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Bis(2,4-Dinitrophenyl)amine

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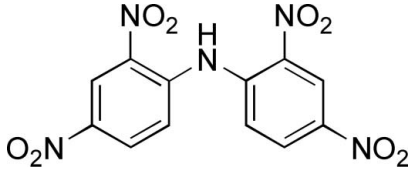
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.002 Å; R factor = 0.046; wR factor = 0.135; data-to-parameter ratio = 12.1.

In the title compound, $C_{12}H_7N_5O_8$, the dihedral angle between the two benzene rings is 56.3 (2)°. The crystal packing is stabilized by intramolecular N—H···O and intermolecular C—H···O hydrogen bonds.

Related literature

For general background, see Elliot & Smith (2000); Espinoza & Thornton (1994); Farrell *et al.* (1985); Chattanathan & Kalidas (1971); Southgate & Hall (1971); Stewart & O'Donnell (1964). For reference bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{12}H_7N_5O_8$
M_r = 349.23
Monoclinic, $P2_1/n$
a = 8.4987 (9) Å
b = 14.7982 (15) Å
c = 11.1828 (12) Å
β = 95.395 (1)°
V = 1400.2 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.14 mm^{-1}
T = 291 (2) K
0.36 × 0.32 × 0.28 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.953, T_{max} = 0.964
7449 measured reflections
2745 independent reflections
2384 reflections with $I > 2\sigma(I)$
R_{int} = 0.085

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.135
S = 1.01
2745 reflections
227 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5′···O1	0.87	2.09	2.6853 (18)	125
N5—H5′···O5	0.87	2.06	2.6321 (19)	123
C6—H6···O8^{i}	0.93	2.54	3.464 (2)	170
C11—H11···O2^{ii}	0.93	2.44	3.144 (2)	132

Symmetry codes: (i) $-x+1, -y+2, -z$; (ii) $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2406).

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supplementary materials

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Bis(2,4-Dinitrophenyl)amine

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Comment

The title compound, (I), is a derivative of nitrodiphenylamines which were used in nonlinear optical materials (Southgate & Hall, 1971). They were known as stabilizers incorporated into propellant formulations and smokeless gunpowder (Elliot & Smith, 2000; Espinoza & Thornton, 1994). And they were acted as indicators to study the H acidity function in ethylene and propylene glycols (Chattanathan & Kalidas, 1971). Their structure–acidity correlation test indicated that the effect of substituents on the acidity of diphenylamines (Stewart & O'Donnell 1964). Simultaneously, the study on the effects of solvation upon the acidities of nitroaromatics shows that the nitrobenzyl anions are suggested to be essentially charge-delocalized (Farrell *et al.*, 1985).

The bond lengths and angles in (I) (Table 1) are in good agree with expected values (Allen *et al.*, 1987). The dihedral angle between the two benzene rings is 56.3 (2)°. The packing is stabilized by intramolecular N—H···O and intermolecular C—H···O interactions in the crystal structure (Table 2).

Experimental

2,4-Dinitroaniline (0.183 g, 1 mmol) was added to a solution of 1-chloro-2,4-dinitrobenzene (0.202 g, 1 mmol) in DMF (2 ml). The resulting solution was applied to a column of basic alumina (5 g) with DMF (20 ml) as eluent. The dark red eluent was concentrated and dissolved in acetone (15 ml). Crude product was obtained by the addition of water (20 ml). Recrystallization from glacial acetic acid (8 ml) furnished the title compound (I) as yellow needles (2.41 g), in yield of 67.5%. Single crystals of (I) were obtained by slow evaporation from a petroleum ether–ethyl acetate (2:1 *v*/*v*) solution system.

Refinement

The H atoms were geometrically placed and were treated as riding, with C—H = 0.93 Å, N—H = 0.87 Å, and with U_{iso}(H) = 1.2U_{eq}(C) or 1.6U_{eq}(N).

Figures

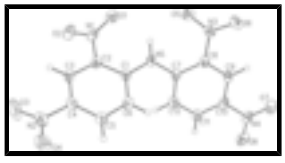


Fig. 1. The molecular structure of (I), with atom labels and 30% probability displacement ellipsoids for non-H atoms.

Bis(2,4-Dinitrophenyl)amine

Crystal data

$C_{12}H_7N_5O_8$	F_{000} = 712
M_r = 349.23	D_x = 1.657 Mg m^{-3}
Monoclinic, $P2_1/n$	Melting point: 472.2 K
Hall symbol: -P 2yn	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 8.4987 (9) Å	Cell parameters from 4779 reflections
b = 14.7982 (15) Å	θ = 2.3–28.1º
c = 11.1828 (12) Å	μ = 0.14 mm^{-1}
β = 95.3950 (10)º	T = 291 (2) K
V = 1400.2 (3) Å^3	Block, orange
Z = 4	0.36 × 0.32 × 0.28 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	2745 independent reflections
Radiation source: sealed tube	2384 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.085
T = 291(2) K	θ_{max} = 26.0º
φ and ω scans	θ_{min} = 2.3º
Absorption correction: multi-scan (SADABS; Bruker, 2000)	h = −10→10
T_{min} = 0.953, T_{max} = 0.964	k = −18→18
7449 measured reflections	l = −5→13

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.046	H-atom parameters constrained
$wR(F^2)$ = 0.135	$w = 1/[\sigma^2(F_o^2) + (0.0813P)^2 + 0.2007P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.01	$(\Delta/\sigma)_{max} < 0.001$
2745 reflections	$\Delta\rho_{max}$ = 0.19 e Å^{-3}
227 parameters	$\Delta\rho_{min}$ = −0.36 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 $F^2 > 2\text{sigma}(F^2)$ 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	0.24828 (18)	0.90522 (9)	0.39789 (12)	0.0352 (3)
C2	0.18191 (17)	0.85746 (9)	0.48995 (12)	0.0345 (3)
C3	0.27475 (19)	0.81680 (9)	0.58238 (12)	0.0383 (3)
H3	0.2293	0.7842	0.6414	0.046*
C4	0.43599 (19)	0.82557 (9)	0.58523 (13)	0.0397 (3)
C5	0.5073 (2)	0.87074 (10)	0.49629 (14)	0.0427 (4)
H5	0.6167	0.8750	0.4992	0.051*
C6	0.4129 (2)	0.90907 (10)	0.40393 (14)	0.0417 (4)
H6	0.4602	0.9387	0.3432	0.050*
C7	0.19498 (17)	0.96538 (9)	0.19386 (12)	0.0355 (3)
C8	0.14268 (17)	1.04179 (9)	0.12616 (12)	0.0351 (3)
C9	0.18928 (18)	1.05794 (10)	0.01239 (13)	0.0385 (3)
H9	0.1571	1.1100	−0.0297	0.046*
C10	0.28348 (18)	0.99575 (10)	−0.03651 (12)	0.0390 (3)
C11	0.3306 (2)	0.91681 (11)	0.02370 (14)	0.0424 (4)
H11	0.3903	0.8739	−0.0127	0.051*
C12	0.2881 (2)	0.90291 (10)	0.13758 (14)	0.0412 (4)
H12	0.3219	0.8507	0.1786	0.049*
N1	0.01119 (16)	0.84928 (9)	0.49229 (11)	0.0415 (3)
N2	0.5346 (2)	0.78806 (11)	0.68694 (13)	0.0556 (4)
N3	0.03468 (16)	1.10760 (9)	0.17095 (12)	0.0426 (3)
N4	0.33458 (17)	1.01266 (11)	−0.15575 (12)	0.0480 (4)
N5	0.15513 (16)	0.95046 (9)	0.30872 (11)	0.0412 (3)
H5'	0.0696	0.9737	0.3334	0.066 (6)*
O1	−0.07352 (14)	0.91080 (9)	0.45042 (11)	0.0538 (3)
O2	−0.03902 (16)	0.78209 (9)	0.53913 (13)	0.0649 (4)
O3	0.4751 (2)	0.73510 (14)	0.75172 (17)	0.1018 (7)
O4	0.67277 (18)	0.81174 (12)	0.70251 (14)	0.0761 (5)
O5	−0.04027 (15)	1.08548 (9)	0.25453 (11)	0.0536 (3)
O6	0.0202 (2)	1.18043 (9)	0.12207 (15)	0.0749 (5)
O7	0.2970 (2)	1.08398 (12)	−0.20501 (13)	0.0772 (5)
O8	0.41639 (18)	0.95593 (10)	−0.19853 (11)	0.0632 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0474 (8)	0.0319 (7)	0.0264 (6)	−0.0017 (5)	0.0039 (6)	−0.0020 (5)
C2	0.0440 (8)	0.0324 (6)	0.0275 (6)	−0.0054 (5)	0.0054 (6)	−0.0050 (5)
C3	0.0558 (9)	0.0319 (7)	0.0275 (6)	−0.0034 (6)	0.0062 (6)	−0.0006 (5)
C4	0.0515 (9)	0.0342 (7)	0.0324 (7)	0.0051 (6)	−0.0013 (6)	−0.0045 (6)
C5	0.0440 (8)	0.0432 (8)	0.0408 (8)	−0.0011 (6)	0.0033 (6)	−0.0060 (6)
C6	0.0482 (9)	0.0434 (8)	0.0344 (7)	−0.0064 (6)	0.0090 (6)	0.0019 (6)
C7	0.0428 (8)	0.0357 (7)	0.0275 (7)	−0.0047 (6)	0.0011 (6)	0.0001 (5)
C8	0.0390 (7)	0.0362 (7)	0.0294 (7)	−0.0020 (6)	−0.0001 (6)	−0.0011 (5)
C9	0.0431 (8)	0.0404 (7)	0.0311 (7)	−0.0038 (6)	−0.0019 (6)	0.0061 (6)
C10	0.0442 (8)	0.0475 (8)	0.0251 (7)	−0.0087 (6)	0.0023 (6)	−0.0011 (6)
C11	0.0510 (9)	0.0413 (7)	0.0352 (8)	−0.0013 (6)	0.0062 (7)	−0.0066 (6)
C12	0.0547 (9)	0.0341 (7)	0.0347 (8)	0.0012 (6)	0.0039 (7)	0.0007 (6)
N1	0.0474 (7)	0.0477 (7)	0.0298 (6)	−0.0099 (6)	0.0059 (5)	−0.0071 (5)
N2	0.0664 (10)	0.0524 (8)	0.0458 (8)	0.0117 (7)	−0.0061 (7)	0.0016 (7)
N3	0.0446 (7)	0.0440 (7)	0.0384 (7)	0.0043 (5)	−0.0002 (6)	0.0005 (6)
N4	0.0500 (8)	0.0640 (9)	0.0299 (7)	−0.0103 (7)	0.0035 (6)	0.0004 (6)
N5	0.0486 (7)	0.0463 (7)	0.0292 (6)	0.0050 (6)	0.0069 (5)	0.0061 (5)
O1	0.0453 (7)	0.0685 (8)	0.0477 (7)	0.0023 (6)	0.0055 (5)	−0.0006 (6)
O2	0.0664 (8)	0.0640 (8)	0.0658 (8)	−0.0275 (7)	0.0140 (7)	0.0067 (7)
O3	0.1026 (13)	0.1026 (13)	0.0942 (13)	−0.0066 (11)	−0.0224 (10)	0.0621 (11)
O4	0.0589 (9)	0.0992 (12)	0.0659 (9)	0.0112 (8)	−0.0170 (7)	−0.0015 (8)
O5	0.0555 (7)	0.0629 (7)	0.0441 (7)	0.0117 (6)	0.0137 (6)	−0.0005 (5)
O6	0.0939 (11)	0.0520 (8)	0.0818 (10)	0.0279 (7)	0.0238 (9)	0.0236 (7)
O7	0.0902 (11)	0.0960 (11)	0.0474 (8)	0.0149 (9)	0.0177 (7)	0.0318 (8)
O8	0.0791 (9)	0.0717 (8)	0.0420 (7)	−0.0090 (7)	0.0234 (6)	−0.0128 (6)

Geometric parameters (Å, °)

C1—N5	1.386 (2)	C9—C10	1.367 (2)
C1—C6	1.396 (2)	C9—H9	0.9300
C1—C2	1.4095 (19)	C10—C11	1.389 (2)
C2—C3	1.378 (2)	C10—N4	1.4623 (18)
C2—N1	1.459 (2)	C11—C12	1.372 (2)
C3—C4	1.374 (2)	C11—H11	0.9300
C3—H3	0.9300	C12—H12	0.9300
C4—C5	1.384 (2)	N1—O2	1.2196 (18)
C4—N2	1.457 (2)	N1—O1	1.2260 (19)
C5—C6	1.369 (2)	N2—O3	1.210 (2)
C5—H5	0.9300	N2—O4	1.222 (2)
C6—H6	0.9300	N3—O6	1.2094 (19)
C7—N5	1.3766 (18)	N3—O5	1.2240 (18)
C7—C12	1.404 (2)	N4—O8	1.2163 (19)
C7—C8	1.409 (2)	N4—O7	1.219 (2)
C8—C9	1.388 (2)	N5—H5'	0.8718
C8—N3	1.4590 (19)		

N5—C1—C6	121.15 (13)	C8—C9—H9	120.7
N5—C1—C2	121.81 (14)	C9—C10—C11	121.70 (13)
C6—C1—C2	116.96 (14)	C9—C10—N4	119.01 (14)
C3—C2—C1	121.77 (14)	C11—C10—N4	119.29 (14)
C3—C2—N1	116.78 (12)	C12—C11—C10	119.16 (14)
C1—C2—N1	121.45 (13)	C12—C11—H11	120.4
C4—C3—C2	118.40 (13)	C10—C11—H11	120.4
C4—C3—H3	120.8	C11—C12—C7	121.76 (14)
C2—C3—H3	120.8	C11—C12—H12	119.1
C3—C4—C5	122.13 (14)	C7—C12—H12	119.1
C3—C4—N2	118.75 (14)	O2—N1—O1	123.57 (14)
C5—C4—N2	119.11 (15)	O2—N1—C2	117.65 (14)
C6—C5—C4	118.51 (15)	O1—N1—C2	118.75 (12)
C6—C5—H5	120.7	O3—N2—O4	123.38 (16)
C4—C5—H5	120.7	O3—N2—C4	118.19 (17)
C5—C6—C1	122.18 (14)	O4—N2—C4	118.43 (16)
C5—C6—H6	118.9	O6—N3—O5	123.06 (15)
C1—C6—H6	118.9	O6—N3—C8	118.69 (14)
N5—C7—C12	120.75 (13)	O5—N3—C8	118.23 (13)
N5—C7—C8	122.49 (13)	O8—N4—O7	123.72 (14)
C12—C7—C8	116.75 (13)	O8—N4—C10	118.06 (14)
C9—C8—C7	121.85 (14)	O7—N4—C10	118.19 (15)
C9—C8—N3	116.27 (13)	C7—N5—C1	125.08 (13)
C7—C8—N3	121.87 (13)	C7—N5—H5'	121.2
C10—C9—C8	118.61 (14)	C1—N5—H5'	113.5
C10—C9—H9	120.7		
N5—C1—C2—C3	−176.25 (13)	C10—C11—C12—C7	1.6 (2)
C6—C1—C2—C3	0.4 (2)	N5—C7—C12—C11	−179.32 (15)
N5—C1—C2—N1	3.3 (2)	C8—C7—C12—C11	2.0 (2)
C6—C1—C2—N1	179.98 (12)	C3—C2—N1—O2	−29.46 (18)
C1—C2—C3—C4	1.6 (2)	C1—C2—N1—O2	150.96 (14)
N1—C2—C3—C4	−177.94 (12)	C3—C2—N1—O1	148.60 (14)
C2—C3—C4—C5	−2.5 (2)	C1—C2—N1—O1	−30.98 (19)
C2—C3—C4—N2	175.88 (13)	C3—C4—N2—O3	15.0 (2)
C3—C4—C5—C6	1.2 (2)	C5—C4—N2—O3	−166.57 (17)
N2—C4—C5—C6	−177.18 (14)	C3—C4—N2—O4	−164.90 (16)
C4—C5—C6—C1	1.0 (2)	C5—C4—N2—O4	13.5 (2)
N5—C1—C6—C5	174.90 (14)	C9—C8—N3—O6	−16.4 (2)
C2—C1—C6—C5	−1.8 (2)	C7—C8—N3—O6	164.47 (16)
N5—C7—C8—C9	177.20 (13)	C9—C8—N3—O5	161.71 (14)
C12—C7—C8—C9	−4.2 (2)	C7—C8—N3—O5	−17.4 (2)
N5—C7—C8—N3	−3.7 (2)	C9—C10—N4—O8	−178.92 (15)
C12—C7—C8—N3	174.86 (13)	C11—C10—N4—O8	0.6 (2)
C7—C8—C9—C10	2.6 (2)	C9—C10—N4—O7	3.3 (2)
N3—C8—C9—C10	−176.46 (13)	C11—C10—N4—O7	−177.19 (16)
C8—C9—C10—C11	1.2 (2)	C12—C7—N5—C1	31.8 (2)
C8—C9—C10—N4	−179.33 (13)	C8—C7—N5—C1	−149.61 (14)
C9—C10—C11—C12	−3.3 (2)	C6—C1—N5—C7	32.3 (2)

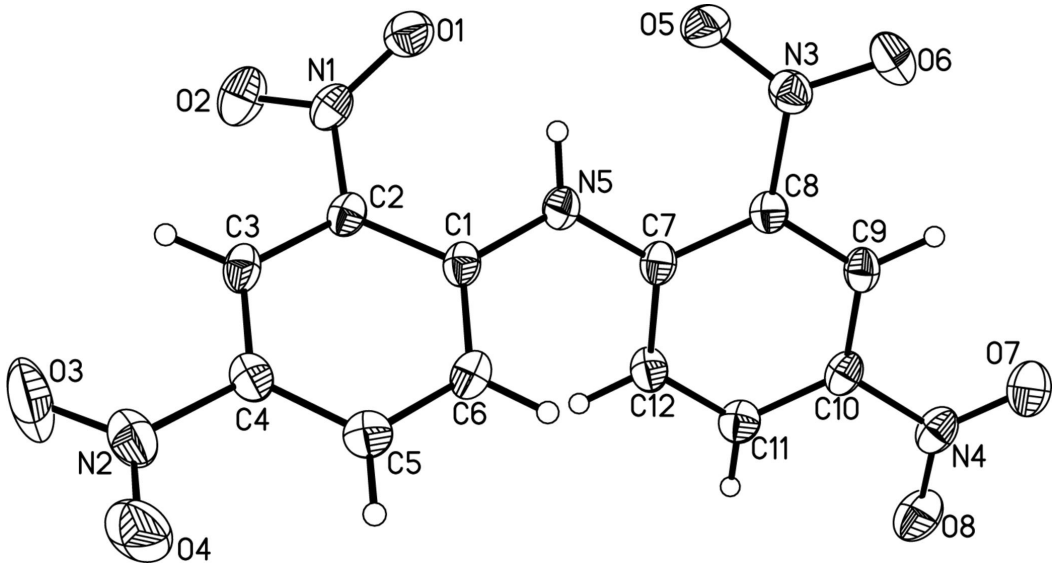
N4—C10—C11—C12	177.26 (14)	C2—C1—N5—C7	−151.20 (14)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5'···O1	0.87	2.09	2.6853 (18)	125
N5—H5'···O5	0.87	2.06	2.6321 (19)	123
C6—H6···O8^{i}	0.93	2.54	3.464 (2)	170
C11—H11···O2^{ii}	0.93	2.44	3.144 (2)	132

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

Fig. 1


O1
N1
O2
O5
N3
O6
N5
C2
C8
C3
C1
C7
C9
O3
O7
C4
C6
C12
C10
N2
C5
C11
N4
O4
O8