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2,4,5-Triphenyl-4*H*-imidazol-4-yl hydroperoxide–dichloromethane (2/1)

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2,4,5-Triphenyl-4*H*-imidazol-4-yl
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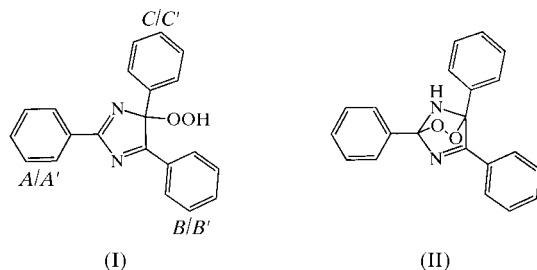
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The structure of lophine peroxide was confirmed to be 2,4,5-triphenyl-4*H*-imidazol-4-yl hydroperoxide and not the 2,5-endoperoxide. The asymmetric unit is composed of an O—H···N hydrogen-bonded dimer of lophine peroxide with an *R/R* or *S/S* configuration and a CH₂Cl₂ solvent molecule, *i.e.* 2C₂₁H₁₆N₂O₂·CH₂Cl₂.

Comment

In lophine chemiluminescence, the peroxide is known to be the critical intermediate. Lophine peroxide was originally formulated as the 2,5-endoperoxide, (II), by Dufraisse *et al.* (1957), but this structure is invalidated by the ¹H NMR and UV spectra, and the hydroperoxide structure (I) was established by White & Harding (1965). X-ray analysis of the lophine peroxide has long been required for structure confirmation. However, only silk-hair-type crystals have grown from ethanol solution. Recently, we obtained prismatic crystals from a CH₂Cl₂ solution. The melting point of the crystals is higher (388 K) than that of silk-hair-type crystals (383 K). We report here the structure of the prismatic crystal and discuss the structure of lophine peroxide, (I).



The *S/S* dimer is bonded by two hydrogen bonds and the π – π stacking between the phenyl groups (*A* and *A'*) on the

second position of each imidazole ring. The angle between the planes of rings *A* and *A'* is 11.19 (4)°. The center-to-center distance between rings *A* and *A'* is 3.84 (5) Å. The bond lengths of 1.470 (2) Å for O1–O2 and 1.464 (2) Å for O1'–O2' agree with the average value for RO–OH of 1.465 Å (Boche *et al.*, 1996), and are shorter than the range 1.496–1.550 Å for R¹O–OR² (Suzuki *et al.*, 2000; Izuoka *et al.*, 1997; Coughlin *et al.*, 1979; Sander *et al.*, 1997; Adam *et al.*, 1983). The C2–O1 [1.419 (3) Å] and C2'–O1' bond lengths [1.418 (2) Å] are shorter than the mean value of those of R–OOR (1.455 Å; Suzuki *et al.*, 2000).

The unit cell consists of an *S/S* domain and an *R/R* domain. These domains are formed by two kinds of inter-domain π – π stacking. An intra-domain π – π stacking center-to-center distance between the phenyl groups (*B*) of an *R/R* dimer or an *S/S* dimer is 3.99 (4) Å along the *a* axis. Another inter-domain π – π stacking is observed between the phenyl group (*A*) of an *R/R* dimer and the phenyl group (*A'*) of an *S/S* dimer. The angle between the molecular axes of a lophine peroxide moiety between adjacent *R/R* or *S/S* dimers is about 60°.

Experimental

The title compound was prepared according to the method of White & Harding (1964). Crystallization from CH₂Cl₂ yielded colorless needles (89%) which showed identical ¹H NMR, IR, and UV spectral data to those of a verified sample obtained from ethanol (Kimura *et al.*, 1993; White & Harding, 1964). The melting point of this crystals is higher (388 K) than that of silk-hair-type crystals obtained from ethanol (383 K). HRMS (FAB) *m/z*: calculated for C₂₁H₁₆N₂O₂ 329.1290; found 329.1265.

Crystal data

2C₂₁H₁₆N₂O₂·CH₂Cl₂
M_r = 741.67
 Monoclinic, *C2/c*
a = 19.519 (1) Å
b = 14.269 (1) Å
c = 26.068 (2) Å
 β = 94.456 (2)°
V = 7238.5 (8) Å³
Z = 8

D_x = 1.361 Mg m^{−3}
 Cu *K*α radiation
 Cell parameters from 14799 reflections
 θ = 4.1–68.0°
 μ = 2.021 mm^{−1}
T = 123.2 K
 Prism, colorless
 0.34 × 0.33 × 0.32 mm

Data collection

Rigaku RAXIS–RAPID Imaging
 Plate diffractometer
 ω scans
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
T_{min} = 0.460, *T_{max}* = 0.524
 33 961 measured reflections
 6464 independent reflections

4887 reflections with *I* > 2σ(*I*)
R_{int} = 0.078
 θ_{\max} = 68.0°
h = −22 → 23
k = −17 → 17
l = −31 → 31
 Intensity decay: none

Refinement

Refinement on *F*²
R(*F*) = 0.051
wR(*F*²) = 0.142
S = 1.149
 6464 reflections
 479 parameters
 H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + \{0.06 \times [\text{Max}(F_o^2, 0) + 2F_c^2]/3\}^2]$
 $(\Delta/\sigma)_{\max} = 0.0010$
 $\Delta\rho_{\max} = 0.65 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.99 \text{ e \AA}^{-3}$
 Extinction correction: Zachariasen
 (1967) type 2 Gaussian isotropic
 Extinction coefficient: 0.0048 (6)

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Table 1

Selected geometric parameters (Å, °).

O1—O2	1.470 (2)	O1'—O2'	1.464 (2)
O1—C2	1.419 (3)	O1'—C2'	1.418 (2)
O2—O1—C2	107.2 (1)	O1—O2—H2o	103
O2'—O1'—C2'	107.7 (1)	O1'—O2'—H2o'	103

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2'—H2o'...N1	1.00	1.76	2.760 (2)	174
O2—H2o...N1'	1.01	1.77	2.773 (2)	176

The positional parameters of the H atoms attached to C atoms were calculated geometrically and fixed with $U_{\text{iso}} = 0.048 \text{ \AA}^2$. The H atoms of the peroxide groups were found by difference syntheses and their positional parameters were somewhat refined and fixed.

Data collection: *MSC/RAXIS-RAPID Imaging Plate Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/RAXIS-RAPID Imaging Plate Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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