

Crystal Structure of 1,1'-Dihydroperoxycyclododecanylperoxide-1,1' at $-160\text{ }^{\circ}\text{C}$

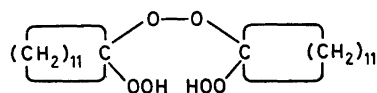
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The crystals are triclinic with dimensions $a=8.657(6)\text{ \AA}$, $b=11.808(4)\text{ \AA}$, $c=12.526(5)\text{ \AA}$, $\alpha=77.22(3)^{\circ}$, $\beta=77.54(4)^{\circ}$, $\gamma=81.68(4)^{\circ}$ for Dirichlet's reduced cell. The space group is $P\bar{1}$ with two 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 5.7% ($R_w=4.4\%$) for 2254 observed reflections measured on an automatic four-circle diffractometer. Mean values of O—O, C—O, and C—C bond distances are 1.474, 1.427, and 1.526 \AA , respectively. The C—O—O angles of the hydroxyperoxy groups are 110.0 and 109.1 $^{\circ}$. The corresponding angles of the peroxy bridge are 108.2 and 108.4 $^{\circ}$. The asymmetric environments of the non-methylene carbon atoms resemble those observed for trimeric acetone peroxide and 1,1'-dihydroperoxycyclohexanyl-

peroxide-1,1'. The conformation of the molecule is *cis*, and the dihedral angle C—O—O—C is 124.3 $^{\circ}$. There are possibly two *intra*-molecular hydrogen bonds of lengths 2.870 and 2.765 \AA , respectively.

A crystal structure determination of 1,1'-dihydroperoxycyclododecanylperoxide-1,1' has



been carried out in order to study the hydroperoxy group, especially its ability to form

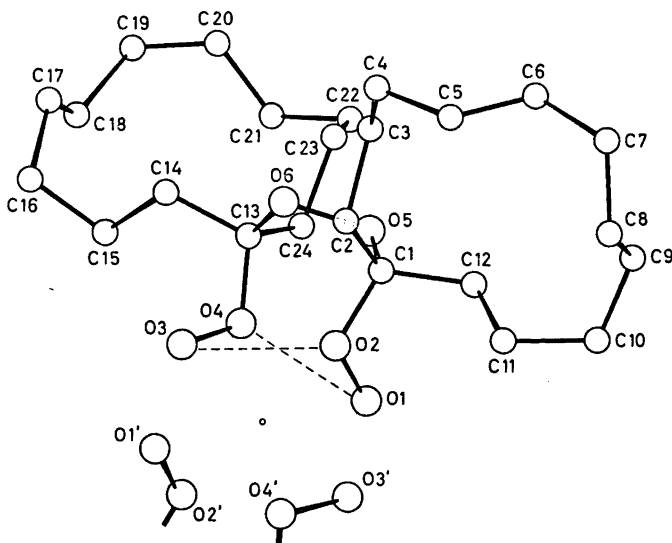


Fig. 1. Schematic drawing of the molecule.

Table 1. Final fractional coordinates and thermal parameters with estimated standard deviations (multiplied by 10^6 for O- and C-atoms and by 10^4 for H-atoms). Hmn is bonded to Cm. The expression for anisotropic vibration is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
O1	112471(32)	49335(22)	16781(20)	1448(53)	586(25)	395(22)	668(58)	-219(55)	-417(36)
O2	9933(31)	59577(22)	25469(19)	1418(61)	398(24)	329(21)	62(54)	-271(53)	-120(35)
O3	77948(34)	49422(21)	13873(21)	1916(58)	368(24)	521(24)	-1015(62)	-454(59)	218(36)
O4	86693(29)	57458(20)	5845(19)	1243(48)	274(23)	342(21)	-217(53)	-356(58)	-89(34)
O5	96782(28)	72242(20)	16628(19)	728(43)	377(23)	318(20)	-126(48)	-398(46)	19(33)
O6	80880(27)	71896(20)	15862(19)	644(44)	473(24)	383(20)	-173(49)	-355(46)	-224(33)
C1	99919(44)	64287(30)	26462(28)	1846(73)	248(33)	292(31)	77(75)	-464(75)	-81(58)
C2	87277(44)	65545(32)	36812(28)	1831(70)	443(36)	127(29)	-189(68)	-178(72)	-180(61)
C3	82973(46)	78897(34)	38864(31)	1114(74)	597(38)	488(33)	539(64)	-598(80)	-223(56)
C4	77687(46)	78547(35)	51211(31)	968(73)	666(40)	338(32)	483(86)	-180(78)	-315(58)
C5	89889(46)	74818(33)	88384(29)	1112(73)	447(36)	281(30)	168(82)	-389(75)	-221(52)
C6	102862(48)	82676(33)	85698(31)	1245(77)	398(37)	454(34)	112(85)	-394(83)	-247(56)
C7	117897(49)	77779(36)	61161(33)	1338(81)	667(43)	493(36)	-414(94)	-399(88)	-357(63)
C8	127141(46)	67524(35)	56588(31)	1031(79)	743(43)	349(33)	-115(89)	-583(78)	-86(60)
C9	135898(44)	78962(37)	44451(32)	671(67)	874(46)	422(35)	-562(89)	-394(77)	55(64)
C10	139259(45)	61138(30)	37941(31)	737(71)	1034(58)	331(33)	688(93)	-317(76)	-91(64)
C11	124666(46)	57421(34)	35328(31)	1178(78)	515(38)	487(32)	494(85)	-648(81)	-270(56)
C12	116472(44)	66748(32)	27175(29)	817(65)	436(35)	386(30)	53(75)	-384(71)	-91(60)
C13	79836(42)	69193(30)	8332(28)	853(70)	292(34)	283(30)	-113(75)	-421(71)	-156(49)
C14	62218(44)	71887(33)	4922(28)	842(68)	988(38)	366(31)	-293(86)	-232(73)	-151(64)
C15	67894(45)	66585(33)	-4477(31)	913(71)	543(38)	489(34)	-491(83)	-437(79)	-215(57)
C16	48819(45)	78491(37)	-6877(31)	875(72)	804(46)	485(33)	-673(98)	-292(78)	-331(61)
C17	37263(44)	83553(36)	-9881(32)	694(66)	695(43)	495(35)	-255(83)	-445(77)	-288(60)
C18	45335(46)	86397(38)	-21793(32)	1182(77)	837(47)	419(35)	-681(96)	-687(83)	-182(63)
C19	49888(47)	101828(38)	-23768(32)	944(75)	750(48)	457(35)	178(91)	-429(81)	54(62)
C20	61823(46)	103888(32)	-17898(30)	964(72)	443(36)	399(33)	-15(82)	-332(78)	-98(54)
C21	78465(44)	97785(31)	-22458(29)	1079(72)	364(35)	289(30)	-157(79)	-338(75)	1(51)
C22	98965(44)	97478(31)	-15496(30)	1089(70)	377(35)	426(33)	-386(79)	-466(78)	2(54)
C23	88038(44)	89438(31)	-4819(29)	1141(71)	314(33)	328(31)	-186(77)	-58(75)	-192(58)
C24	98289(41)	76489(30)	-4392(27)	711(63)	355(34)	258(28)	-99(72)	-223(68)	-138(49)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H21	9128(35)	6878(26)	4328(24)	2,8(.7)	H141	8934(35)	7955(27)	432(25)	2,8(.7)
H22	7753(35)	6216(26)	3588(24)	2,7(.7)	H142	5646(35)	6666(26)	1289(25)	2,4(.7)
H31	7483(36)	8173(26)	3491(24)	3,1(.7)	H151	5974(35)	8715(27)	-280(25)	2,8(.7)
H32	9253(36)	8386(26)	3685(25)	2,9(.7)	H152	6553(35)	6857(26)	-1123(24)	2,3(.7)
H41	6786(35)	7335(26)	5439(24)	2,3(.7)	H161	3321(34)	8782(26)	116(24)	2,3(.8)
H42	7287(35)	8783(27)	5178(25)	2,8(.7)	H162	3616(35)	6597(26)	-1149(25)	2,8(.7)
H51	9436(35)	6629(26)	5759(24)	1,3(.7)	H171	4845(35)	8796(26)	-462(25)	2,1(.7)
H52	8454(35)	7346(26)	6651(25)	2,8(.7)	H172	2574(36)	8572(26)	-915(25)	1,7(.7)
H61	9896(35)	9836(26)	5783(25)	2,8(.7)	H181	3889(36)	8729(26)	-2696(24)	3,2(.7)
H62	18661(35)	8496(26)	4722(25)	2,3(.7)	H182	8526(36)	8329(26)	-2376(25)	2,1(.7)
H71	11336(38)	7496(26)	6929(25)	2,7(.7)	H191	3944(36)	10881(26)	-2188(25)	4,3(.7)
H72	12439(35)	8413(26)	5985(24)	2,7(.7)	H192	8269(36)	18366(26)	-3193(25)	3,2(.7)
H81	12873(35)	6153(26)	5697(25)	2,4(.7)	H201	5881(35)	9969(27)	-981(24)	1,2(.7)
H82	13498(35)	6408(26)	6186(24)	3,8(.7)	H202	6247(35)	11168(26)	-1866(25)	1,9(.7)
H91	14588(36)	7357(26)	4468(25)	2,3(.7)	H211	8174(35)	18272(27)	-3829(25)	1,9(.7)
H92	12962(38)	7854(26)	4898(25)	1,8(.7)	H212	7788(35)	8967(27)	-2315(25)	3,8(.7)
H101	14548(35)	5377(26)	4229(24)	3,8(.7)	H221	9805(35)	18848(26)	-8141(25)	3,1(.7)
H102	14747(35)	6322(26)	3883(24)	2,8(.7)	H222	18251(36)	9488(26)	-1075(25)	2,7(.7)
H111	11663(35)	5588(26)	4239(25)	1,8(.7)	H231	7768(36)	9141(26)	46(24)	1,4(.7)
H112	12782(35)	4968(26)	3211(24)	3,0(.7)	H232	9564(36)	9114(26)	58(24)	1,0(.7)
H121	12354(35)	6786(26)	1989(25)	2,2(.7)	H241	18171(36)	7346(26)	-451(25)	2,1(.7)
H122	11532(35)	7489(26)	2936(24)	1,2(.7)	H242	8793(36)	7567(26)	-1153(24)	3,8(.7)

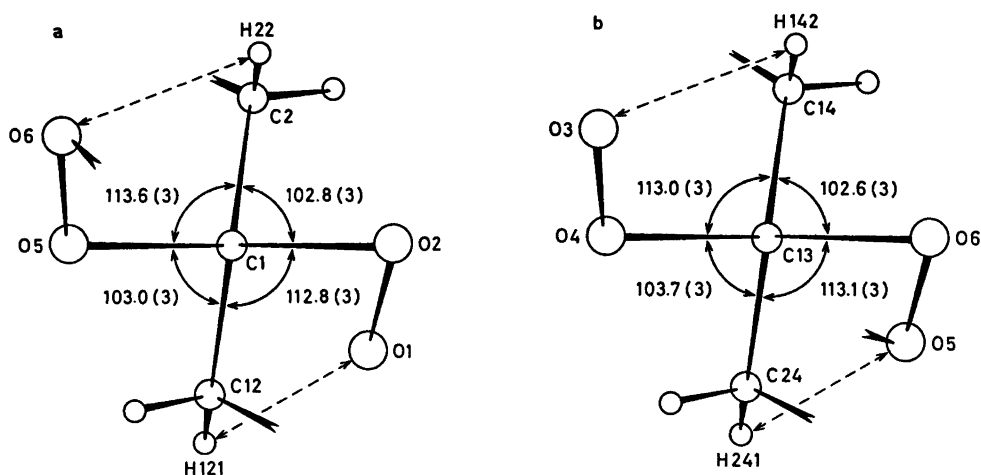


Fig. 2. Schematic drawing showing the asymmetric environments of the carbon atoms C1 and C13.

Table 2. Bond distances and angles and dihedral angles with estimated standard deviations.

Distance	Å	Distance	Å
01 - 02	1.470(3)	C12 - C1	1.527(5)
05 - 06	1.476(3)	C13 - C14	1.519(5)
03 - 04	1.475(3)	C14 - C15	1.528(5)
02 - C1	1.424(4)	C15 - C16	1.527(5)
05 - C1	1.426(4)	C16 - C17	1.517(5)
04 - C13	1.428(4)	C17 - C18	1.532(5)
06 - C13	1.431(4)	C18 - C19	1.520(6)
C1 - C2	1.525(5)	C19 - C20	1.526(5)
C2 - C3	1.539(5)	C20 - C21	1.525(5)
C3 - C4	1.531(5)	C21 - C22	1.521(5)
C4 - C5	1.531(5)	C22 - C23	1.530(5)
C5 - C6	1.521(5)	C23 - C24	1.532(5)
C6 - C7	1.518(5)	C24 - C13	1.521(5)
C7 - C8	1.529(5)	O1 - O4	2.870(4)
C8 - C9	1.539(5)	O1 - O5	2.845(3)
C9 - C10	1.521(6)	O3 - O2	2.765(4)
C10 - C11	1.515(5)	O3 - O6	2.774(3)
C11 - C12	1.532(5)	O1 - O4*	2.987(3)

Angle	(°)	Angle	(°)
01 - 02 - C1	110.0(2)	C12 - C1 - C2	114.3(3)
05 - 04 - C13	109.1(2)	C13 - C14 - C15	114.5(3)
02 - C1 - O5	110.6(3)	C14 - C15 - C16	113.2(3)
04 - C13 - O6	109.9(3)	C15 - C16 - C17	114.8(3)
C2 - C1 - O5	113.6(3)	C16 - C17 - C18	114.5(3)
C12 - C1 - O5	103.0(3)	C17 - C18 - C19	114.3(3)
C24 - C13 - O4	105.7(3)	C18 - C19 - C20	114.6(3)
C14 - C13 - O4	113.0(3)	C19 - C20 - C21	114.0(3)
C13 - O6 - O5	108.4(2)	C20 - C21 - C22	115.6(3)
C1 - O5 - O6	108.2(2)	C21 - C22 - C23	114.3(3)
C2 - C1 - O2	102.8(3)	C22 - C23 - C24	114.1(3)
C12 - C1 - O2	112.8(3)	C23 - C24 - C13	113.1(3)
C14 - C13 - O6	102.6(3)	C24 - C13 - C14	114.8(3)
C24 - C13 - O6	113.1(3)	O2 - O1 - O4	76.9(1)
C1 - O2 - O3	114.9(3)	O2 - O1 - O5	55.3(1)
O2 - C3 - O4	112.8(3)	O4 - O3 - O2	80.6(1)
C3 - O4 - O5	114.2(3)	O4 - O3 - O6	57.5(1)
O4 - O5 - C6	113.4(3)	O1 - O4 - O3	87.1(2)
O5 - O6 - C7	114.1(3)	O1 - O4 - C13	115.9(2)
C6 - O7 - C8	114.3(3)	O3 - O2 - O1	91.3(2)
C7 - C8 - O9	113.4(3)	O3 - O2 - C1	115.5(2)
C8 - O9 - C10	114.4(3)	O2 - O1 - O4*	133.0(2)
O9 - C10 - C11	114.8(3)	O1 - O4* - O3*	107.9(2)
C10 - C11 - C12	113.8(3)	O1 - O4 - C13*	113.0(2)
C11 - C12 - C1	114.3(3)		

Dihedral angle	(°)
C1 - O5 - O6 - C13	-124.3(3)
C1 - O2 - O3 - C4	-152.3(3)
C2 - O3 - C4 - O5	68.0(4)
C3 - O4 - O5 - C6	67.5(4)
O4 - O5 - O6 - C7	-169.4(3)
O5 - C6 - C7 - O8	68.9(4)
O6 - C7 - O8 - C9	67.4(4)
C7 - O8 - C9 - C10	-152.4(3)
O8 - C9 - C10 - C11	69.2(4)
O9 - C10 - C11 - C12	67.0(4)
C10 - C11 - C12 - C1	-167.0(3)
C11 - C12 - C1 - O2	70.6(4)
C12 - C1 - O2 - C3	67.8(4)
C13 - C14 - C15 - C16	-168.9(3)
C14 - C15 - C16 - C17	65.0(4)
C15 - C16 - C17 - C18	68.5(4)
C16 - C17 - C18 - C19	-151.3(3)
C17 - C18 - C19 - C20	69.4(4)
C18 - C19 - C20 - C21	68.0(4)
C19 - C20 - C21 - C22	-168.7(3)
C20 - C21 - C22 - C23	65.7(4)
C21 - C22 - C23 - C24	69.4(4)
C22 - C23 - C24 - C13	-150.3(3)
C23 - C24 - C13 - C14	71.1(4)
C24 - C13 - C14 - C15	68.0(4)

hydrogen bonds, and to establish the cyclododecane ring conformation.

The crystals of $C_{24}H_{46}O_6$ are triclinic. Dimensions for Dirichlet's reduced cell are $a = 8.657(6)$ Å, $b = 11.808(4)$ Å, $c = 12.526(5)$ Å, $\alpha = 77.22(3)^\circ$, $\beta = 77.54(4)^\circ$, $\gamma = 81.68(4)^\circ$. Statistical tests indicate the space group $P\bar{1}$. There are two molecules in the unit cell ($\rho_c = 1.18$ g/cm³, $\rho_0 = 1.16$ g/cm³). The intensities were measured (at -160°C) on a Syntex $P\bar{1}$ diffractometer with an Enraf-Nonius liquid-nitrogen cooling device (modified by H. Hope.) With an observed-unobserved cutoff at $1.5\sigma(I)$, 2254 reflections were recorded as observed. The radiation was $\text{MoK}\alpha$ ($\lambda = 0.71069$ Å) and $2\theta_{\text{max}} = 45^\circ$. No corrections for absorption or secondary extinction effects have been carried out.

The structure was solved by direct methods¹ and refined by full-matrix least squares techniques.^{2*} Anisotropic temperature factors were introduced for oxygen and carbon atoms. Weights in least squares were obtained from the standard deviations in intensities, $\sigma(I)$,

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

taken as where C_T is the total number of counts and C_N the net count. The final R -value

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

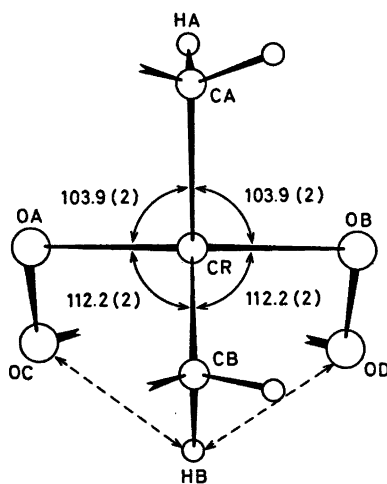


Fig. 3. Schematic drawing showing the asymmetric environment of the spiro carbon atom, CR, of dimeric peroxides. OH, OB, OC, and OD are oxygens of the peroxy bridges.

was $R = 5.7\%$ ($R_w = 4.5\%$) for 2254 observed reflections.

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 r.m.s. amplitudes range from 0.177 to 0.262 Å. Due to 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, 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.

Fig. 1 shows that the conformation of the molecule with respect to the hydroperoxy group is *cis*. Average bond distances and angles of the hydroperoxy group and the peroxy bridge of the present compound, (I), may be compared with those of 1,1'-dihydroperoxycyclohexanylperoxide-1,1'³ (II):

	(I)	(II)
O—O	1.474(3) Å	1.477(4) Å
C—O	1.427(4) Å	1.437(5) Å
C—O—O		
(hydroperoxy)	109.6(3)°	110.4(3)°
C—O—O		
(peroxy)	108.2(2)°	107.9(3)°

Although no significant differences occur among bond distances and angles, the dihedral angle C—O—O—C is somewhat smaller in I (124.3(3)°) than in II (126.3(3)°).

As in the case of II, the hydroperoxy hydrogen atoms could not be localized in the difference Fourier map. Table 2 indicates that there are two *intra*-molecular hydrogen bonds, O1...O4 (2.870 Å) and O3...O2 (2.765 Å). Since the O—O...O angles are as small as 76.9 and 80.6°, respectively, this cannot, however, be stated with confidence. In II one of the two hydrogen bonds was *inter*-molecular.

The arrangements around the carbon atoms C1 and C13 are asymmetric as shown in Fig. 2 (a) and (b). The angles C12—C1—O5, C2—C1—O2, C24—C13—O4 and C14—C13—O6 have an average value of 103.0°, while the average of C2—C1—O5, C12—C1—O2, C14—

C13—O4, and C24—C13—O6 is 113.1°. The distortions may roughly be described as "rotations" (*ca.* 7°) about axes through C1 and C13 normal to the paper plane (Fig. 2). Similar results were obtained for II, and also for trimeric acetone peroxide.⁴ In dimeric peroxides⁵⁻⁷ the corresponding axes of "rotation" are normal to the C—C—C planes (see Fig. 3). It seems reasonable to relate the effects to *intra*-molecular oxygen-hydrogen repulsions (as indicated by the dotted lines in the figures).

Deviations of the 12-membered ring conformation from the idealized "square" model with 422-symmetry (containing eight synclinal and four anti-periplanar partial conformations) are in good agreement with earlier findings. In 2,12-dibromocyclododecanone⁸ the average synclinal torsional angle is 68.4°, in azacyclododecane hydrochloride⁹ 68.4°, and in the title compound it is 68.2°. Corresponding values for antiperiplanar dihedral angles (°) are

—171.6,	—150.2,	—170.7,	—153.8
—168.6,	—153.4,	—168.2,	—155.1
—169.4,	—152.4,	—167.0,	—152.3
—168.9,	—151.3,	—168.7,	—150.3

The mean value of the C—C—C angles (114.2°) agrees closely with that of 2,12-dibromocyclododecanone (114.1°).

No short *inter*-molecular contacts are observed.

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