4	118.15 (18)	C12—C13—H13	119.8
C6—C5—H5	120.9	C14—C13—H13	119.8
C4—C5—H5	120.9	C13—C14—C9	121.41 (17)
C5—C6—C1	121.73 (18)	C13—C14—H14	119.3
C5—C6—H6	119.1	C9—C14—H14	119.3
C1—C6—H6	119.1	C12—O15—C16	118.13 (15)
N8—C7—C1	112.89 (16)	O15—C16—H16A	109.5
N8—C7—H7A	109.0	O15—C16—H16B	109.5
C1—C7—H7A	109.0	H16A—C16—H16B	109.5
N8—C7—H7B	109.0	O15—C16—H16C	109.5
C1—C7—H7B	109.0	H16A—C16—H16C	109.5
H7A—C7—H7B	107.8	H16B—C16—H16C	109.5
C9—N8—C7	119.94 (16)		

C6—C1—C2—C3	−0.5 (3)	C1—C7—N8—C9	178.22 (17)
C7—C1—C2—C3	−178.52 (19)	C7—N8—C9—C14	166.83 (19)
C1—C2—C3—C4	−0.1 (3)	C7—N8—C9—C10	−16.1 (3)
C2—C3—C4—C5	0.8 (3)	C14—C9—C10—C11	0.7 (3)

C2—C3—C4—N1	−179.66 (18)	N8—C9—C10—C11	−176.45 (18)
O2—N1—C4—C3	−179.1 (2)	C9—C10—C11—C12	−0.1 (3)
O1—N1—C4—C3	−1.3 (3)	C10—C11—C12—C13	−0.7 (3)
O2—N1—C4—C5	0.5 (3)	C10—C11—C12—O15	−179.83 (17)
O1—N1—C4—C5	178.3 (2)	O15—C12—C13—C14	179.92 (17)
C3—C4—C5—C6	−0.8 (3)	C11—C12—C13—C14	0.9 (3)
N1—C4—C5—C6	179.63 (17)	C12—C13—C14—C9	−0.3 (3)
C4—C5—C6—C1	0.1 (3)	C10—C9—C14—C13	−0.5 (3)
C2—C1—C6—C5	0.5 (3)	N8—C9—C14—C13	176.68 (17)
C7—C1—C6—C5	178.53 (18)	C13—C12—O15—C16	7.4 (3)
C6—C1—C7—N8	138.5 (2)	C11—C12—O15—C16	−173.61 (18)
C2—C1—C7—N8	−43.5 (3)		

Hydrogen-bond geometry (Å, º)

Cg1 and Cg2 are the centroids of the nitrophenyl (C1–C6) and methoxyphenyl (C9–C14) rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N8—H8···O1^{i}	0.89 (2)	2.42 (3)	3.231 (2)	152.8 (19)
C16—H16*B*···O2^{ii}	0.96	2.47	3.372 (3)	155
C3—H3···*Cg*2^{iii}	0.93	2.77	3.560 (2)	143
C6—H6···*Cg*2^{iv}	0.93	2.87	3.524 (2)	129
C16—H16*A*···*Cg*1^{v}	0.96	2.96	3.830 (2)	151

Symmetry codes: (i) −*x*, −*y*, −*z*+1; (ii) *x*+2, *y*, *z*+1; (iii) −*x*, −*y*+1, −*z*; (iv) *x*−1/2, −*y*+1/2, *z*−1/2; (v) *x*+1, *y*, *z*+1.