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Dicyclohexylamine hydrogen peroxide hemisolvate

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.044
wR factor = 0.130
Data-to-parameter ratio = 12.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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The molecules of the title complex, $C_{12}H_{23}N{\cdot}0.5H_2O_2$, are linked together by O—H···N and N—H···O hydrogen bonds to give ten-membered rings, which form flat ribbons parallel to the *a* axis. Centrosymmetric H_2O_2 molecules, as well as amino groups, act as both donors and acceptors of hydrogen bonds.

Comment

Hydrogen peroxide solvates are widely used as environmentally friendly bleaching compounds (Pritchard & Islam, 2003; Cosgrove & Jones, 1998) and oxidation agents in organic synthesis (McKillop & Sanderson, 2000). Hydrogen bonding plays the main role in forming crystals of peroxosolvates. It was supposed that it might be possible to design stable hydrogen peroxide carriers by maximizing the number of hydrogen bonds in the structure (Adams & Ramdas, 1978). However, due to their low stability, very few organic peroxosolvates have been structurally characterized to date – there are 19 entries in Cambridge Structural Database (CSD, Version 5.27, January 2006; Allen, 2002). Here, we report the structure of the title new peroxosolvate molecular complex of dicyclohexylamine with hydrogen peroxide, (I).

(I)

In the structure of (I), the dicyclohexylamine molecule exhibits the expected molecular geometry and both cyclohexyl rings adopt a chair conformation, with the amine group occupying equatorial positions (Fig. 1).

The H_2O_2 molecule has an anti-periplanar conformation, with the H—O—O—H torsion angle equal to 180° as a consequence of the crystallographically imposed centre of symmetry. This feature was previously found in hydrogen peroxide solvates of guanidinium oxalate (Adams & Pritchard, 1976), guanidinium pyromellitate (Adams & Ramdas, 1979) and tetraphenylarsonium chloride (Churakov *et al.*, 2005). The O—O bond length [1.4748 (15) Å] is somewhat longer than that observed for crystalline hydrogen peroxide [1.461 (3) Å; Savariault & Lehmann, 1980] and is comparable with the value found for guanidinium oxalate peroxosolvate dihydrate [1.468 (9) Å; Adams & Pritchard, 1976].

Both components of complex (I) are linked together by a system of hydrogen bonds (Fig. 2). Atom N1 acts as both a donor and an acceptor of hydrogen bonds for adjacent H_2O_2 molecules. The amine group of dicyclohexylamine also forms

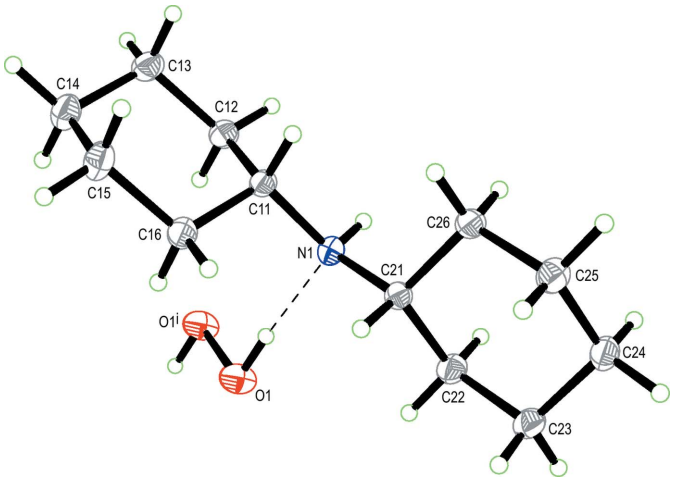

Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates a hydrogen bond. [Symmetry code: (i) $-x, 1-y, 1-z$.]

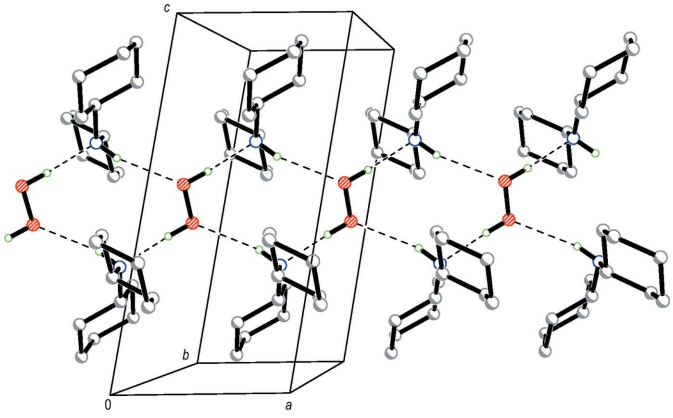

Figure 2
The hydrogen-bonded (dashed lines) chains in (I), parallel to the *a* axis. H atoms not involved in hydrogen bonds have been omitted.

two hydrogen bonds with cocrystallized molecules in the structures of crystalline complexes with 2,4-di-*tert*-butylphenol (Komissarova *et al.*, 2003) and cyclohexanone oxime (Chetina *et al.*, 2006). The H_2O_2 molecule of (I) is involved in four hydrogen bonds with adjacent dicyclohexylamine molecules, forming two donor and two acceptor interactions. Thus, all 'active' H atoms (both amino and peroxo) are engaged in hydrogen bonding in (I).

Two dicyclohexylamine molecules and two H_2O_2 molecules are linked by hydrogen bonds into a ten-membered ring. Peroxide molecules fuse these rings together, forming flat ribbons or tapes parallel to the *a* axis.

During the preparation of this manuscript, the latest update of the CSD has been released (May 2006), which contains the structure of compound (I) as a private communication (refcode VAYGUY; Hursthouse *et al.*, 2006). The reported structure was determined at a different temperature to the present work, but the main structural features are similar to those we have found in (I).

Experimental

Dicyclohexylamine (99%) and 50% hydrogen peroxide were purchased from Aldrich. Hydrogen peroxide (50%, 0.2 ml; ρ = 1.18 Mg m^{-3}) was placed in a sample bottle (9 mm diameter) and covered with a 1:2 mixture of dichloromethane and benzene (approximately 1 ml; $\rho \simeq 1.0$ Mg m^{-3}). Finally, the organic layer was carefully covered with dicyclohexylamine (0.1 ml; ρ = 0.91 Mg m^{-3}). After a few hours, several crystals (up to 5 mm in length) were observed on the wall of the sample bottle. Crystals of (I) decompose slowly in air.

Crystal data

$C_{12}H_{23}N{\cdot}0.5H_2O_2$
M_r = 198.32
Triclinic, $P\overline{1}$
a = 5.2113 (2) Å
b = 10.2567 (4) Å
c = 11.4044 (5) Å
α = 84.034 (1)°
β = 80.011 (1)°
γ = 79.400 (1)°
V = 588.45 (4) Å^3
Z = 2
D_x = 1.119 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 120 (2) K
Block, colourless
0.32 × 0.24 × 0.18 mm

Data collection

Bruker SMART CCD 6000 area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.978, T_{max} = 0.988
4519 measured reflections
2802 independent reflections
2199 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 28.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.130
S = 1.08
2802 reflections
223 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0709P)^2 + 0.0609P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—O1^{i}	1.4748 (15)	N1—C21	1.4808 (13)
O1—H1	0.91 (2)	N1—H2	0.870 (16)
N1—C11	1.4791 (14)		
O1^{i}—O1—H1	99.4 (11)	C11—N1—H2	106.7 (10)
C11—N1—C21	116.48 (8)	C21—N1—H2	106.6 (9)

Symmetry code: (i) $-x, -y+1, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.91 (2)	1.87 (2)	2.7733 (12)	175.8 (16)
N1—H2···O1^{ii}	0.870 (16)	2.391 (16)	3.2388 (13)	164.9 (13)

Symmetry code: (ii) $x+1, y, z$.

All H atoms were located in a difference Fourier map and refined isotropically. In the final stages of the refinement, no residual peaks with intensity greater than 0.13 e A^{-3} were found in the hydrogen peroxide region, indicating the complete occupancy of this site by

H_2O_2 molecules and the absence of partial peroxide/water substitution (Churakov *et al.*, 2005).

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

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$C_{12}H_{23}N{\cdot}0.5H_2O_2$
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Hall symbol: -P 1
$a = 5.2113$ (2) Å
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$c = 11.4044$ (5) Å
$\alpha = 84.034$ (1)°
$\beta = 80.011$ (1)°
$\gamma = 79.400$ (1)°
$V = 588.45$ (4) Å^3
$Z = 2$
$F(000) = 222$
$D_x = 1.119$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1920 reflections
$\theta = 2.8$–$30.0°$
$\mu = 0.07$ mm^{-1}
$T = 120$ K
Block, colourless
0.32 × 0.24 × 0.18 mm

Data collection

Bruker SMART CCD 6000 area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2003)
$T_{min} = 0.978$, $T_{max} = 0.988$
4519 measured reflections
2802 independent reflections
2199 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 28.0°$, $\theta_{min} = 1.8°$
$h = -6 \rightarrow 6$
$k = -13 \rightarrow 12$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.130$
$S = 1.08$
2802 reflections
223 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0709P)^2 + 0.0609P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.02665 (17)	0.45770 (9)	0.55559 (7)	0.0257 (2)
N1	0.35999 (19)	0.49679 (9)	0.68121 (8)	0.0168 (2)
C11	0.3104 (2)	0.63840 (10)	0.70704 (9)	0.0163 (2)
C12	0.3710 (2)	0.72101 (11)	0.58902 (10)	0.0197 (3)
C13	0.3087 (2)	0.87000 (12)	0.60482 (11)	0.0230 (3)
C14	0.0221 (2)	0.91188 (12)	0.66185 (11)	0.0250 (3)
C15	−0.0372 (3)	0.83146 (12)	0.78098 (11)	0.0243 (3)
C16	0.0241 (2)	0.68175 (11)	0.76548 (10)	0.0202 (3)
C21	0.3732 (2)	0.39791 (10)	0.78521 (9)	0.0162 (2)
C22	0.3926 (2)	0.25921 (11)	0.74285 (10)	0.0208 (3)
C23	0.4090 (2)	0.15064 (12)	0.84557 (11)	0.0226 (3)
C24	0.6419 (2)	0.15434 (11)	0.90936 (11)	0.0217 (3)
C25	0.6217 (3)	0.29192 (11)	0.95341 (10)	0.0216 (3)
C26	0.6050 (2)	0.40046 (11)	0.85117 (10)	0.0190 (3)
H21	0.207 (3)	0.4184 (13)	0.8420 (11)	0.018 (3)*
H222	0.554 (3)	0.2418 (13)	0.6803 (12)	0.020 (3)*
H11	0.425 (3)	0.6570 (14)	0.7637 (12)	0.019 (3)*
H122	0.262 (3)	0.7010 (15)	0.5310 (13)	0.029 (4)*
H132	0.429 (3)	0.8914 (15)	0.6553 (13)	0.031 (4)*
H142	−0.091 (3)	0.8943 (15)	0.6059 (13)	0.030 (4)*
H121	0.554 (3)	0.6934 (15)	0.5552 (13)	0.029 (4)*
H162	−0.090 (3)	0.6583 (15)	0.7140 (13)	0.031 (4)*
H232	0.243 (3)	0.1638 (14)	0.9028 (12)	0.024 (3)*
H161	−0.014 (3)	0.6294 (15)	0.8456 (13)	0.030 (4)*
H252	0.462 (3)	0.3095 (14)	1.0150 (13)	0.026 (4)*
H262	0.769 (3)	0.3890 (14)	0.7917 (12)	0.021 (3)*
H131	0.350 (3)	0.9203 (15)	0.5246 (13)	0.029 (4)*
H152	0.068 (3)	0.8541 (14)	0.8390 (13)	0.025 (3)*
H251	0.775 (3)	0.2960 (15)	0.9926 (14)	0.033 (4)*
H2	0.513 (3)	0.4825 (15)	0.6357 (13)	0.026 (4)*
H242	0.807 (3)	0.1335 (15)	0.8507 (13)	0.029 (4)*
H261	0.589 (3)	0.4886 (16)	0.8811 (13)	0.029 (4)*
H241	0.643 (3)	0.0839 (16)	0.9786 (14)	0.033 (4)*
H231	0.419 (3)	0.0646 (16)	0.8135 (13)	0.029 (4)*
H151	−0.219 (3)	0.8541 (16)	0.8172 (14)	0.035 (4)*
H221	0.241 (3)	0.2549 (15)	0.7033 (12)	0.028 (4)*
H1	0.102 (4)	0.4736 (18)	0.5937 (15)	0.047 (5)*
H141	−0.016 (3)	1.0087 (17)	0.6736 (14)	0.040 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0280 (5)	0.0340 (5)	0.0185 (4)	−0.0128 (4)	−0.0088 (4)	0.0052 (4)
N1	0.0186 (5)	0.0154 (5)	0.0160 (4)	−0.0017 (3)	−0.0031 (4)	−0.0008 (3)
C11	0.0180 (5)	0.0147 (5)	0.0170 (5)	−0.0031 (4)	−0.0053 (4)	−0.0006 (4)
C12	0.0206 (6)	0.0188 (5)	0.0195 (5)	−0.0044 (4)	−0.0027 (4)	0.0008 (4)
C13	0.0259 (6)	0.0185 (6)	0.0254 (6)	−0.0068 (4)	−0.0052 (5)	0.0027 (4)
C14	0.0274 (6)	0.0186 (6)	0.0274 (6)	−0.0004 (5)	−0.0057 (5)	0.0018 (5)
C15	0.0261 (6)	0.0186 (6)	0.0249 (6)	0.0015 (5)	−0.0005 (5)	−0.0016 (5)
C16	0.0192 (5)	0.0178 (5)	0.0224 (6)	−0.0022 (4)	−0.0017 (4)	−0.0002 (4)
C21	0.0164 (5)	0.0163 (5)	0.0163 (5)	−0.0033 (4)	−0.0038 (4)	−0.0004 (4)
C22	0.0255 (6)	0.0167 (5)	0.0230 (6)	−0.0047 (4)	−0.0095 (5)	−0.0023 (4)
C23	0.0259 (6)	0.0165 (5)	0.0277 (6)	−0.0059 (4)	−0.0086 (5)	−0.0005 (4)
C24	0.0246 (6)	0.0173 (5)	0.0235 (6)	−0.0018 (4)	−0.0080 (5)	0.0010 (4)
C25	0.0279 (6)	0.0199 (6)	0.0188 (5)	−0.0046 (4)	−0.0086 (5)	−0.0003 (4)
C26	0.0218 (6)	0.0175 (5)	0.0196 (5)	−0.0050 (4)	−0.0079 (4)	0.0005 (4)

Geometric parameters (Å, º)

O1—O1^{i}	1.4748 (15)	C16—H162	0.980 (16)
O1—H1	0.91 (2)	C16—H161	1.018 (15)
N1—C11	1.4791 (14)	C21—C22	1.5299 (15)
N1—C21	1.4808 (13)	C21—C26	1.5351 (15)
N1—H2	0.870 (16)	C21—H21	0.990 (14)
C11—C16	1.5298 (16)	C22—C23	1.5325 (15)
C11—C12	1.5308 (14)	C22—H222	1.004 (14)
C11—H11	1.005 (14)	C22—H221	0.984 (15)
C12—C13	1.5255 (16)	C23—C24	1.5275 (16)
C12—H122	1.001 (15)	C23—H232	0.988 (15)
C12—H121	0.965 (16)	C23—H231	0.979 (16)
C13—C14	1.5245 (17)	C24—C25	1.5260 (16)
C13—H132	0.987 (16)	C24—H242	0.997 (15)
C13—H131	1.012 (15)	C24—H241	1.013 (15)
C14—C15	1.5287 (16)	C25—C26	1.5284 (14)
C14—H142	0.991 (16)	C25—H252	0.992 (15)
C14—H141	0.995 (17)	C25—H251	0.991 (16)
C15—C16	1.5321 (16)	C26—H262	0.990 (14)
C15—H152	0.998 (15)	C26—H261	0.984 (16)
C15—H151	0.964 (17)		
O1^{i}—O1—H1	99.4 (11)	C15—C16—H161	110.4 (9)
C11—N1—C21	116.48 (8)	H162—C16—H161	106.7 (12)
C11—N1—H2	106.7 (10)	N1—C21—C22	108.81 (8)
C21—N1—H2	106.6 (9)	N1—C21—C26	113.46 (8)
N1—C11—C16	111.14 (9)	C22—C21—C26	109.77 (9)
N1—C11—C12	107.90 (9)	N1—C21—H21	107.8 (7)
C16—C11—C12	110.41 (9)	C22—C21—H21	108.9 (8)

N1—C11—H11	112.5 (8)	C26—C21—H21	108.0 (8)
C16—C11—H11	106.3 (8)	C21—C22—C23	112.04 (9)
C12—C11—H11	108.5 (8)	C21—C22—H222	108.7 (8)
C13—C12—C11	112.02 (9)	C23—C22—H222	109.7 (7)
C13—C12—H122	108.6 (9)	C21—C22—H221	110.8 (9)
C11—C12—H122	109.2 (8)	C23—C22—H221	109.6 (8)
C13—C12—H121	111.6 (9)	H222—C22—H221	105.8 (11)
C11—C12—H121	108.7 (9)	C24—C23—C22	111.13 (9)
H122—C12—H121	106.6 (12)	C24—C23—H232	109.6 (8)
C14—C13—C12	111.20 (9)	C22—C23—H232	109.1 (8)
C14—C13—H132	110.0 (9)	C24—C23—H231	112.5 (9)
C12—C13—H132	108.7 (9)	C22—C23—H231	108.4 (8)
C14—C13—H131	111.4 (9)	H232—C23—H231	105.9 (12)
C12—C13—H131	109.1 (9)	C25—C24—C23	110.24 (10)
H132—C13—H131	106.3 (12)	C25—C24—H242	110.1 (9)
C13—C14—C15	110.36 (10)	C23—C24—H242	107.3 (8)
C13—C14—H142	107.4 (9)	C25—C24—H241	110.6 (9)
C15—C14—H142	109.7 (8)	C23—C24—H241	109.2 (9)
C13—C14—H141	110.7 (10)	H242—C24—H241	109.3 (12)
C15—C14—H141	110.3 (9)	C24—C25—C26	111.40 (9)
H142—C14—H141	108.3 (13)	C24—C25—H252	109.4 (8)
C14—C15—C16	111.27 (10)	C26—C25—H252	109.3 (8)
C14—C15—H152	109.6 (8)	C24—C25—H251	110.7 (9)
C16—C15—H152	110.3 (8)	C26—C25—H251	109.4 (9)
C14—C15—H151	111.7 (9)	H252—C25—H251	106.5 (12)
C16—C15—H151	108.6 (10)	C25—C26—C21	111.98 (9)
H152—C15—H151	105.3 (12)	C25—C26—H262	110.7 (8)
C11—C16—C15	111.57 (9)	C21—C26—H262	107.3 (8)
C11—C16—H162	107.3 (9)	C25—C26—H261	110.5 (8)
C15—C16—H162	110.3 (9)	C21—C26—H261	110.0 (8)
C11—C16—H161	110.3 (9)	H262—C26—H261	106.1 (12)

Symmetry code: (i) $-x$, $-y+1$, $-z+1$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.91 (2)	1.87 (2)	2.7733 (12)	175.8 (16)
N1—H2···O1^{ii}	0.870 (16)	2.391 (16)	3.2388 (13)	164.9 (13)

Symmetry code: (ii) $x+1$, y, z.