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trans-Diphenyldiazene oxide

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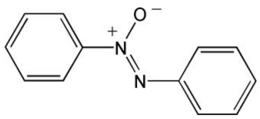
Key indicators: single-crystal X-ray study; T = 299 K; mean σ(C–C) = 0.004 Å; disorder in main residue; R factor = 0.055; wR factor = 0.156; data-to-parameter ratio = 12.0.

The crystal structure of the title compound (common name: *trans*-azoxybenzene, *t*-AXB), $C_{12}H_{10}N_2O$, was determined at 299 ± 0.5 K, *i.e.* 6 K below its melting point. The azoxy group has the expected geometry, and the O atom is affected by libration normal to the N=N—O plane. The O atom is disordered over two positions; the site-occupancy ratio is ~3:2. Phenyl rings are out of the NNO plane, with dihedral angles ranging from 20 (1) to 34 (1)°. The dihedral angle between the two phenyl rings is 46.19 (11)°. This geometry contrasts strongly with the gas-phase conformation of *t*-AXB, previously determined by electron diffraction combined with *ab initio* calculations, which showed that the stable conformation is planar. This discrepancy is, however, consistent with low rotational barriers for phenyl rings. These features could be of interest in relation to the actual reaction mechanism of the Wallach rearrangement (acid-catalyzed isomerization of *t*-AXB into 4-hydroxyazobenzene), which remains a controversial matter.

Related literature

The vibrational spectra of the title molecule have been analyzed (Gruger & Le Calvé, 1972). Preliminary X-ray data were reported by Herrington & Bernard (1966) and the molecular structure in the gas-phase was established on the basis of gas-phase electron diffraction studies combined with *ab initio* calculations (Tsuji *et al.*, 2000). Two coordination complexes including the title molecule have been structurally characterized (Bassi & Scordamaglia, 1975; Cambie *et al.*, 1996). For structures of *para*-substituted azoxybenzenes, see: Ejsmont *et al.* (2000, 2002, 2004, 2005); Domański *et al.* (2001).



Experimental

Crystal data

$C_{12}H_{10}N_2O$
M_r = 198.22
Monoclinic, $P2_1/n$
a = 5.844 (3) Å
b = 15.864 (7) Å
c = 11.073 (5) Å
β = 103.30 (4)°
V = 998.9 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 299 (1) K
0.60 × 0.20 × 0.16 mm

Data collection

Siemens *P*4 diffractometer
Absorption correction: none
4750 measured reflections
1746 independent reflections
1034 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.115
2 standard reflections
every 48 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.156
S = 1.05
1746 reflections
145 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.16 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.15 e Å^{-3}

Data collection: *XSCANS* (Siemens, 1999); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2265).

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supplementary materials

Acta Cryst. (2007). E**63**, o3639 [**doi:10.1107/S1600536807035787**]

***trans*-Diphenyldiazene oxide**

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Comment

The title molecule, (I), has been structurally characterized using a variety of techniques, *e.g.* IR and Raman spectroscopy (Gruger & Le Calvé, 1972), or gas electron diffraction combined with *ab initio* calculations (Tsuji *et al.*, 2000). However, the X-ray structure has not been determined so far, probably because of the low melting point of this compound, 305–309 K. A preliminary study about space group determination, $P2_1/a$ was done by Herrington & Bernard (1966). This reference is however not quoted in the CSD (Version 5.28, updated May 2007).

Two complexes including (I) as ligand are reported, with W^{VI} (Bassi & Scordamaglia, 1975) and Ru^{I} (Cambie *et al.*, 1996). In both complexes, azoxybenzene is found in an almost planar conformation, the dihedral angle between phenyl rings being 13.2 and 7.4°, respectively. The same conformation has been observed in derivatives of (I) including a *para*-substituted phenyl ring (Ejsmont *et al.*, 2000, 2002, 2004, 2005 Domański *et al.*, 2001). Non-planar conformations have been observed *e.g.* in the case of *trans*-4-aminoazoxybenzene: the α isomer is stabilized in a planar (2.6°) conformation at 293 K (Domański *et al.*, 2001) but is twisted [43.7 (1)°] at 90 K (Ejsmont *et al.*, 2002). A similar flexible behavior is described for the β isomer.

Unexpectedly, the title molecule is found to belong to non-planar azoxybenzene family. The dihedral angle between phenyl rings is 46.19 (11)° (Fig. 1), while electron diffraction studies showed that the molecule is stabilized in a planar conformation in the gas phase. This difference confirms that rotational barriers for phenyl rings in (I) are low (Tsuji *et al.*, 2000). Such a flexibility may be of interest regarding the actual mechanism of the Wallach rearrangement [acid-catalyzed isomerization of (I) into 4-hydroxyazobenzene], which still remains controversial, despite of a number of experimental evidences.

Otherwise, the geometry of (I) is as expected, for example for the central azoxy functionality, with bond lengths and angles similar to those found in above cited derivatives. A feature deserves however to be commented, regarding the O atom, which is disordered over two sites. This disorder seems to be a consequence of a libration motion normal to the N═N—O plane for this atom, which, in turn, may be related with the low melting point of this molecule.

Experimental

A sample of (I) was donated by the Chemistry Stores at Universidad Autónoma de Nuevo León, and recrystallized from ethanol. Batch used for X-ray crystallography was checked by I·*R*. spectroscopy (solid sample, cm^{-1}): ν(N═N) = 1436, ν (N—O) = 1328 (assignation follows studies published by Gruger & Le Calvé, 1972).

Refinement

Single crystals systematically decomposed on contact with all available glues we attempted. A single-crystal was then transferred in a capillary tube, and data collected without special precautions regarding the atmosphere around the sample. Data collection was carried out avoiding continuous irradiation, by closing the shutter during dead times. Azoxy O atom is disordered over two sites, O1A and O1B, with fixed site occupancies 0.6 and 0.4, respectively. All H atoms were placed in idealized positions, and refined using a riding model approximation, with C—H bond lengths constrained to 0.97 Å and isotropic displacement parameters set to $U_{\rm iso}$(H) = 1.2 $U_{\rm eq}$(carrier C).

Figures

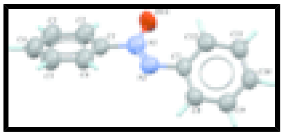

Fig. 1. The structure of (I), with displacement ellipsoids at the 50% probability level. Atom O1B, disordered with O1A, has been omitted for clarity.

trans-Diphenyldiazene oxide

Crystal data

$C_{12}H_{10}N_2O$

M_r = 198.22

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

a = 5.844 (3) Å

b = 15.864 (7) Å

c = 11.073 (5) Å

β = 103.30 (4)°

V = 998.9 (8) Å^3

Z = 4

F_{000} = 416

D_x = 1.318 Mg m^{-3}

Melting point: 305-309 K

Mo $K\alpha$ radiation
λ = 0.71073 Å

Cell parameters from 68 reflections

θ = 4.5–12.0°

μ = 0.09 mm^{-1}

T = 299 (1) K

Needle, yellow

0.60 × 0.20 × 0.16 mm

Data collection

Siemens P4
diffractometer

Monochromator: graphite

T = 299(1) K

ω scans

Absorption correction: none

4750 measured reflections

1746 independent reflections

1034 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.115

$\theta_{\rm max}$ = 25.1°

$\theta_{\rm min}$ = 2.3°

$h = -6 \rightarrow 6$

$k = -17 \rightarrow 18$

$l = -13 \rightarrow 13$

2 standard reflections

every 48 reflections

intensity decay: 1%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.055

$wR(F^2)$ = 0.156

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.043P)^2 + 0.2419P]$

	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
1746 reflections	$\Delta\rho_{max} = 0.16$ e Å^{-3}
145 parameters	$\Delta\rho_{min} = -0.15$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1A	−0.0378 (16)	0.4162 (9)	0.5903 (12)	0.080 (3)	0.60
O1B	−0.015 (3)	0.3914 (15)	0.6080 (18)	0.109 (7)	0.40
N1	0.1816 (4)	0.42455 (16)	0.6174 (2)	0.0637 (7)	
N2	0.3345 (4)	0.39334 (15)	0.5698 (2)	0.0634 (7)	
C1	0.2717 (5)	0.48817 (17)	0.7134 (3)	0.0566 (7)	
C2	0.1399 (6)	0.50318 (19)	0.7979 (3)	0.0713 (9)	
H2	−0.0068	0.4734	0.7936	0.086*	
C3	0.2203 (6)	0.5616 (2)	0.8893 (3)	0.0805 (10)	
H3	0.1325	0.5713	0.9525	0.097*	
C4	0.4186 (6)	0.6056 (2)	0.8930 (3)	0.0819 (10)	
H4	0.4712	0.6475	0.9573	0.098*	
C5	0.5464 (6)	0.5911 (2)	0.8052 (3)	0.0792 (9)	
H5	0.6882	0.6232	0.8067	0.095*	
C6	0.4729 (5)	0.53096 (18)	0.7152 (3)	0.0663 (8)	
H6	0.5638	0.5194	0.6539	0.080*	
C7	0.2709 (5)	0.32809 (17)	0.4804 (2)	0.0551 (7)	
C8	0.4621 (5)	0.28069 (19)	0.4705 (3)	0.0621 (8)	
H8	0.6153	0.2926	0.5236	0.075*	
C9	0.4369 (5)	0.2169 (2)	0.3863 (3)	0.0658 (8)	
H9	0.5719	0.1826	0.3815	0.079*	
C10	0.2243 (5)	0.20073 (18)	0.3086 (3)	0.0627 (8)	
H10	0.2077	0.1550	0.2490	0.075*	
C11	0.0350 (5)	0.24936 (18)	0.3153 (3)	0.0645 (8)	
H11	−0.1155	0.2389	0.2586	0.077*	
C12	0.0550 (5)	0.31344 (18)	0.4019 (3)	0.0615 (7)	
H12	−0.0804	0.3474	0.4071	0.074*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1A	0.041 (3)	0.096 (7)	0.101 (4)	−0.014 (3)	0.011 (3)	−0.035 (4)
O1B	0.114 (11)	0.106 (13)	0.140 (11)	−0.055 (9)	0.094 (10)	−0.062 (9)
N1	0.0650 (16)	0.0607 (15)	0.0694 (16)	−0.0037 (13)	0.0234 (13)	0.0043 (13)
N2	0.0612 (14)	0.0642 (15)	0.0664 (14)	0.0049 (13)	0.0179 (12)	0.0031 (13)
C1	0.0650 (16)	0.0479 (15)	0.0564 (16)	−0.0003 (14)	0.0125 (14)	0.0005 (14)
C2	0.0797 (19)	0.0635 (19)	0.077 (2)	−0.0014 (17)	0.0313 (17)	−0.0041 (17)
C3	0.096 (2)	0.076 (2)	0.076 (2)	0.004 (2)	0.033 (2)	−0.0108 (19)
C4	0.094 (2)	0.068 (2)	0.081 (2)	0.002 (2)	0.014 (2)	−0.0191 (18)

C5	0.079 (2)	0.069 (2)	0.090 (2)	−0.0103 (17)	0.0196 (19)	−0.0081 (19)
C6	0.0767 (19)	0.0585 (18)	0.0676 (18)	−0.0028 (15)	0.0247 (16)	−0.0053 (16)
C7	0.0698 (17)	0.0515 (16)	0.0449 (14)	−0.0079 (14)	0.0150 (13)	−0.0028 (13)
C8	0.0591 (16)	0.0658 (19)	0.0599 (16)	−0.0018 (15)	0.0105 (14)	−0.0029 (16)
C9	0.0684 (18)	0.0688 (19)	0.0629 (17)	0.0038 (16)	0.0205 (16)	−0.0032 (16)
C10	0.0743 (18)	0.0572 (18)	0.0568 (16)	−0.0059 (16)	0.0157 (15)	−0.0073 (14)
C11	0.0696 (18)	0.0638 (18)	0.0570 (16)	−0.0062 (15)	0.0083 (14)	−0.0020 (15)
C12	0.0659 (17)	0.0625 (18)	0.0568 (16)	0.0046 (15)	0.0156 (14)	0.0051 (15)

Geometric parameters (Å, °)

O1A—N1	1.255 (10)	C5—H5	0.9700
O1B—N1	1.243 (18)	C6—H6	0.9700
N1—N2	1.240 (3)	C7—C8	1.372 (4)
N1—C1	1.473 (4)	C7—C12	1.378 (4)
N2—C7	1.421 (3)	C8—C9	1.361 (4)
C1—C6	1.354 (4)	C8—H8	0.9700
C1—C2	1.363 (4)	C9—C10	1.363 (4)
C2—C3	1.373 (5)	C9—H9	0.9700
C2—H2	0.9700	C10—C11	1.364 (4)
C3—C4	1.346 (5)	C10—H10	0.9700
C3—H3	0.9700	C11—C12	1.384 (4)
C4—C5	1.375 (5)	C11—H11	0.9700
C4—H4	0.9700	C12—H12	0.9700
C5—C6	1.374 (4)		

N2—N1—O1B	122.4 (10)	C1—C6—C5	118.9 (3)
N2—N1—O1A	130.7 (6)	C1—C6—H6	120.5
N2—N1—C1	114.0 (2)	C5—C6—H6	120.5
O1B—N1—C1	121.3 (9)	C8—C7—C12	120.1 (3)
O1A—N1—C1	114.9 (6)	C8—C7—N2	111.6 (3)
N1—N2—C7	119.2 (2)	C12—C7—N2	128.1 (3)
C6—C1—C2	121.9 (3)	C9—C8—C7	120.0 (3)
C6—C1—N1	121.3 (3)	C9—C8—H8	120.0
C2—C1—N1	116.8 (3)	C7—C8—H8	120.0
C1—C2—C3	118.2 (3)	C8—C9—C10	120.8 (3)
C1—C2—H2	120.9	C8—C9—H9	119.6
C3—C2—H2	120.9	C10—C9—H9	119.6
C4—C3—C2	121.3 (3)	C9—C10—C11	119.5 (3)
C4—C3—H3	119.4	C9—C10—H10	120.3
C2—C3—H3	119.4	C11—C10—H10	120.3
C3—C4—C5	119.7 (3)	C10—C11—C12	120.8 (3)
C3—C4—H4	120.2	C10—C11—H11	119.6
C5—C4—H4	120.2	C12—C11—H11	119.6
C6—C5—C4	120.0 (3)	C7—C12—C11	118.7 (3)
C6—C5—H5	120.0	C7—C12—H12	120.6
C4—C5—H5	120.0	C11—C12—H12	120.6

O1B—N1—N2—C7	13.5 (13)	C2—C1—C6—C5	0.2 (5)
O1A—N1—N2—C7	−10.0 (10)	N1—C1—C6—C5	178.5 (3)
C1—N1—N2—C7	176.8 (2)	C4—C5—C6—C1	1.4 (5)

N2—N1—C1—C6	23.9 (4)	N1—N2—C7—C8	−158.1 (3)
O1B—N1—C1—C6	−172.6 (13)	N1—N2—C7—C12	27.2 (4)
O1A—N1—C1—C6	−150.4 (8)	C12—C7—C8—C9	−2.5 (4)
N2—N1—C1—C2	−157.7 (3)	N2—C7—C8—C9	−177.7 (2)
O1B—N1—C1—C2	5.8 (13)	C7—C8—C9—C10	1.8 (4)
O1A—N1—C1—C2	28.0 (8)	C8—C9—C10—C11	0.3 (4)
C6—C1—C2—C3	−2.2 (5)	C9—C10—C11—C12	−1.6 (4)
N1—C1—C2—C3	179.4 (3)	C8—C7—C12—C11	1.2 (4)
C1—C2—C3—C4	2.7 (5)	N2—C7—C12—C11	175.5 (2)
C2—C3—C4—C5	−1.2 (5)	C10—C11—C12—C7	0.9 (4)
C3—C4—C5—C6	−0.9 (5)		

Fig. 1