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6,6-Diisopropyl-3,3′-dimethyl-2,2′-azinodiphenol

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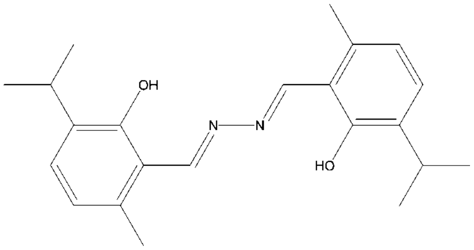
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.059; wR factor = 0.181; data-to-parameter ratio = 15.3.

In the centrosymmetric title compound, $C_{22}H_{28}N_2O_2$, the H atom of the phenol OH group forms a strong intramolecular O—H···N hydrogen bond, with an O···N distance of 2.578 (2) Å, which is in the middle of the expected range for such hydrogen bonds.

Related literature

For related literature, see: Kumbhar & Dewang (2001); Pelizzi & Pelizzi (1980); Rastogi *et al.* (1979); Satapathy & Sahoo (1970); Sinn & Harris (1969); Yamada *et al.* (1968).



Experimental

Crystal data

$C_{22}H_{28}N_2O_2$
M_r = 352.46
Monoclinic, $P2_1/n$
a = 11.925 (2) Å
b = 6.0622 (12) Å
c = 14.152 (2) Å
β = 98.763 (10)°

V = 1011.2 (3) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 0.58 mm^{-1}
T = 293 (2) K
0.60 × 0.55 × 0.10 mm

Data collection

Bruker *P*4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.330, T_{max} = 0.758 (expected range = 0.411–0.943)
1958 measured reflections

1869 independent reflections
1507 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
3 standard reflections every 97 reflections intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.181
S = 1.06
1869 reflections

122 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.10 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O—H1O···N	0.82	1.85	2.578 (2)	148

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

RJB acknowledges the Laboratory for the Structure of Matter at the Naval Research Laboratory for access to their diffractometers.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2250).

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supplementary materials

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6,6-Diisopropyl-3,3'-dimethyl-2,2'-azinodiphenol

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Comment

Hydrazides have interesting ligational properties due to presence of several potential coordination sites and transitional metal complexes of this ligand have been studied (Rastogi *et al.*, 1979; Pelizzi & Pelizzi, 1980). Selection of the title compound was based on its broad spectrum activity and important role in plants as well as natural occurrence of the parent compound thymol (2-hydroxy-3-isopropyl-6-methylbenzene) (Kumbhar & Dewang, 2001). Hydrazones are a class of compounds obtained by condensation of aldehyde or ketone with appropriate amines. The types of hydrazone produced depend upon the amines used and may include simple amines like aniline or hydrazine. When the terminal NH_2 group is condensed with aldehydes or ketones, the proton of NH group become more labile and acyl hydrazones react with metal ions in the enol form (Satapathy & Sahoo, 1970; Yamada *et al.*, 1968; Sinn & Harris, 1969).

Elemental analysis of title compound gave a satisfactory fit to the formula $C_{22}H_{28}N_2O_2$. Table 1 contains selected bond lengths and angles. Views of the molecule and unit-cell contents are shown in Figs 1 and 2 respectively.

Hydrogen bonding is major feature of the structure of phenolic hydrazines. Invariably, the phenolic H atom forms an intramolecular hydrogen bond to the N atom of hydrazine group, giving a six membered ring. This interaction is usually characterized in terms of phenolic O to hydrazine N separation. This distance varies little between structures, with maximum value of 2.65 Å and minimum of 2.51 Å. In all free ligand structures, the molecules associate *via* intramolecular hydrogen bonding.

The structure of the title compound $C_{22}H_{28}N_2O_2$ exhibits intramolecular hydrogen bonding (Table 2) where the H atom of the phenolic hydroxyl group forms a strong O—H······N intramolecular hydrogen bond with an O···N distance 2.578 (2)Å which is in the middle of expected range of such hydrogen bonds.

Experimental

A solution of hydrazine hydrate (0.001 *M*) was added to a solution 2-formyl thymol (0.002 *M*) in ethanol (50 ml) and mixture was heated on a water bath for 8 hr. Yellow crystals deposited at room temperature which were filtered and recrystallized from ethanol, (yield 83%). Yellow crystals suitable for *x*- ray diffraction were obtained.

Elemental analysis - Found (cal) C − 75.15 (74.96), H − 8.76 (8.33), N − 7.64 (7.97). IR (KBr, cm $^{-1}$) 3420 (–OH), 1600 (–C=N–). NMR- ($CDCl_3$, dppm)- 1.22 (d, 12H, gem CH_3), 2.37 (S, 6H, Ar- CH_3) 3.33 {(heptane, 2H, CH)}, 6.68–7.110 (d, 4H, Ar—H), 9.1 (S, 2H, CH=N).

Refinement

The H atoms were idealized with an O—H distance of 0.82 and C—H distances of 0.93 (aromatic C—H), 0.96 (CH_3), and 0.98 (CH) Å and $U_{iso}(H) = 1.2U_{eq}(C)$ ($1.5U_{eq}(C)$ for the CH_3 protons).

Figures

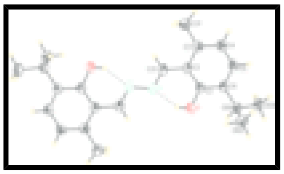

Fig. 1. The title compound with numbering scheme used. Hydrogen bonding interactions shown as dotted lines. Ellipsoids are drawn at the 20% probabilty level.

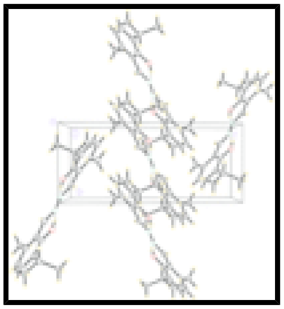

Fig. 2. The packing arrangement viewed down the *a* axis showing the intramolecular N—H···O hydrogen bonding interactions (dashed bonds).

6,6-Diisopropyl-3,3′-dimethyl-2,2′-azinodiphenol

Crystal data

$C_{22}H_{28}N_2O_2$
$M_r = 352.46$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 11.925$ (2) Å
$b = 6.0622$ (12) Å
$c = 14.152$ (2) Å
$\beta = 98.763$ (10)°
$V = 1011.2$ (3) Å^3
$Z = 2$

$F_{000} = 380$
$D_x = 1.158$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 65 reflections
$\theta = 3.2$–28.0°
$\mu = 0.58$ mm^{-1}
$T = 293$ (2) K
Plate, yellow
0.60 × 0.55 × 0.10 mm

Data collection

Bruker P4
diffractometer
Radiation source: fine-focus sealed tube
Monochromator: graphite
$T = 293(2)$ K
ω scans
Absorption correction: empirical (using intensity measurements)
via ψ scans (North *et al.*, 1968)
$T_{min} = 0.330$, $T_{max} = 0.758$
1958 measured reflections
1869 independent reflections
1507 reflections with $I > 2\sigma(I)$

$R_{int} = 0.036$
$\theta_{max} = 69.0°$
$\theta_{min} = 7.5°$
$h = -14\rightarrow0$
$k = 0\rightarrow7$
$l = -16\rightarrow17$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.059$	H-atom parameters constrained
$wR(F^2) = 0.181$	$w = 1/[\sigma^2(F_o^2) + (0.0834P)^2 + 0.14P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
1869 reflections	$\Delta\rho_{max} = 0.13$ e Å^{-3}
122 parameters	$\Delta\rho_{min} = -0.10$ 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}
O	0.22448 (12)	0.2919 (2)	0.98676 (12)	0.0945 (5)
H1O	0.1826	0.1917	0.9987	0.142*
N	0.03674 (14)	0.0815 (3)	0.98764 (12)	0.0828 (5)
C1	0.16522 (16)	0.4342 (3)	0.92369 (13)	0.0746 (5)
C2	0.04839 (16)	0.4043 (3)	0.89208 (13)	0.0745 (5)
C21	−0.01234 (18)	0.2229 (3)	0.92723 (14)	0.0799 (6)
H21A	−0.0896	0.2079	0.9054	0.096*
C3	−0.00895 (17)	0.5556 (4)	0.82627 (13)	0.0812 (6)
C31	−0.13374 (19)	0.5317 (5)	0.78758 (18)	0.1100 (8)
H31A	−0.1566	0.6481	0.7428	0.165*
H31B	−0.1771	0.5401	0.8393	0.165*
H31C	−0.1468	0.3917	0.7561	0.165*
C4	0.05091 (19)	0.7293 (4)	0.79547 (15)	0.0882 (6)
H4A	0.0137	0.8309	0.7524	0.106*
C5	0.16609 (19)	0.7543 (3)	0.82806 (15)	0.0844 (6)
H5A	0.2042	0.8726	0.8057	0.101*
C6	0.22623 (17)	0.6100 (3)	0.89244 (13)	0.0757 (5)
C61	0.35080 (17)	0.6367 (4)	0.93133 (15)	0.0864 (6)

H61A	0.3843	0.4888	0.9364	0.104*
C62	0.3655 (2)	0.7337 (5)	1.03203 (17)	0.1066 (8)
H62A	0.3250	0.6448	1.0717	0.160*
H62B	0.3362	0.8814	1.0294	0.160*
H62C	0.4446	0.7358	1.0583	0.160*
C63	0.4165 (2)	0.7718 (5)	0.8680 (2)	0.1156 (9)
H63A	0.4026	0.7148	0.8039	0.173*
H63B	0.4961	0.7630	0.8919	0.173*
H63C	0.3924	0.9228	0.8679	0.173*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O	0.0887 (9)	0.0828 (9)	0.1125 (11)	−0.0062 (7)	0.0172 (8)	0.0219 (8)
N	0.0919 (11)	0.0713 (10)	0.0910 (11)	−0.0131 (8)	0.0326 (8)	−0.0045 (8)
C1	0.0848 (12)	0.0698 (10)	0.0714 (10)	−0.0033 (9)	0.0190 (8)	−0.0002 (8)
C2	0.0846 (12)	0.0719 (11)	0.0704 (10)	−0.0072 (9)	0.0221 (9)	−0.0069 (8)
C21	0.0863 (12)	0.0783 (12)	0.0796 (12)	−0.0087 (9)	0.0268 (9)	−0.0095 (10)
C3	0.0874 (12)	0.0900 (13)	0.0682 (10)	−0.0044 (10)	0.0183 (9)	−0.0037 (9)
C31	0.0914 (15)	0.136 (2)	0.1000 (16)	−0.0058 (14)	0.0078 (12)	0.0137 (15)
C4	0.1015 (15)	0.0890 (14)	0.0735 (12)	−0.0008 (11)	0.0113 (10)	0.0087 (10)
C5	0.1018 (15)	0.0780 (12)	0.0757 (11)	−0.0094 (10)	0.0211 (10)	0.0034 (9)
C6	0.0855 (11)	0.0711 (10)	0.0735 (10)	−0.0079 (9)	0.0214 (9)	−0.0027 (9)
C61	0.0828 (12)	0.0834 (13)	0.0963 (14)	−0.0080 (10)	0.0241 (10)	0.0047 (11)
C62	0.0906 (14)	0.131 (2)	0.0956 (16)	−0.0111 (14)	0.0072 (11)	−0.0023 (14)
C63	0.1092 (17)	0.124 (2)	0.1194 (19)	−0.0348 (15)	0.0353 (14)	0.0092 (16)

Geometric parameters (Å, °)

O—C1	1.359 (2)	C4—C5	1.389 (3)
O—H1O	0.8200	C4—H4A	0.9300
N—C21	1.287 (3)	C5—C6	1.382 (3)
N—N^{i}	1.400 (3)	C5—H5A	0.9300
C1—C6	1.400 (3)	C6—C61	1.512 (3)
C1—C2	1.409 (3)	C61—C63	1.518 (3)
C2—C3	1.408 (3)	C61—C62	1.527 (3)
C2—C21	1.446 (3)	C61—H61A	0.9800
C21—H21A	0.9300	C62—H62A	0.9600
C3—C4	1.380 (3)	C62—H62B	0.9600
C3—C31	1.512 (3)	C62—H62C	0.9600
C31—H31A	0.9600	C63—H63A	0.9600
C31—H31B	0.9600	C63—H63B	0.9600
C31—H31C	0.9600	C63—H63C	0.9600
C1—O—H1O	109.5	C6—C5—H5A	118.7
C21—N—N^{i}	113.4 (2)	C4—C5—H5A	118.7
O—C1—C6	116.59 (18)	C5—C6—C1	116.59 (19)
O—C1—C2	121.14 (17)	C5—C6—C61	123.68 (18)
C6—C1—C2	122.27 (18)	C1—C6—C61	119.70 (18)

C3—C2—C1	118.94 (17)	C6—C61—C63	114.18 (19)
C3—C2—C21	120.31 (18)	C6—C61—C62	110.35 (17)
C1—C2—C21	120.75 (18)	C63—C61—C62	110.4 (2)
N—C21—C2	122.29 (19)	C6—C61—H61A	107.2
N—C21—H21A	118.9	C63—C61—H61A	107.2
C2—C21—H21A	118.9	C62—C61—H61A	107.2
C4—C3—C2	118.93 (18)	C61—C62—H62A	109.5
C4—C3—C31	119.1 (2)	C61—C62—H62B	109.5
C2—C3—C31	121.95 (19)	H62A—C62—H62B	109.5
C3—C31—H31A	109.5	C61—C62—H62C	109.5
C3—C31—H31B	109.5	H62A—C62—H62C	109.5
H31A—C31—H31B	109.5	H62B—C62—H62C	109.5
C3—C31—H31C	109.5	C61—C63—H63A	109.5
H31A—C31—H31C	109.5	C61—C63—H63B	109.5
H31B—C31—H31C	109.5	H63A—C63—H63B	109.5
C3—C4—C5	120.7 (2)	C61—C63—H63C	109.5
C3—C4—H4A	119.6	H63A—C63—H63C	109.5
C5—C4—H4A	119.6	H63B—C63—H63C	109.5
C6—C5—C4	122.52 (19)		

O—C1—C2—C3	−179.61 (17)	C31—C3—C4—C5	−178.8 (2)
C6—C1—C2—C3	0.5 (3)	C3—C4—C5—C6	−0.4 (3)
O—C1—C2—C21	1.0 (3)	C4—C5—C6—C1	0.2 (3)
C6—C1—C2—C21	−178.88 (17)	C4—C5—C6—C61	−178.17 (19)
N^{i}—N—C21—C2	−179.80 (17)	O—C1—C6—C5	179.78 (16)
C3—C2—C21—N	−179.75 (17)	C2—C1—C6—C5	−0.3 (3)
C1—C2—C21—N	−0.4 (3)	O—C1—C6—C61	−1.7 (3)
C1—C2—C3—C4	−0.6 (3)	C2—C1—C6—C61	178.18 (17)
C21—C2—C3—C4	178.78 (17)	C5—C6—C61—C63	−23.7 (3)
C1—C2—C3—C31	178.73 (18)	C1—C6—C61—C63	158.0 (2)
C21—C2—C3—C31	−1.9 (3)	C5—C6—C61—C62	101.3 (2)
C2—C3—C4—C5	0.5 (3)	C1—C6—C61—C62	−77.0 (2)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O—H1O···N	0.82	1.85	2.578 (2)	148

Fig. 1

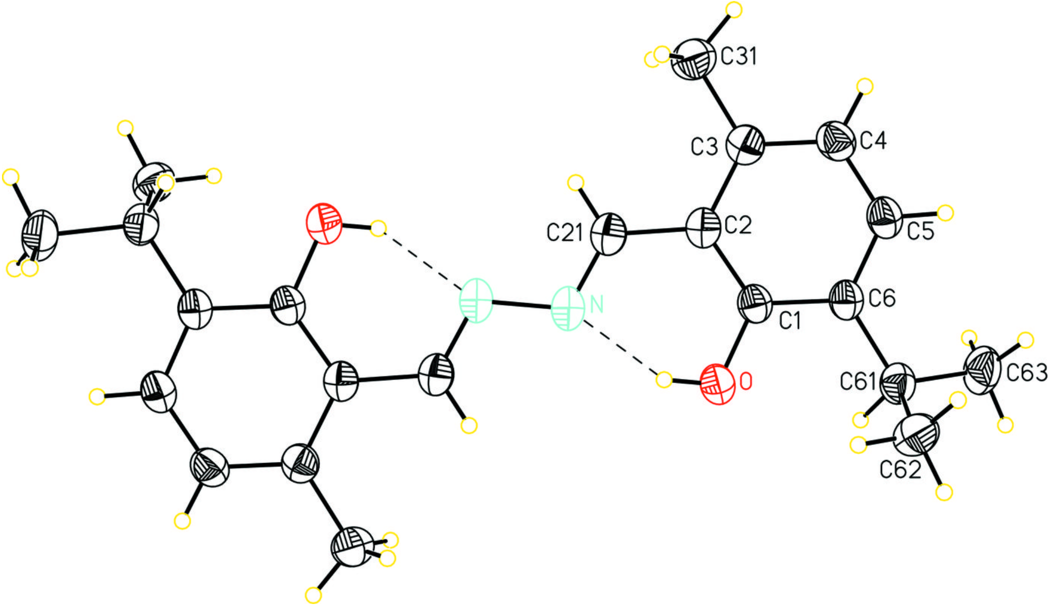

Fig. 2