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The solid dihydrate of *N,N*-dimethyl-*n*-tetradecylamine oxide

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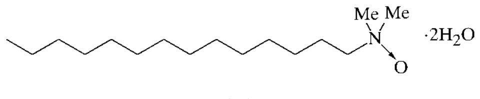
Crystalline *N*,*N*-dimethyl-*n*-tetradecylamine oxide has been prepared by reaction of liquid *N*,*N*-dimethyl-*n*-tetradecylamine with 70% H_2O_2 in the presence of CO_2 as catalyst. The resulting soft low-melting solid was crystallized as the dihydrate, *viz*. $C_{16}H_{35}NO\cdot 2H_2O$. The extended hydrocarbon chains pack in a parallel fashion, with the *N*-oxide ends of the molecules forming hydrogen bonds with the water molecules in hydrophilic layers. The N—O distance is 1.411 (3) Å.

Comment

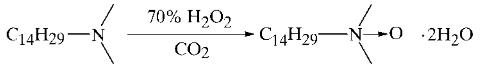
There is a paucity of structural data in the literature on fatty amine oxides. These compounds are commercially important surfactants because of their extensive use in detergents (Maisonneuve, 1991) and surfactant compositions. As a class, they have been both known and commercially available since the mid 1960s (Devinsky, 1986). End uses for these materials generally vary with respect to the length of the included alkyl chain, with 'light' chains (C_8 and C_{10}) being especially effective in hard surface degreasers and specialty cleaners (Miller *et al.*, 1995), 'medium' chains (C_{12} and C_{14}) finding broad usage in light-duty detergents and dishwash formulations (Edward, 1963), and 'heavy' chains (C_{16}, C_{18} and higher) having useful properties in fiber treatments, such as fabric softeners, antistatic treatments, and hair-conditioner products (Shapiro, 1970).



(II)

Generally, these tertiary amine oxides are manufactured, supplied, and formulated as aqueous solutions. A major departure from this trend was developed by workers at Ethyl Corporation when they were able to produce a family of stable easy-to-handle liquid and solid compositions with a broad spectrum of tertiary amine oxides dissolved in non-aqueous 'solvents' or co-surfactants (Sauer *et al.*, 1991; Hughes *et al.*, 1992). Additional work, at least with several of the medium and heavy alkyl-chain systems, also demonstrated the possibility for the production of essentially solvent-free solid non-hygroscopic powdered forms of these amine oxide surfactants (Smith *et al.*, 1991). Based upon elemental analysis and indirect spectral evidence, it was postulated by these workers that the actual form of these 'solid' materials approximated that of an alkyldimethylamine oxide dihydrate. Extensive characterization of these amorphous powders provided much useful data for the formulator, such as melting point, critical micelle concentration (CMC), hydrophile–lipophile balance data (HLB), and solubility data. To date, however, no direct evidence for the exact physical and chemical structures of these solvent-free solid species has been available. We have determined the structure of the title compound, *N*,*N*-dimethyl-*n*-tetradecylamine oxide dihydrate, (II), to better characterize this family of compounds, to provide a more exact understanding of the nature of one of its members, and, at least inferentially, to shed light on the probable structures of other homologues in this family.

The title compound, (II), was prepared by reaction of the starting liquid amine, (I), with 70% H_2O_2 in the presence of CO_2 as catalyst (see reaction *Scheme* below). By using 70% H_2O_2, the 30% available water is apparently sufficient for formation of the solid dihydrate as thin fragile plates. It is fortuitous that the dihydrate is crystalline, as *N*,*N*-dimethylalkylamine oxides are notoriously difficult to crystallize. None are present in the Cambridge Structural Database (CSD; Allen, 2002), except for trimethylamine oxide (Caron *et al.*, 1964). The structure of *N*,*N*-dimethylethanolamine *N*-oxide (Maia *et al.*, 1984) has also been reported. Ammonium salts of *N*,*N*-dimethylalkylamines are common in the CSD, with ten entries present for alkyl = *n*-tetradecyl.



(I) (II)

The asymmetric unit for (II) is shown in Fig. 1 and selected geometrical data are given in Table 1. The alkyl group is extended and slightly bowed, with atoms C2, C13 and C14 lying 0.084 (3), 0.071 (3) and 0.064 (3) Å, respectively, on one side of the best plane of atoms C2–C14, while atoms C7 and C8 lie 0.046 (4) and 0.058 (4) Å on the opposite side of this plane. The C—C distances in the hydrocarbon chain vary in the range 1.512 (4)–1.526 (4) Å, with a mean value of

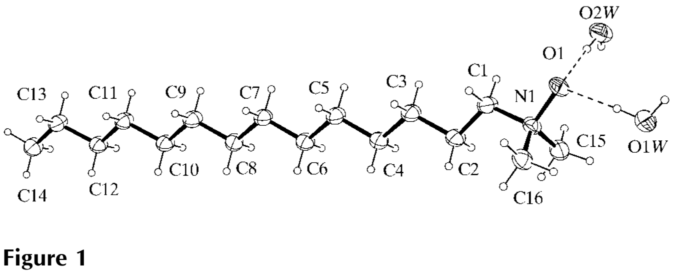


Figure 1
A view of the title compound, with displacement ellipsoids at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

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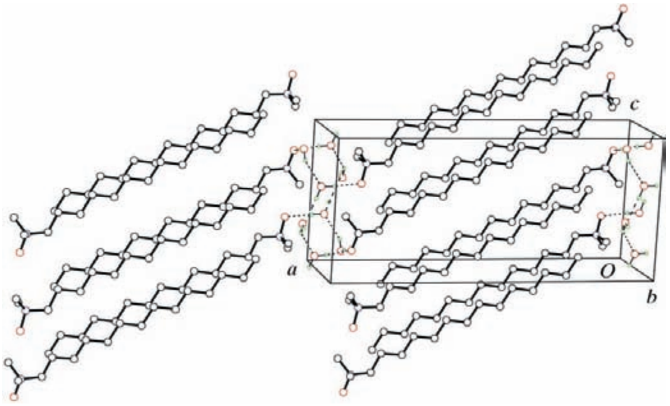

Figure 2
The unit cell in the title compound. Only water H atoms are shown.

1.5180 (11) Å. Most intrachain bond angles of the hydrocarbon chain fall within the narrow range 113.7 (3)–114.8 (3)°, with N1—C1—C3 slightly larger and C1—C2—C3 slightly smaller. The N—O distance compares with a value of 1.404 Å (corrected for libration) in trimethylamine oxide (Caron *et al.*, 1964) and a value of 1.399 Å (mean of three) in *N*,*N*-dimethylethanolamine *N*-oxide (Maia *et al.*, 1984).

The unit cell is shown in Fig. 2, which illustrates the hydrogen-bonded regions near $x = 0$, where the water molecules associate with the head-to-head hydrophilic ends of the fatty amine *N*-oxide molecules. In the interior of the cell, the parallel hydrocarbon chains interdigitate along the [010] direction. The hydrophilic region is shown in Fig. 3. Each water molecule donates two hydrogen bonds and accepts one, linking the *N*-oxide groups into six-oxygen centrosymmetric rings. These rings are further linked by $H_2O\cdots H_2O$ hydrogen bonds to form two-dimensional arrays (see Table 2 for hydrogen-bond details).

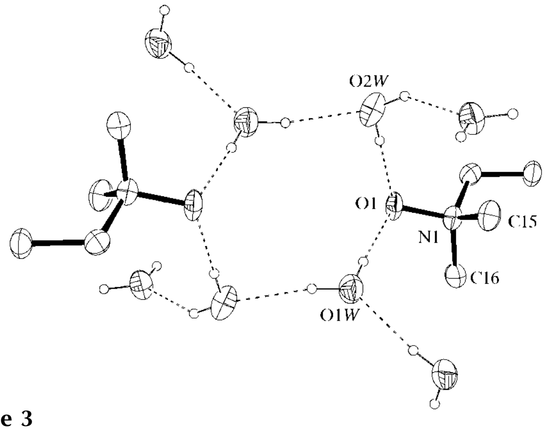

Figure 3
The hydrogen bonding in the title compound. Only the first two C atoms of the C_{14} chain are illustrated.

Experimental

The title compound was prepared by reacting liquid *N*,*N*-dimethyl-*n*-tetradecylamine with 70% hydrogen peroxide in the presence of CO_2 as catalyst. A blanket of CO_2 was maintained throughout the addition of the peroxide to the liquid amine. The amine oxidation process is strongly exothermic and the reaction temperature was regulated by the rate of peroxide addition (Elnagar, 2000). The resulting soft solid (m.p. 317 K) was crystallized from ethyl methyl ketone.

Crystal data

$C_{16}H_{35}NO\cdot 2H_2O$
$M_r = 293.48$
Monoclinic, $P2_1/c$
$a = 22.782$ (8) Å
$b = 8.110$ (5) Å
$c = 9.995$ (5) Å
$\beta = 91.19$ (2)°
$V = 1846.3$ (16) Å^3
$Z = 4$
$D_x = 1.056$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3471 reflections
$\theta = 2.5$–26.0°
$\mu = 0.07$ mm^{-1}
$T = 100$ K
Plate, colorless
0.48 × 0.17 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer (with an Oxford Cryosystems Cryostream cooler)
ω scans with κ offsets
15 919 measured reflections
3508 independent reflections
1746 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.076$
$\theta_{\rm max} = 26.0°$
$h = -28 \rightarrow 28$
$k = -10 \rightarrow 10$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.086$
$wR(F^2) = 0.195$
$S = 1.06$
3508 reflections
196 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0530P)^2 + 1.8197P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.004$
$\Delta\rho_{\rm max} = 0.32$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—N1	1.411 (3)	N1—C15	1.489 (4)
N1—C16	1.477 (4)	N1—C1	1.494 (4)
O1—N1—C16	108.0 (2)	C16—N1—C1	111.8 (3)
O1—N1—C15	109.7 (2)	C15—N1—C1	111.6 (3)
C16—N1—C15	109.4 (3)	N1—C1—C2	117.0 (2)
O1—N1—C1	106.3 (2)	C3—C2—C1	109.5 (2)
O1—N1—C1—C2	173.4 (3)	N1—C1—C2—C3	172.1 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1$W\cdots$O1	0.88	1.85	2.727 (3)	174
O1W—H2$W\cdots$O2$W^{\rm i}$	0.87	1.97	2.832 (4)	170
O2W—H3$W\cdots$O1	0.88	1.87	2.741 (4)	177
O2W—H4$W\cdots$O1$W^{\rm ii}$	0.88	2.07	2.829 (4)	144

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

H atoms on C atoms were placed in calculated positions, with C—H distances in the range 0.98–0.99 Å, and thereafter treated as riding. A torsional parameter was refined for each methyl group. Water H atoms were located in difference maps, and their O—H distances were restrained. For all H atoms, $U_{\rm iso} = 1.5U_{\rm eq}$ of the attached atom for methyl and water H atoms or $1.2U_{\rm eq}$ for all other H atoms.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1004). Services for accessing these data are described at the back of the journal.

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