Crystal and Molecular Structure of 10,10-Dimethyl-3,4-dioxatricyclo-[5.2.1.$0^{1,5}$]decane-2-spiro-2′-adamantane and a Comparison of C–O and O–O Bond Lengths in Small Rings as a Function of Ring Size †

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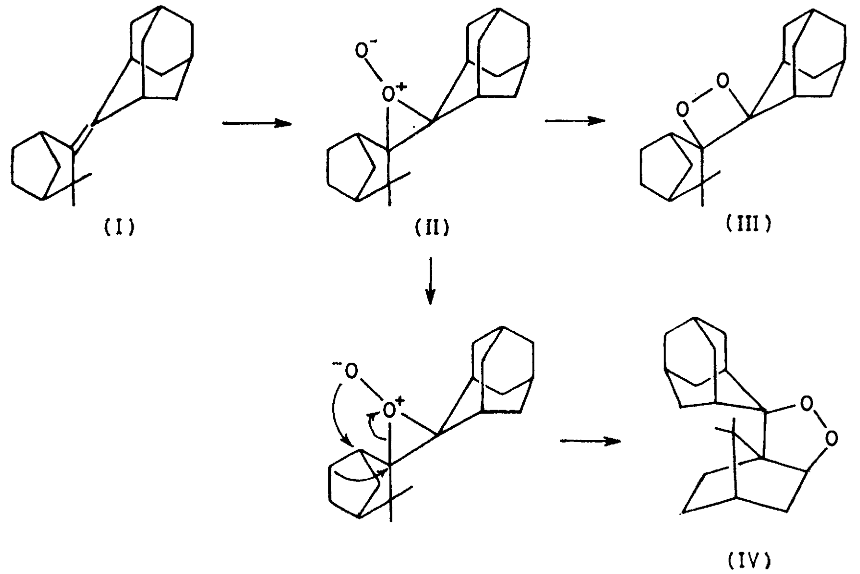
The crystal structure of the title compound (IV) formed by reaction of singlet oxygen with camphenylideneadamantane (I) shows it to be a 1,2-dioxolan in which the camphane framework has rearranged to norbornane. Crystals are orthorhombic, space group $P2_12_12_1$, with a = 23.17(2), b = 9.76(1), c = 6.74(1) Å, Z = 4; the structure was refined to R 0.062 based on 783 counter reflections. From comparisons with other structures it is shown that in small-ring cyclic peroxides and related molecules the C–O and O–O follow the trend of C–C bonds in being longer in four- than in either three- or five-membered rings. However the differences in bond length with ring size appear to be larger for C–O and smaller for O–O bonds by comparison with C–C bonds.

It has been reported[1] that the reaction of camphenylideneadamantane (I) with singlet oxygen produces two crystalline isomeric products, one of which is the dioxetan (III) and the other is a rather unexpected rearrangement product (IV) containing a dioxolan ring. The identification of (IV), which has implications for the mechanism of the reaction, rests on the crystal structure analysis described here. We have also compared bond lengths in several small-ring oxygen heterocycles to establish the trends in C–O and O–O bond lengths with ring size.



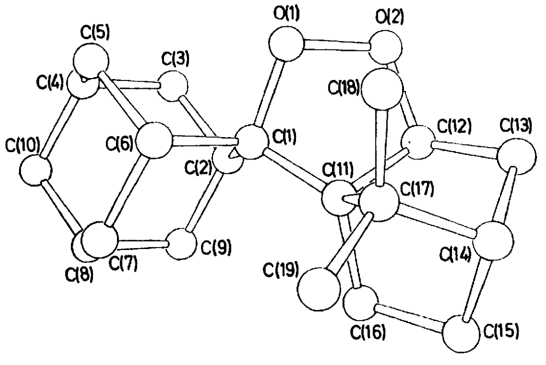


FIGURE 1 Molecular conformation and atom numbering scheme

Molecular Structure and Mechanism of Formation.—The molecular conformation and atom-numbering scheme are shown in Figure 1 and relevant molecular parameters are listed in Tables 1 and 2. It can be seen that the peroxide group forms part of a five-membered dioxolan ring of which one carbon atom comes from the adamantane group and two from the norbornane group. The dioxolan ring has an envelope conformation with C(1) the out-of-plane atom (Table 3). The O–O distance is 1.483(7) and the mean C–O distance is 1.451(10) Å. These may be compared with those in the dioxolan ring of 8-acetyl-1,2,6,7,8-pentamethyl-2,4,5,9-tetraoxatricyclo[4.2.1.$0^{3,7}$]nonane[2] where O–O is 1.476(4) and mean C–O 1.418(6) Å, the former showing good and the latter rather poorer agreement.

The adamantane cage system has mean bond lengths of 1.542(22) Å and internal bond angles of 109.4(1.4)° in good agreement with those in similar molecules.[3] The angle C(2)–C(1)–C(6) at the spiro-junction is at the low end of the range but is not significantly different from the

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† Reprints not available.

average. The other cage framework is now a norbornane cage which again has dimensions comparable to those in similar molecules.[4] The bridgehead angle C(11)–C(17)–C(14) is 94.5(6)° compared to a usual angle of *ca.* 96°.

TABLE 1

Final atom co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses

	x	*y*	*z*
C(1)	3 684(4)	4 303(10)	4 087(12)
C(2)	3 541(3)	5 815(8)	4 727(15)
C(3)	3 777(4)	6 811(10)	3 169(16)
C(4)	4 436(4)	6 656(11)	3 065(16)
C(5)	4 589(4)	5 143(12)	2 471(15)
C(6)	4 337(4)	4 158(10)	3 969(15)
C(7)	4 602(4)	4 525(12)	6 027(14)
C(8)	4 472(4)	5 983(12)	6 607(15)
C(9)	3 806(3)	6 158(10)	6 782(15)
C(10)	4 705(4)	7 001(10)	5 096(15)
C(11)	3 324(3)	3 213(8)	5 088(12)
C(12)	2 735(3)	3 360(9)	4 020(13)
C(13)	2 465(6)	1 965(10)	4 103(15)
C(14)	2 882(4)	1 145(8)	5 483(14)
C(15)	2 835(4)	1 844(10)	7 553(13)
C(16)	3 156(4)	3 199(9)	7 316(13)
C(17)	3 472(4)	1 665(9)	4 767(14)
C(18)	3 605(4)	1 208(9)	2 662(15)
C(19)	3 958(4)	1 109(10)	6 048(18)
O(1)	3 499(2)	4 135(6)	2 035(8)
O(2)	2 873(2)	3 829(6)	2 054(9)

TABLE 2

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses, and torsion angles (°) for the dioxolan ring

(*a*) Bonds

O(1)–O(2)	1.483(7)	C(17)–C(19)	1.522(14)
C(1)–O(1)	1.459(10)	C(1)–C(2)	1.571(12)
C(12)–O(2)	1.443(11)	C(2)–C(3)	1.533(14)
C(1)–C(11)	1.512(12)	C(3)–C(4)	1.540(13)
C(11)–C(12)	1.553(10)	C(4)–C(5)	1.569(16)
C(12)–C(13)	1.499(13)	C(5)–C(6)	1.512(15)
C(13)–C(14)	1.564(13)	C(6)–C(7)	1.561(14)
C(14)–C(15)	1.558(13)	C(7)–C(8)	1.505(16)
C(15)–C(16)	1.525(13)	C(8)–C(9)	1.561(12)
C(11)–C(16)	1.554(12)	C(2)–C(9)	1.554(14)
C(11)–C(17)	1.563(12)	C(4)–C(10)	1.544(15)
C(14)–C(17)	1.539(13)	C(8)–C(10)	1.522(15)
C(17)–C(18)	1.521(14)	C(1)–C(6)	1.526(13)

(*b*) Angles

C(1)–O(1)–O(2)	107.6(5)	C(6)–C(7)–C(8)	111.6(8)
C(12)–O(2)–O(1)	106.8(4)	C(7)–C(8)–C(9)	108.8(7)
C(1)–C(2)–C(3)	109.3(6)	C(7)–C(8)–C(10)	111.7(7)
C(1)–C(2)–C(9)	111.3(6)	C(8)–C(10)–C(4)	108.0(7)
C(1)–C(6)–C(5)	111.2(6)	C(11)–C(12)–C(13)	105.5(6)
C(1)–C(6)–C(7)	108.9(7)	C(11)–C(16)–C(15)	103.4(6)
C(1)–C(11)–C(12)	102.4(5)	C(11)–C(17)–C(14)	94.5(6)
C(1)–C(11)–C(16)	125.3(6)	C(11)–C(17)–C(18)	117.2(6)
C(2)–C(3)–C(4)	109.0(6)	C(11)–C(12)–O(2)	105.1(5)
C(2)–C(9)–C(8)	107.6(6)	C(11)–C(17)–C(19)	115.4(6)
C(2)–C(1)–C(6)	108.1(6)	C(12)–C(11)–C(17)	102.6(6)
C(2)–C(1)–O(1)	107.7(5)	C(12)–C(13)–C(14)	103.1(6)
C(2)–C(1)–C(11)	114.8(5)	C(12)–C(11)–C(16)	103.2(6)
C(3)–C(4)–C(5)	109.2(8)	C(13)–C(14)–C(15)	105.5(6)
C(3)–C(4)–C(10)	109.9(8)	C(13)–C(14)–C(17)	101.3(6)
C(3)–C(2)–C(9)	109.5(6)	C(14)–C(15)–C(16)	104.5(6)
C(5)–C(4)–C(10)	109.9(7)	C(14)–C(17)–C(18)	112.2(6)
C(14)–C(17)–C(19)	111.4(6)	C(18)–C(17)–C(19)	106.0(6)

(*c*) Torsion angles

C(1)–O(1)–O(2)–C(12)	−20	O(1)–C(1)–C(11)–C(12)	−41
O(2)–O(1)–C(1)–C(11)	38	C(1)–C(11)–C(12)–O(2)	30
O(1)–O(2)–C(12)–C(11)	−7		

As noted by McCapra and Beheshti[1] the observed product is indicative of a Wagner–Meerwein type rearrangement involving a positively charged intermediate.

TABLE 3

Deviations (Å) of atoms from their mean plane of C(11), C(12), O(1), O(2)

C(11) 0.02, C(12), −0.04, O(1) −0.03, O(2) 0.04, C(1) −0.61 C(13) 1.12

This would be consistent with a mechanism involving the initial formation of perepoxide (II), which then rearranges to give either the observed dioxetan or dioxolan. Consideration of the interactions between the frontier orbitals of ethylene and singlet oxygen has led Inagaki and his co-workers[5] to suggest that the initial intermediate formed should be perepoxide. Calculations by Dewar[6] using MINDO/3 programs have concluded that such a perepoxide intermediate may be energetically favoured as an initial product with subsequent decomposition to give a dioxetan or an epoxide. However, later calculations by Harding and Goddard[7] using a generalised valence bond (GVB) method with extensive configuration interaction disagree with Dewar's results and think a perepoxide intermediate unlikely.

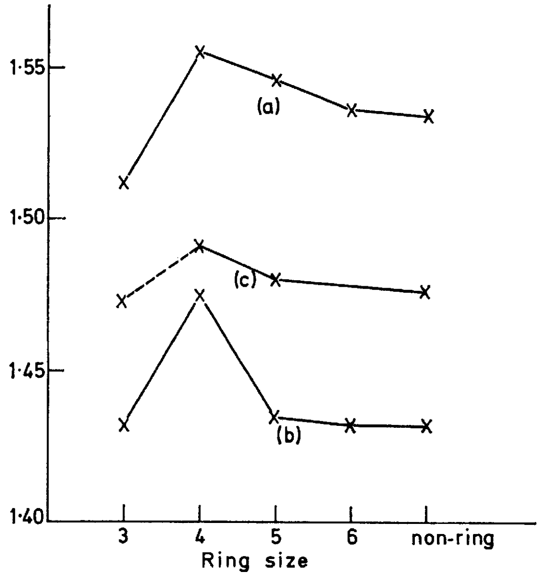

FIGURE 2 Variation of bond length with ring size for a, C–C, b, C–O, and c, O–O bonds

Comparison of Bond lengths in Small Rings.—In a recently published crystal structure of a 1,2-dioxetan[8] the authors note that the O–O bond length of 1.491(7) is not significantly different from that in H_2O_2 [1.47(s) Å], but that the C–O bond length [1.475(7) Å] is significantly longer than that of 1.42(3) Å in dioxan. We feel that the comparison used is not an apt one since C–C bond lengths are known to vary with ring size in small rings. This has prompted us to compare the three types of bond lengths C–C, C–O, and O–O in small-ring cyclic peroxides and related molecules. Some representative values have been plotted as a function of ring size in Figure 2 and a clear trend emerges. In each case there is a small increase from non-ring to six- and five-membered rings, followed by a large increase on going to the four- and a fall again to the three-membered ring. It appears that C–O bond lengths are more sensitive to ring size than are C–C bonds, and that either the O–O bond length in dioxetan is underestimated or that such bond lengths are less sensitive to ring size than are C–C bonds. Within the limits of accuracy of the dioxetan structure determination either interpretation is possible. The overall trend of bond length with ring size is of course understandable on the basis of the use of sp^3 hybrid orbitals in five- and six-membered rings and non-ring molecules, but the necessity to use more-nearly pure *p* orbitals to get bond angles of 90° in a four-membered ring with the concomitant increase in orbital radius and hence bond length. In the three-membered ring one can assume the bent-broad arrangement in which the expected bond length is approximately that of the four-membered ring multiplied by the cosine of the angle (15°) between the orbital direction and the atom–atom vector, *i.e.* 0.966, in good agreement with the experimental ratio of bond lengths in three- and four-membered rings of 0.97 for both C–C and C–O.

For the purposes of this comparison the bond lengths plotted were chosen in a somewhat arbitrary way, where possible from peroxide structures, but also from rings with ether linkages, and whilst not the result of an exhaustive search are, we hope, reasonably characteristic of the relevant ring size. The C–C bond lengths were taken from the electron-diffraction results for the simple cyclic alkanes as compiled by Kuchitsu.[9] For the non-ring values of 1.432 and 1.476 Å for C–O and O–O we took the mean for two non-ring peroxide molecules [10] which were in good agreement. For the six-membered rings we could not find data for a peroxide group, and for C–O we took 1.432 Å which is the mean for a large number of pyranose rings.[11] For five-membered rings we took the mean values for the present work and for the other dioxolan molecule already mentioned.[2] The two O–O bonds (1.476 and 1.483 Å) agree well and whilst the C–O bonds (1.418 and 1.451 Å) differ somewhat their mean (1.435 Å) agrees well with that for furanose rings.[12] For four-membered rings the O–O and C–O values of 1.491 and 1.475 Å are taken from the only known structure of a dioxetan,[8] the C–O length being in good agreement with those observed (1.475 Å) in an oxetan.[13] For a three-membered ring the C–O bond length of 1.432 Å was taken from that in the ethylene oxide ring of *p*-nitrostyrene oxide.[14] Since no three-membered ring organic peroxides exist we have taken 1.473 Å from the means of six structures [15] of transition-metal sideways-bonded dioxygen complexes; this is obviously open to criticism but does give some order of magnitude value.

The C–O bond lengths are consistently lower than the means of the C–C and O–O bonds owing to the electronegativity difference between C and O. The wider variation with ring size of the C–O bonds might possibly be due to a change in the electronegativity difference between C and O when the hybridisation changes from sp^3 to more-nearly *p* orbital character.

EXPERIMENTAL

The title compound was separated from the dioxetan by t.l.c. (hexane–ether, 9 : 1) [16] and recrystallised twice from acetonitrile as long white needles, m.p. 116—117 °C.

Crystal Data.—$C_{19}H_{28}O_2$, $M = 288.5$. Orthorhombic, $a = 23.17(2)$, $b = 9.76(1)$, $c = 6.74(1)$ Å, $U = 1\,524.8$ Å^3, $Z = 4$, $D_c = 1.26$ g cm^{-3}, $F(000) = 632$. Mo-K_α radiation $\lambda = 0.7107$ Å; μ(Mo-K_α) $= 0.85$ cm^{-1}. Space group $P2_12_12_1$ from systematic absences; $h00$ for h odd, $0k0$ for k odd, $00l$ for l odd.

A long crystal of cross-section 0.2 × 0.1 mm was cut to a length of 0.5 mm, sealed in a capillary tube, and used for data collection on a Hilger and Watts Y 290 four-circle diffractometer. Cell dimensions were calculated by least-squares treatment of setting angles for 12 reflections. Since the crystal decomposed at room temperature during *ca.* 48 h it was decided to keep the data collection time to a minimum. Intensity data for $2 < \theta < 22°$ were measured for *ca.* 12 h by an ω–2θ step-scan and with graphite-monochromated Mo-K_α radiation. Peak counts were measured over 15 s with 7.5 s each for background counts at either end of the scan. Three standard reflections remeasured every 100 reflections showed no significant variation. The 1 148 reflections measured were corrected for Lorentz and polarisation effects but not for absorption. For the structure refinement the 783 reflections with $I > 3\sigma(I)$ were used, where $\sigma(I)$ was calculated from counting statistics.

The structure was solved by direct methods and carbon and oxygen atoms refined anisotropically by full-matrix least-squares to R 0.094. A weighted difference-Fourier map showed the positions of all the hydrogen atoms which were included in further refinements at fixed positions with isotropic thermal parameters equal to those of the carbon atoms to which they were attached. Convergence was reached at R 0.062, R' 0.077, when the maximum shift-to-error ratio was 0.05. A final difference map was everywhere < 0.2 eÅ^{-3}.

In the least-squares refinement neutral atom scattering factors were taken from ref. 17 and the weighting scheme used was $w = 1.97/[\sigma^2(F) + 0.000\,94F^2]$. No attempt was made to define the absolute configuration. The structure analysis was done with the SHELX program system.[18] Final atomic co-ordinates are listed in Table 1. Anisotropic thermal parameters, H atom positions, torsion angles, and a listing of final structure factors have been deposited as Supplementary Publication No. SUP 22356 (9 pp., 1 microfiche).*

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