Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

2,2′-Dimethoxy-6,6′-dinitrobiphenyl

Shao-Bin Miao, Dong-Sheng Deng, Xian-Ming Liu and Bao-Ming Ji*

College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471022, People's Republic of China
Correspondence e-mail: lyhxxjbm@126.com

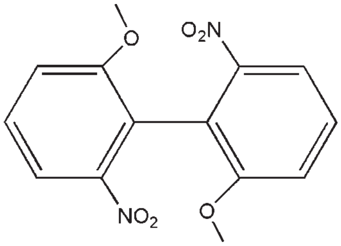
Received 28 July 2009; accepted 24 August 2009

Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.002 Å; R factor = 0.035; wR factor = 0.097; data-to-parameter ratio = 12.9.

In the title compound, $C_{14}H_{12}N_2O_6$, the half molecule in the asymmetric unit of the cell is completed by a crystallographic twofold rotation axis, and the two benzene rings of the complete molecule make a dihedral angle of 60.5 (3)°. Furthermore, intermolecular weak C—H⋯O hydrogen bonds link adjacent molecules, forming a two-dimensional sheet. These sheets are stablized by face-to-face weak π–π contacts [centroid–centroid distance = 3.682 (1) Å] between the nearly parallel [dihedral angle = 0.12 (7)°] benzene rings of the neighboring molecules, resulting in a three-dimensional network.

Related literature

For the synthesis of the title compound, see: Chen *et al.* (2001). For asymmetric synthesis using chiral ligands with C_2 symmetry, see: Jiang *et al.* (2001); García *et al.* (2002). For synthetic methods for chiral compounds, see: Brunel (2005); Kočovský *et al.* (2003). For related biphenyl structures, see: Fischer *et al.* (2007). For related structural data see: Yang *et al.* (2005).



Experimental

Crystal data

$C_{14}H_{12}N_2O_6$
M_r = 304.26
Monoclinic, $C2/c$
a = 18.236 (3) Å
b = 7.7826 (12) Å
c = 10.9079 (17) Å
β = 115.089 (2)°
V = 1402.0 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 294 K
0.30 × 0.18 × 0.18 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) T_{min} = 0.966, T_{max} = 0.979
5102 measured reflections
1298 independent reflections
1009 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.097
S = 1.03
1298 reflections
101 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C7—H7B⋯O3^{i}	0.96	2.48	3.426 (3)	169

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

This work was supported by the Youth Foundation of Luoyang Normal University (No. 10000409).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2193).

References

Bruker (2004). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Brunel, J. M. (2005). *Chem. Rev.* **105**, 857–897.
Chen, Y. X., Li, Y. M., Lam, k. H., & Chan, A. S. C. (2001). *Chin. J. Chem.* **19**, 794–799.
Fischer, A., Yathirajan, H. S., Ashalatha, B. V., Narayana, B. & Sarojini, B. K. (2007). *Acta Cryst.* E**63**, o1357–o1358.
García, C., LaRochelle, L. K. & Walsh, P. J. (2002). *J. Am. Chem. Soc.* **124**, 10970–10971.
Jiang, B., Feng, Y. & Hang, J. F. (2001). *Tetrahedron Asymmetry*. **12**, 2323–2329.
Kočovský, P., Vyskočil, Š. & Smrčina, M. (2003). *Chem. Rev.* **103**, 3213–3245.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Yang, D. S., Ma, H. X., Hu, R. Z., Song, J. R. & Zhao, F. Q. (2005). *J. Mol. Struct.* **779**, 49–54.

supplementary materials

Acta Cryst. (2009). E**65**, o2314 [**doi:10.1107/S1600536809033790**]

2,2'-Dimethoxy-6,6'-dinitrobiphenyl

S.-B. Miao, D.-S. Deng, X.-M. Liu and B.-M. Ji

Comment

A large number of chiral compounds with C_2-symmetry are widely used as chiral auxiliaries and ligands in asymmetric synthesis and have shown high stereocontrol properties in a wide range of asymmetric transformations (Jiang *et al.* 2001; García *et al.* 2002). Design and synthesis of such compounds play a very important role in the development of highly enantioselective asymmetric reactions. Thus, it is not surprising that a lot of methods have been developed to obtain these chiral compounds (Brunel 2005; Kočovský *et al.* 2003). In this paper, we report the synthesis and crystal structure of the title compound with C_2-symmetry.

A view of the molecular structure of the title compound is given in Fig.1. All bond lengths and angles are in the expected range and in good agreement with those reported previously (Yang *et al.* 2005). The dihedral angle between two benzene rings is 60.5 (3)°, which is considerable larger than those found in other biphenyls (Fischer *et al.* 2007), possibly due to the concomitant effects of the steric hindrance of adjacent methoxy and nitro groups.

In the crystal structure, each molecule is connected by four adjacent molecules through intermolecular C—H···O hydrogen bonds (Table 1), between methoxy groups and O atoms of the adjacent nitro groups, leading to the formation of a two-dimensional sheet in the *ac* plane. The sheets are further connected into a three-dimensional network(Fig.2) by the face-to-face weak π–π contacts between nearly parallel benzene rings of the neighboring title molecules. The $Cg1\cdots Cg1^{iii}$ distance is 3.6823 (11) Å, the perpendicular distance between the rings is 3.410 Å, and the slippage between the rings is 1.389 Å. *Cg*1 is the centroid of the benzene ring C1 - C6, the symmetry code iii = 1 - *x*, -*y*, 1 - *z*.

Experimental

The title compound was synthesized by a reported method (Chen, *et al.* 2001),namely, a mixture of 2-iodo-3-nitroanisol (14 g, 0.05 mol) and activated copper brone (9.5 g, 0.15 mol), 50 ml of dimethylformamide was stirried at 140°C for 4 h under nitrogen atmosphere. Yellow crystals suitable for X-ray diffraction study were obtained from a solution in acetic ester.

Refinement

All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned with common isotropic displacement factors $U_{iso}(H)$ = 1.2 times $U_{eq}(C,N)$ and 1.5 times $U_{eq}(O)$, respectively, and included in the final refinement by using geometrical restraints, with C–H distances of 0.93 Å.

Figures

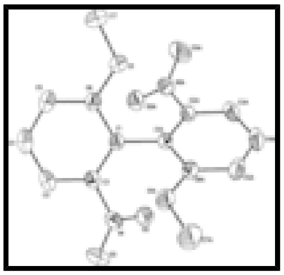


Fig. 1. *ORTEP* drawing (30% probability displacement ellipsoids) of a single molecule of the title compound.

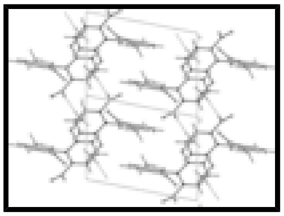


Fig. 2. three-dimensional structures of the title compound.

2,2'-Dimethoxy-6,6'-dinitrobiphenyl

Crystal data

$C_{14}H_{12}N_2O_6$

$M_r = 304.26$

Monoclinic, $C2/c$

Hall symbol: -C 2yc

$a = 18.236$ (3) Å

$b = 7.7826$ (12) Å

$c = 10.9079$ (17) Å

$\beta = 115.089$ (2)°

$V = 1402.0$ (4) Å^3

$Z = 4$

$F_{000} = 632$

$D_x = 1.441$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1790 reflections

$\theta = 2.5$–25.7°

$\mu = 0.12$ mm^{-1}

$T = 294$ K

Block, yellow

0.30 × 0.18 × 0.18 mm

Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 294$ K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.966$, $T_{\max} = 0.979$

5102 measured reflections

1298 independent reflections

1009 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 25.5$°

$\theta_{\min} = 2.5$°

$h = -22 \rightarrow 22$

$k = -9 \rightarrow 9$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.035$	H-atom parameters constrained
$wR(F^2) = 0.097$	$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 0.8036P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
1298 reflections	$\Delta\rho_{max} = 0.14$ e Å^{-3}
101 parameters	$\Delta\rho_{min} = -0.13$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes)

are estimated using the full covariance matrix. The cell e.s.d.'s are taken

into account individually in the estimation of e.s.d.'s in distances, angles

and torsion angles; correlations between e.s.d.'s in cell parameters are only

used when they are defined by crystal symmetry. An approximate (isotropic)

treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.49134 (9)	0.22562 (19)	0.67636 (14)	0.0387 (4)
C2	0.54245 (9)	0.2962 (2)	0.62577 (15)	0.0434 (4)
C3	0.52777 (12)	0.2896 (2)	0.49065 (17)	0.0546 (5)
H3	0.5639	0.3378	0.4607	0.066*
C4	0.45847 (12)	0.2102 (2)	0.40223 (17)	0.0588 (5)
H4	0.4471	0.2058	0.3107	0.071*
C5	0.40569 (11)	0.1370 (2)	0.44656 (16)	0.0540 (5)
H5	0.3589	0.0835	0.3852	0.065*
C6	0.42203 (9)	0.1426 (2)	0.58296 (15)	0.0444 (4)
C7	0.30000 (13)	−0.0071 (4)	0.5464 (2)	0.0944 (8)
H7A	0.2673	0.0767	0.4817	0.142*
H7B	0.2716	−0.0485	0.5971	0.142*

H7C	0.3110	−0.1012	0.4998	0.142*
N1	0.61559 (9)	0.3880 (2)	0.71661 (15)	0.0557 (4)
O1	0.37432 (7)	0.06986 (18)	0.63620 (11)	0.0594 (4)
O2	0.61327 (8)	0.47507 (17)	0.80791 (13)	0.0615 (4)
O3	0.67594 (9)	0.3739 (3)	0.69543 (17)	0.0967 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0399 (8)	0.0425 (8)	0.0345 (8)	0.0057 (6)	0.0166 (7)	0.0011 (6)
C2	0.0464 (9)	0.0454 (9)	0.0426 (8)	0.0044 (7)	0.0229 (7)	0.0023 (7)
C3	0.0722 (12)	0.0549 (10)	0.0508 (10)	0.0071 (9)	0.0399 (9)	0.0053 (8)
C4	0.0853 (14)	0.0566 (11)	0.0369 (8)	0.0117 (10)	0.0283 (10)	0.0036 (8)
C5	0.0610 (11)	0.0545 (10)	0.0372 (8)	0.0046 (9)	0.0119 (8)	−0.0031 (8)
C6	0.0452 (9)	0.0473 (9)	0.0388 (8)	0.0033 (7)	0.0159 (7)	0.0004 (7)
C7	0.0600 (13)	0.142 (2)	0.0750 (14)	−0.0445 (14)	0.0224 (12)	−0.0253 (15)
N1	0.0500 (8)	0.0679 (10)	0.0571 (9)	−0.0031 (7)	0.0302 (7)	0.0073 (8)
O1	0.0473 (7)	0.0794 (9)	0.0474 (7)	−0.0193 (6)	0.0162 (6)	−0.0058 (6)
O2	0.0612 (8)	0.0665 (8)	0.0570 (7)	−0.0133 (6)	0.0253 (6)	−0.0081 (7)
O3	0.0604 (9)	0.1503 (16)	0.0999 (12)	−0.0197 (10)	0.0538 (9)	−0.0120 (11)

Geometric parameters (Å, °)

C1—C2	1.383 (2)	C5—C6	1.389 (2)
C1—C6	1.400 (2)	C5—H5	0.9300
C1—C1^{i}	1.500 (3)	C6—O1	1.3576 (19)
C2—C3	1.383 (2)	C7—O1	1.424 (2)
C2—N1	1.466 (2)	C7—H7A	0.9600
C3—C4	1.370 (3)	C7—H7B	0.9600
C3—H3	0.9300	C7—H7C	0.9600
C4—C5	1.371 (3)	N1—O2	1.2200 (18)
C4—H4	0.9300	N1—O3	1.2217 (18)
C2—C1—C6	116.51 (13)	C6—C5—H5	120.0
C2—C1—C1^{i}	123.77 (15)	O1—C6—C5	124.06 (15)
C6—C1—C1^{i}	119.63 (14)	O1—C6—C1	115.19 (13)
C1—C2—C3	123.51 (15)	C5—C6—C1	120.75 (15)
C1—C2—N1	119.86 (13)	O1—C7—H7A	109.5
C3—C2—N1	116.60 (14)	O1—C7—H7B	109.5
C4—C3—C2	118.11 (16)	H7A—C7—H7B	109.5
C4—C3—H3	120.9	O1—C7—H7C	109.5
C2—C3—H3	120.9	H7A—C7—H7C	109.5
C3—C4—C5	121.01 (15)	H7B—C7—H7C	109.5
C3—C4—H4	119.5	O2—N1—O3	123.39 (16)
C5—C4—H4	119.5	O2—N1—C2	119.06 (13)
C4—C5—C6	120.08 (17)	O3—N1—C2	117.55 (16)
C4—C5—H5	120.0	C6—O1—C7	118.46 (14)
C6—C1—C2—C3	0.7 (2)	C2—C1—C6—O1	178.01 (14)
C1^{i}—C1—C2—C3	177.26 (13)	C1^{i}—C1—C6—O1	1.26 (19)

C6—C1—C2—N1	178.92 (14)	C2—C1—C6—C5	−1.6 (2)
C1^{i}—C1—C2—N1	−4.5 (2)	C1^{i}—C1—C6—C5	−178.36 (13)
C1—C2—C3—C4	0.6 (3)	C1—C2—N1—O2	−36.5 (2)
N1—C2—C3—C4	−177.73 (16)	C3—C2—N1—O2	141.90 (16)
C2—C3—C4—C5	−0.9 (3)	C1—C2—N1—O3	144.16 (17)
C3—C4—C5—C6	0.0 (3)	C3—C2—N1—O3	−37.5 (2)
C4—C5—C6—O1	−178.25 (16)	C5—C6—O1—C7	−4.5 (3)
C4—C5—C6—C1	1.3 (3)	C1—C6—O1—C7	175.90 (18)

Symmetry codes: (i) −*x*+1, *y*, −*z*+3/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7B···O3^{ii}	0.96	2.48	3.426 (3)	169

Symmetry codes: (ii) *x*−1/2, *y*−1/2, *z*.

Fig. 1

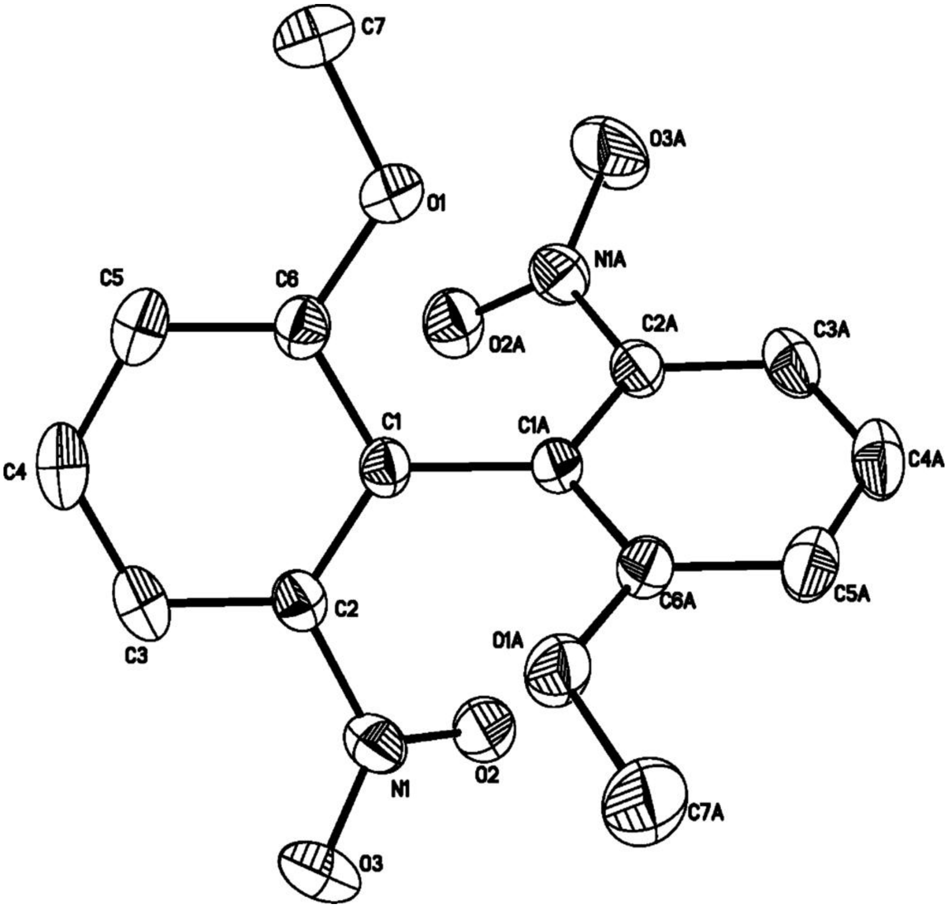

C7
O3A
O1
N1A
C5
C6
C2A
C3A
O2A
C1
C1A
C4
C4A
C2
C6A
C5A
C3
O1A
N1
O2
C7A
O3

Fig. 2