

Crystal Structure of 1,1-Dihydroperoxycyclododecane at -160°C

P. GROTH

Department of Chemistry, University of Oslo, Oslo 3, Norway

The crystals are orthorhombic with cell dimensions $a=5.973(1)$ Å, $b=13.140(4)$ Å, $c=16.164(4)$ Å, space group $P2_12_12_1$, and four molecules in the unit cell. The structure was solved by direct methods and refined by full-matrix least squares technique to an R -value of 2.4 % ($R_w=2.3$ %) for 896 observed reflections measured on an automatic four circle diffractometer. The two O-O distances are 1.462 and 1.467 Å. The significant difference between the two C-O bonds (1.442 and 1.410 Å) is probably related to the hydrogen bonding system, consisting of *inter*-molecular bonds only. The average C-C bond distance and C-C-O angle of the cyclododecane ring are 1.524 Å and 114.3° , respectively.

In two earlier attempts to determine the hydrogen bonding systems formed by hydroperoxy groups,^{1,2} the hydrogen atoms themselves could not be found in the difference

Fourier maps, and the results are therefore somewhat incomplete. In the hope of obtaining a more accurate description, a crystal structure determination of 1,1-dihydroperoxycyclododecane ($\text{C}_{12}\text{H}_{24}\text{O}_4$) has been carried out.

The crystals are orthorhombic with cell dimensions $a=5.973(1)$ Å, $b=13.140(4)$ Å, $c=16.164(4)$ Å. The space group is $P2_12_12_1$ and there are four molecules in the unit cell ($\rho_0=1.22$ g/cm³, $\rho_0=1.21$ g/cm³). The intensities were measured (at -160°C) on a Syntex PI diffractometer with an Enraf-Nonius liquid nitrogen cooling device (modified by H. Hope). The radiation was $\text{MoK}\alpha$ ($\lambda=0.71069$ Å) and $2\theta_{\text{max}}=45^{\circ}$. With an observed-unobserved cutoff at $2.0\sigma(I)$, 896 reflections were recorded as observed. The crystal size was $(0.09 \times 0.16 \times 0.28)$ mm³. No corrections were made for absorption or secondary extinction effects.

Table 1. Final fractional coordinates and thermal parameters with estimated standard deviations. The expression for anisotropic vibration is $\exp[-2\pi^2(h^2a^{*2}U11 + \dots + klb^*c^*U23)]$. Hmn is bonded to Cm and HOM to Om.

| ATOM | X | Y | Z | U11 | U22 | U33 | U12 | U13 | U23 |
|------|------------|------------|-------------|-----------|-----------|-----------|------------|------------|------------|
| O1 | .02178(28) | .36738(11) | .62918(8) | .0218(9) | .0161(8) | .0238(8) | .0009(8) | -.0057(7) | -.0021(7) |
| O2 | .13981(31) | .22819(12) | .06467(10) | .0239(10) | .0170(9) | .0277(10) | .0034(8) | -.0020(9) | .0009(7) |
| O3 | .31899(25) | .41978(11) | .05053(8) | .0193(10) | .0276(8) | .0154(8) | -.0030(8) | .0023(7) | .0018(7) |
| O4 | .33839(31) | .44400(13) | -.03780(10) | .0332(11) | .0312(10) | .0267(9) | .0073(9) | .0005(8) | .0034(8) |
| C1 | .09283(40) | .39971(17) | .06968(13) | .0171(14) | .0194(13) | .0192(13) | -.0010(12) | .0018(11) | -.0010(11) |
| C2 | .06972(47) | .47752(19) | .03451(16) | .0192(16) | .0205(13) | .0211(15) | .0010(13) | .0004(12) | -.0005(11) |
| C3 | .26992(44) | .50848(17) | .05360(13) | .0229(15) | .0207(14) | .0206(15) | -.0012(13) | .0008(14) | .0000(12) |
| C4 | .20885(47) | .66251(18) | .04428(17) | .0402(16) | .0201(15) | .0249(15) | .0003(14) | .0041(14) | .0004(12) |
| C5 | .39410(46) | .64617(21) | .10762(15) | .0185(14) | .0213(15) | .0298(15) | .0032(14) | -.0057(12) | -.0005(12) |
| C6 | .33282(48) | .67751(20) | .19609(15) | .0239(17) | .0211(16) | .0324(16) | .0023(13) | .0050(12) | -.0010(12) |
| C7 | .47458(53) | .62888(20) | .26331(17) | .0271(18) | .0205(18) | .0276(16) | .0040(15) | .0001(14) | .0010(12) |
| C8 | .43723(47) | .51476(21) | .27331(18) | .0211(15) | .0326(17) | .0275(16) | .0020(14) | .0033(14) | .0007(13) |
| C9 | .20365(46) | .40536(19) | .30413(17) | .0233(15) | .0314(16) | .0180(15) | .0004(14) | .0015(13) | .0010(12) |
| C10 | .14798(54) | .37353(20) | .29152(14) | .0254(16) | .0291(16) | .0203(14) | .0000(14) | .0029(14) | .0000(12) |
| C11 | .11616(53) | .34319(23) | .20061(15) | .0262(16) | .0107(16) | .0261(14) | -.0003(14) | .0040(13) | .0000(11) |
| C12 | .09433(45) | .39012(20) | .16306(14) | .0176(14) | .0159(14) | .0215(13) | .0008(13) | -.0001(12) | -.0002(11) |

| ATOM | X | Y | Z | B | ATOM | X | Y | Z | B |
|------|------------|-----------|------------|---------|------|------------|-----------|------------|---------|
| H21 | -.2146(41) | .4633(15) | .0575(13) | .7(4) | H22 | -.0727(37) | .4679(15) | -.0276(14) | 1.3(4) |
| H31 | .1158(42) | .6134(17) | .3138(14) | 1.8(5) | H32 | .0547(37) | .5929(16) | .1112(14) | 1.2(4) |
| H41 | -.2778(48) | .0514(17) | -.0181(15) | 2.4(5) | H42 | -.1483(37) | .7358(17) | .0481(12) | 1.0(4) |
| H51 | -.468(41) | .5771(20) | .1978(14) | 1.8(5) | H52 | -.3293(44) | .6875(17) | .0910(13) | 1.0(5) |
| H61 | -.3511(49) | .7520(18) | .1978(12) | 1.4(5) | H62 | -.1772(44) | .6642(18) | .2078(14) | 1.2(5) |
| H71 | -.6301(45) | .6424(18) | .2490(13) | 1.5(5) | H72 | -.4531(54) | .6650(18) | .3171(15) | 2.5(6) |
| H81 | -.4718(38) | .4786(15) | .2107(15) | 1.2(4) | H82 | -.5493(42) | .4900(17) | .3128(14) | 1.6(5) |
| H91 | -.1998(36) | .4907(15) | .3651(14) | .9(4) | H92 | -.0814(35) | .5317(16) | .2772(13) | .8(4) |
| H101 | -.2757(41) | .3165(18) | .3178(14) | 2.0(5) | H102 | -.0808(48) | .3529(17) | .3210(14) | 1.4(5) |
| H111 | -.2523(38) | .3661(16) | .1690(12) | 1.5(4) | H112 | -.1026(49) | .2705(18) | .1960(12) | .8(4) |
| H121 | .2263(41) | .3484(16) | .1773(12) | .8(4) | H122 | .1224(39) | .4578(18) | .1842(12) | 1.2(5) |
| H02 | .2584(62) | .2159(24) | .6336(19) | 5.5(9) | H04 | .4201(55) | .3932(22) | -.0519(19) | 4.0(8) |

Table 2. Interatomic distances, bond angles and dihedral angles with estimated standard deviations.

| Distance | Å | Distance | Å |
|----------|----------|-----------|----------|
| O1 - O2 | 1.462(2) | O7 - O8 | 1.525(4) |
| O3 - O4 | 1.467(2) | O8 - O9 | 1.520(4) |
| C1 - O1 | 1.442(3) | O9 - C10 | 1.523(4) |
| C1 - O3 | 1.410(3) | C10 - C11 | 1.534(4) |
| C1 - O2 | 1.520(4) | C11 - C12 | 1.526(4) |
| O2 - C3 | 1.531(3) | C12 - C1 | 1.516(3) |
| O3 - C4 | 1.527(3) | O2 - O1' | 2.764(3) |
| O4 - C5 | 1.519(4) | O4 - O2' | 2.843(3) |
| O5 - C6 | 1.532(4) | O2 - HO2 | .870(35) |
| O6 - C7 | 1.519(4) | O4 - HO2 | .858(31) |

| Angle | (°) | Angle | (°) |
|---------------|----------|------------------|-----------|
| O1 - O1 - O2 | 109.8(1) | C7 - O8 - O9 | 114.7(2) |
| O1 - O3 - O4 | 109.2(2) | O8 - O9 - C10 | 114.0(2) |
| O1 - C1 - O3 | 109.9(2) | C9 - C10 - C11 | 114.0(2) |
| O1 - C1 - O2 | 102.1(2) | C10 - C11 - C12 | 112.2(2) |
| O1 - C1 - C12 | 112.5(2) | C11 - C12 - C1 | 115.2(2) |
| O3 - C1 - O2 | 113.9(2) | O1 - O2 - HO2 | 102.5(21) |
| O3 - C1 - C12 | 105.2(2) | O2 - HO2 - O1 | 173.9(31) |
| C12 - C1 - O2 | 115.6(2) | HO2 - O1' - O2' | 118.9(10) |
| C1 - C2 - O3 | 114.6(2) | HO2 - O1' - C1' | 128.5(10) |
| O2 - C3 - O4 | 112.9(2) | O3 - O4 - HO4 | 97.8(21) |
| O3 - C4 - O5 | 115.0(2) | O4 - HO4 - O2' | 169.2(30) |
| O4 - C5 - O6 | 114.9(2) | HO4 - O2' - O1' | 103.1(9) |
| O5 - C6 - O7 | 114.9(2) | HO4 - O2' - HO2' | 115.3(24) |
| O6 - C7 - O8 | 114.1(2) | | |

| Dihedral angle | (°) |
|----------------------|-----------|
| C1 - O2 - O3 - O4 | -160.4(2) |
| O2 - O3 - O4 - O5 | 67.7(3) |
| O3 - O4 - O5 - O6 | 69.4(3) |
| O4 - O5 - O6 - O7 | -158.1(2) |
| O5 - O6 - O7 - O8 | 68.6(3) |
| O6 - O7 - O8 - O9 | 66.1(3) |
| O7 - O8 - O9 - C10 | -164.0(2) |
| O8 - O9 - C10 - C11 | 68.9(3) |
| O9 - C10 - C11 - C12 | 69.0(3) |
| C10 - C11 - C12 - C1 | -156.9(2) |
| C11 - C12 - C1 - O2 | 69.1(3) |
| C12 - C1 - O2 - O3 | 68.4(3) |

The structure was solved by direct methods³ and refined by full-matrix least squares technique.^{4*} Anisotropic temperature factors were introduced for oxygen and carbon atoms. Methylene hydrogen atom positions were calculated, while the two H-atoms of the hydroperoxy groups were seen as the largest peaks in the difference Fourier map. Atomic form factors were those of Hanson *et al.*⁵ except for hydrogen.⁶ Weights used in least squares were obtained from the standard deviations in intensities, $\sigma(I)$, taken as

$$\sigma(I) = [C_T + (0.02C_N)^2]^{\frac{1}{2}}$$

where C_T is the total number of counts and C_N the net count. The final R -value was 2.4% ($R_w = 2.3\%$) for 896 observed reflections.

* All programs used (except those for phase determination) are included in this reference.

Final fractional coordinates and thermal parameters with estimated standard deviations are given in Table 1. The principal axes of the thermal vibration ellipsoids were calculated from the temperature parameters of Table 1. Maximum to r.m.s. amplitudes range from 0.149 to 0.211 Å (corresponding B -values of 1.76 and 3.52 Å²). Because of the size of the molecule, no rigid-body analysis of translational, librational and screw motion has been carried out.

Interatomic distances, bond angles, and dihedral angles are listed in Table 2. The standard deviations, given in parentheses, are estimated from the correlation matrix of the last least squares refinement cycle. A list of observed structure factors is available from the author.

The *inter*-molecular hydrogen bonding system, shown in Fig. 1, forms endless double chains along [100] with O...O distances of 2.764 and 2.843 Å. O2 is an acceptor as well as a donor, while O1 accepts HO4. The fact that O3 is not involved in hydrogen bonding may possibly be related to the significant difference between the bond lengths C1 - O1 (1.442 Å) and C1 - O3 (1.410 Å). A similar, though statistically insignificant, effect was observed in 1,1'-dihydroperoxycyclohexanylperoxide-1,1',¹ (I). In 1,1'-dihydroperoxycyclododecanylperoxide-1,1',² (II), both oxygens are involved in *intra*-molecular hydrogen bonds, and the C - O bonds are equal. Table 2 shows that bond distances and angles involved in the hydrogen bonding system have normal values. Bond distances and angles of the hydroperoxy groups correspond, within three times e.s.d.'s, to those of (I) and (II).

The arrangement around C1 is asymmetric, with angles C2 - C1 - O1 and C12 - C1 - O3 about 10.5° smaller than C2 - C1 - O3 and C12 - C1 - O1. The effect (described in detail elsewhere²) is probably related to *intra*-molecular oxygen-hydrogen repulsions.

Deviations of the 12-membered ring conformation from the idealized "square" model with 422-symmetry (containing eight synclinal and four *anti*-periplanar partial conformations) may be compared with those of (II). The average synclinal torsional angles agree closely (68.4 and 68.2°). However, the *anti*-periplanar dihedral angles (°) are more nearly equal in the title compound:

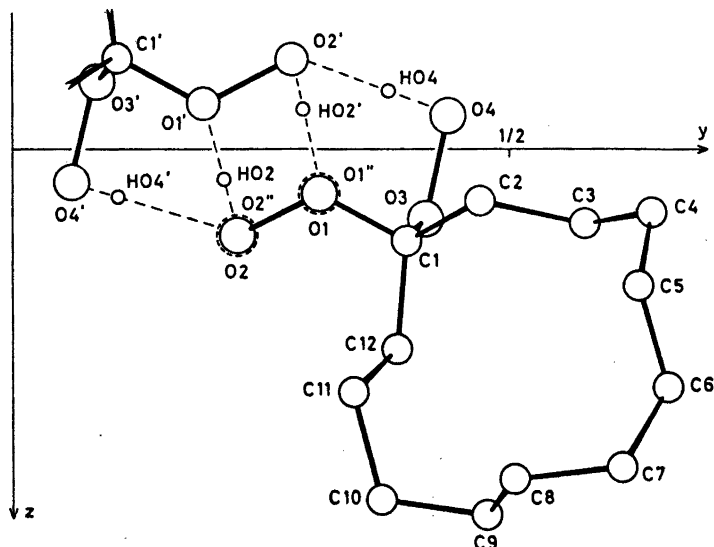


Fig. 1. Schematic drawing of the molecule and the hydrogen bonding system, viewed along [100]. O1'' and O2'' are in the neighbouring cell.

-160.4, -158.1, -164.0, -156.9

than in (II):

-169.4, -152.4, -167.0, -152.3

-168.9, -151.3, -168.7, -150.3

The average C-C bond distance and C-C-C angle (1.524 Å and 114.3°) correspond closely with those of (II) (1.526 Å and 114.1°). Methylene C-H bond distances range from 0.96 to 1.05 Å.

Except for the hydrogen bonds, no short *inter*-molecular contacts are observed.

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