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Key indicators

Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.044
 wR factor = 0.130
Data-to-parameter ratio = 12.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Dicyclohexylamine hydrogen peroxide hemisolvate

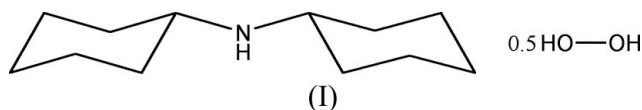
The molecules of the title complex, $\text{C}_{12}\text{H}_{23}\text{N}\cdot 0.5\text{H}_2\text{O}_2$, are linked together by $\text{O}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds to give ten-membered rings, which form flat ribbons parallel to the a axis. Centrosymmetric H_2O_2 molecules, as well as amino groups, act as both donors and acceptors of hydrogen bonds.

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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).



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 $\text{H}-\text{O}-\text{O}-\text{H}$ 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 $\text{O}-\text{O}$ 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

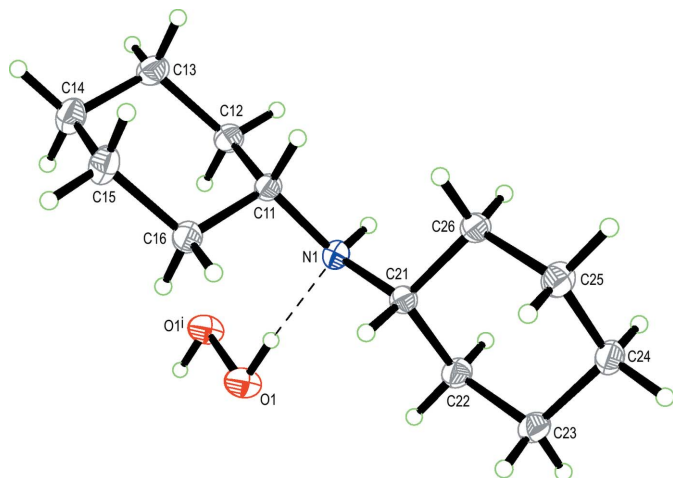


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates a hydrogen bond. [Symmetry code: (i) $-x, 1 - y, 1 - z$.]

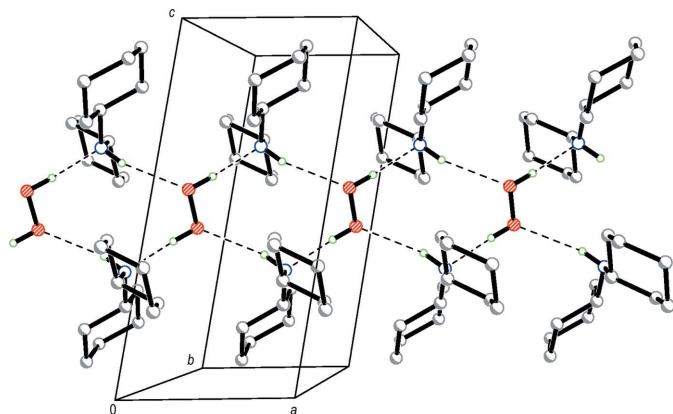


Figure 2
The hydrogen-bonded (dashed lines) chains in (I), parallel to the a axis. H atoms not involved in hydrogen bonds have been omitted.

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 peroxy) 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; $\rho = 1.18 \text{ Mg m}^{-3}$) was placed in a sample bottle (9 mm diameter) and covered with a 1:2 mixture of dichloromethane and benzene (approximately 1 ml; $\rho \approx 1.0 \text{ Mg m}^{-3}$). Finally, the organic layer was carefully covered with dicyclohexylamine (0.1 ml; $\rho = 0.91 \text{ Mg m}^{-3}$). 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

$\text{C}_{12}\text{H}_{23}\text{N}\cdot 0.5\text{H}_2\text{O}_2$	$V = 588.45 (4) \text{ \AA}^3$
$M_r = 198.32$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.119 \text{ Mg m}^{-3}$
$a = 5.2113 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.2567 (4) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$c = 11.4044 (5) \text{ \AA}$	$T = 120 (2) \text{ K}$
$\alpha = 84.034 (1)^\circ$	Block, colourless
$\beta = 80.011 (1)^\circ$	$0.32 \times 0.24 \times 0.18 \text{ mm}$
$\gamma = 79.400 (1)^\circ$	

Data collection

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

Refinement

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

Table 1

Selected geometric parameters (\AA , $^\circ$).

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

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

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1}\cdots\text{N1}$	0.91 (2)	1.87 (2)	2.7733 (12)	175.8 (16)
$\text{N1}-\text{H2}\cdots\text{O1}^{\text{ii}}$	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 \AA^{-3} were found in the hydrogen peroxide region, indicating the complete occupancy of this site by

H₂O₂ molecules and the absence of partial peroxide/water substitution (Churakov *et al.*, 2005).

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2003); data reduction: *SAINTE*; 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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