Crystal and Molecular Structures of 8-Bromo-6,7-dioxabicyclo[3.2.1]octane, 9-Bromo-7,8-dioxabicyclo[4.2.1]nonane, and 10-Bromo-8,9-dioxabicyclo-[5.2.1]decane

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The crystal structures of the title saturated bicyclic [n.2.1] peroxides confirm the previous suggestion, based on n.m.r. data and mechanistic considerations, that in each compound the bromine atom is *syn* to the dioxygen bridge. The C–O–O–C dihedral angles are 0(1), 14(1), and 45(1)° respectively, while the corresponding O–O bond lengths are 1.498(8), 1.447(8), and 1.463(7) Å. The six-, seven-, and eight-membered carbocyclic rings adopt chair, chair, and chair-chair conformations respectively. A comparison of the [3.2.1] compound with its homologues, and with 47 other cyclic or bicyclic peroxides, suggests that its O–O bond is relatively long, and that this arises because of bond angle strain primarily at the bromine-bearing carbon atom.

In the course of our studies on prostaglandin endoperoxide model compounds we prepared a homologous series of $(n + 5)$-bromodioxabicyclo[n.2.1]alkanes $(n = 2—5)$.[1] Mechanistic considerations rendered it likely that in each of these compounds the bromine atom would be *syn* to the dioxygen bridge [*i.e.* structure (2)]. Such a configuration was supported by [1]H n.m.r. data for the [2.2.1] and [3.2.1] peroxides, but no evidence was obtained to confirm analogous structures for the higher homologues. Furthermore, the mechanistic argument was weakened by the fact that the *cis-2-trans*-3, and *trans-2-cis*-3 configurations could not be assigned with certainty to the diastereoisomers of 2,3-dibromocyclo-heptyl and -octyl hydroperoxides [(1; n = 4,5)], and by the fact that both isomers gave the *same* bicyclic peroxides upon treatment with silver trifluoroacetate [equation (1)].

The conformational rigidity of bicyclic peroxides makes them attractive candidates for physicochemical studies aimed at probing the angular dependence of lone pair–lone pair interactions in the O–O bond. Thus, attempts have been made to correlate photoelectron (p.e.) spectra with C–O–O–C dihedral angles,[2] but these were severely handicapped by the lack of experimental structural data, and conflicting conclusions were reached. The crystal structure of 1,4-diphenyl-2,3-dioxabicyclo-[2.2.1]heptane has been investigated[3] to see if the O–O distance provides any evidence for destabilisation of the peroxide bond as a result of vicinal lone pair repulsions being maximised by an enforced dihedral angle of 0°. The O–O bond length was found to be unusually long [1.501(2) Å], but it was conceded that bond angle strain as well as lone pair repulsions contribute to this result.

We have determined the crystal structures of three bromo-dioxabicyclo[n.2.1]alkanes $(n = 3—5)$[1] with the following aims: (i) to confirm the stereochemical disposition of the bromine atoms, (ii) to provide measured C–O–O–C dihedral angles for correlation with p.e. spectroscopic data, (iii) to contribute to attempts to identify the factors which influence O–O bond lengths, and (iv) to provide the first structural study of the 2,3-dioxabicyclo[2.2.1]heptane nucleus of prostaglandin endoperoxides.

Results and Discussion

The bond lengths, bond angles, and the C–O–O–C dihedral angles for the three peroxides are given in Tables 1—3.†
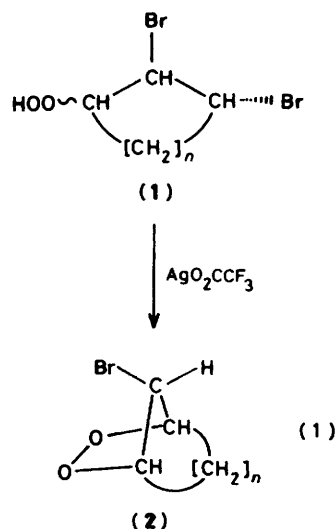
Figures 1–3 are views of the three molecules showing the numbering schemes used for non-hydrogen atoms.

Orientation of the Bromine Atom.—The results show that in all three peroxides the bromine atom is *syn* to the dioxygen bridge. This verifies the assignments previously made and adds support to the suggestion that dioxabicyclisation [equation (1)] occurs by displacement of the 3-bromine with inversion of configuration, the stereochemistry at the 2-position being unaffected.[1]

Correlation with P.e. Spectra.—Calculations suggest that the highest occupied molecular orbital of a dialkyl peroxide arises from the out-of-phase linear combination of the $2p_x$ orbitals on the two oxygen centres.[2c] They also predict a dependence of the difference in energy between this and the next highest peroxide orbital upon the C–O–O–C dihedral angle (θ). This has been

† Crystals of the [3.2.1] bromoperoxide contain two symmetry-unrelated molecules whose structures are the same within experimental error.

Table 1. Bond lengths (Å) and bond angles (°) for the [3.2.1] bromoperoxide

C(11)–Br(1)	1.941(10)	O(12)–O(11)	1.498(8)
C(12)–O(11)	1.435(10)	C(16)–O(12)	1.439(10)
C(12)–C(11)	1.523(13)	C(13)–C(12)	1.488(13)
C(14)–C(13)	1.538(15)	C(15)–C(14)	1.524(16)
C(16)–C(15)	1.488(14)	C(16)–C(11)	1.507(12)
C(21)–Br(2)	1.938(10)	O(22)–O(21)	1.497(8)
C(22)–O(21)	1.446(10)	C(26)–O(22)	1.448(10)
C(22)–C(21)	1.502(13)	C(26)–C(21)	1.471(12)
C(23)–C(22)	1.520(14)	C(24)–C(23)	1.524(14)
C(25)–C(24)	1.491(12)	C(26)–C(25)	1.517(13)

C(12)–O(11)–O(12)	105.8(6)	C(16)–O(12)–O(11)	106.5(6)
C(12)–C(11)–Br(1)	112.3(6)	C(16)–C(11)–Br(1)	111.7(6)
C(16)–C(11)–C(12)	98.6(7)	C(11)–C(12)–O(11)	103.0(7)
C(13)–C(12)–O(11)	111.6(8)	C(13)–C(12)–C(11)	109.9(8)
C(14)–C(13)–C(12)	109.3(9)	C(15)–C(14)–C(13)	112.1(9)
C(16)–C(15)–C(14)	110.3(9)	C(11)–C(16)–O(12)	102.8(7)
C(15)–C(16)–O(12)	110.6(8)	C(15)–C(16)–C(11)	110.2(8)
C(22)–O(21)–O(22)	106.3(6)	C(26)–O(22)–O(21)	104.5(6)
C(22)–C(21)–Br(2)	112.8(6)	C(26)–C(21)–Br(2)	112.6(7)
C(26)–C(21)–C(22)	99.3(8)	C(21)–C(22)–O(21)	102.3(7)
C(23)–C(22)–O(21)	110.9(8)	C(23)–C(22)–C(21)	109.1(7)
C(24)–C(23)–C(22)	110.8(8)	C(25)–C(24)–C(23)	112.4(8)
C(26)–C(25)–C(24)	110.3(8)	C(21)–C(26)–O(22)	104.3(7)
C(25)–C(26)–O(22)	110.3(8)	C(25)–C(26)–C(21)	110.9(8)

C(12)–O(11)–O(12)–C(16)	0(1)
C(22)–O(21)–O(22)–C(26)	1(1)

**Table 2.** Bond lengths (Å) and bond angles (°) for the [4.2.1] bromoperoxide

C(2)–Br	1.931(11)	O(2)–O(1)	1.447(8)
C(7)–O(1)	1.460(12)	C(2)–O(2)	1.424(12)
C(2)–C(1)	1.486(14)	C(7)–C(1)	1.499(13)
C(2)–C(2)	1.512(16)	C(4)–C(3)	1.508(18)
C(5)–C(4)	1.374(19)	C(6)–C(5)	1.513(22)
C(7)–C(6)	1.537(14)		

C(7)–O(1)–O(2)	108.1(6)	C(2)–O(2)–O(1)	107.4(7)
C(2)–C(1)–Br	110.7(7)	C(7)–C(1)–Br	111.9(8)
C(7)–C(1)–C(2)	103.8(9)	C(1)–C(2)–O(2)	103.0(8)
C(3)–C(2)–O(2)	111.2(9)	C(3)–C(2)–C(1)	115.7(10)
C(4)–C(3)–C(2)	117.0(10)	C(5)–C(4)–C(3)	121.5(15)
C(6)–C(5)–C(4)	121.9(13)	C(7)–C(6)–C(5)	117.4(10)
C(1)–C(7)–O(1)	103.6(8)	C(6)–C(7)–O(1)	109.5(8)
C(6)–C(7)–C(1)	115.1(10)		

C(2)–O(1)–O(2)–C(7)	14(1)

Table 3. Bond lengths (Å) and bond angles (°) for the [5.2.1] bromoperoxide

C(1)–Br	1.974(7)	O(2)–O(1)	1.463(7)
C(8)–O(1)	1.434(8)	C(2)–O(2)	1.448(8)
C(2)–C(1)	1.526(9)	C(8)–C(1)	1.495(9)
C(3)–C(2)	1.508(10)	C(4)–C(3)	1.518(10)
C(5)–C(4)	1.520(11)	C(6)–C(5)	1.531(12)
C(7)–C(6)	1.519(10)	C(8)–C(7)	1.511(10)

C(8)–O(1)–O(2)	102.3(5)	C(2)–O(2)–O(1)	105.3(5)
C(2)–C(1)–Br	109.7(4)	C(8)–C(1)–Br	110.9(5)
C(8)–C(1)–C(2)	105.1(6)	C(1)–C(2)–O(2)	103.6(5)
C(3)–C(2)–O(2)	107.4(6)	C(3)–C(2)–C(1)	114.9(6)
C(4)–C(3)–C(2)	118.0(6)	C(5)–C(4)–C(3)	118.8(6)
C(6)–C(5)–C(4)	117.8(7)	C(7)–C(6)–C(5)	117.3(7)
C(8)–C(7)–C(6)	120.3(6)	C(1)–C(8)–O(1)	103.0(5)
C(7)–C(8)–O(1)	113.9(6)	C(7)–C(8)–C(1)	115.3(6)

C(2)–O(1)–O(2)–C(8)	45(1)
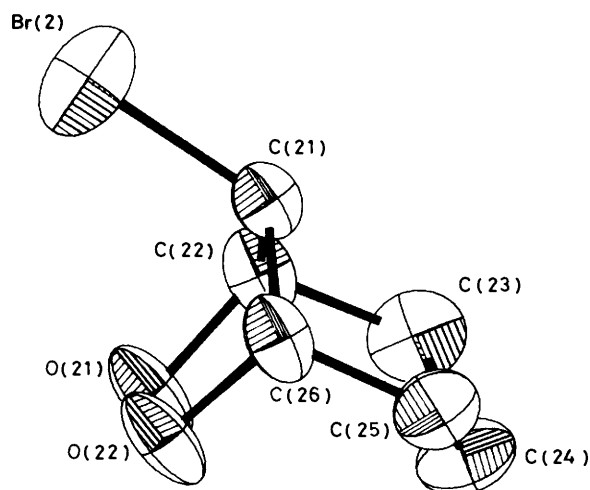
Figure 1. A molecule of 8-bromo-6,7-dioxabicyclo[3.2.1]octane showing the numbering scheme used for non-hydrogen atoms. Thermal ellipsoids are at 50% probability

examined experimentally by measuring the p.e. spectra of several cyclic and bicyclic peroxides, where conformational mobility about the O–O bond is considerably restricted. The results are in broad agreement with theory in that the separation (ΔI) of the bands assigned to ionisation events from the first two peroxide orbitals gets smaller as θ increases in the range 0—90°. However, the exact form of the relationship is uncertain since linear dependencies of ΔI upon θ^{2a} and $\cos \theta^{2b,c}$ have been proposed. That the results appear to fit either correlation stems from the fact that there are large uncertainties in the values of θ taken, since these were merely estimated from Dreiding models.

By measuring the p.e. spectra[4] and the dihedral angles of these three peroxides, we have begun to provide a firm experimental basis upon which to clarify the nature of the relationship between θ and ΔI. However, more such data are required before

a satisfactory conclusion can be reached, and it is also desirable to attempt to establish whether or not there are any significant structural changes upon going from the crystal to the gas phase.

An important conclusion from our p.e. spectroscopic work was that the second band for the [3.2.1] compound (ignoring those due to ionisations from the bromine lone pair orbitals) arises from a high lying σ-orbital and not from a peroxide orbital. This serves as a warning against the indiscriminate use of the ΔI value between the first and second bands to estimate C–O–O–C dihedral angles. Structural parameters for 8-bromo-6,7-dioxabicyclo[3.2.1]octane determined in this work were used in the calculations of orbital energies for the parent [3.2.1] peroxide. A full discussion of these results has appeared elsewhere.[4]

O–O *Bond Lengths.*—A search of the Cambridge Data Centre files provided 45 crystallographic structures in which the C–O–O–C unit is present and incorporated into a ring. These include a wide variety of peroxide types, such as dioxetanes, dioxolanes, ozonides, dioxanes, trioxanes, tetra-oxanes, and seven-, eight-, and nine-membered rings. We were also aware of very recent X-ray work on two unsaturated [3.2.2] endoperoxides[5] and on three dioxetanes.[6b]
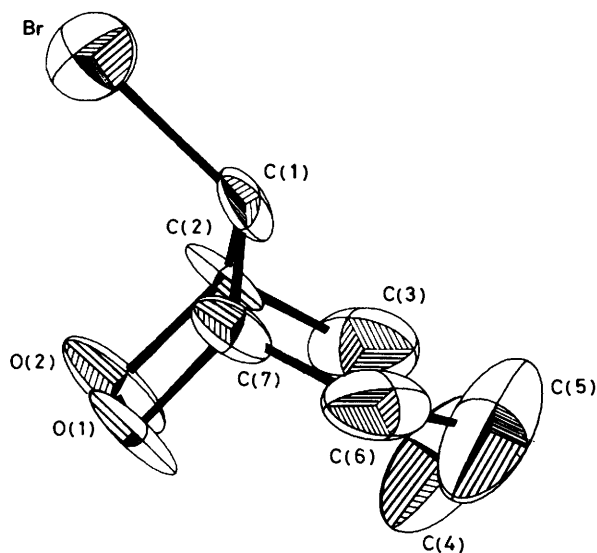
Figure 2. A molecule of 9-bromo-7,8-dioxabicyclo[4.2.1]nonane showing the numbering scheme used for non-hydrogen atoms. Thermal ellipsoids are at 50% probability
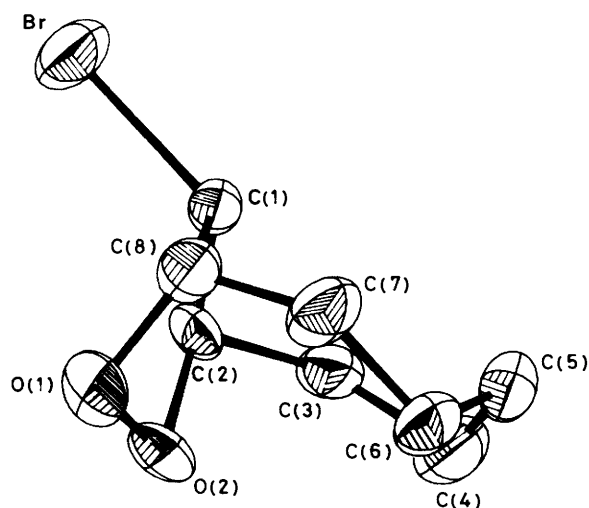

Figure 3. A molecule of 10-bromo-8,9-dioxabicyclo[5.2.1]decane showing the numbering scheme used for non-hydrogen atoms. Thermal ellipsoids are at 50% probability

The reported O–O distances lie between 1.44 and 1.58 Å, but only 10% of them are less than 1.46 Å and only 20% are greater than 1.49 Å. There does not appear to be a common factor for the appearance of 'short' O–O bonds, the relevant compounds being a dioxacyclo-octane,[7] a tetraoxane,[8] a dioxolane,[9] and a dioxetane.[10] However, given that our [4.2.1] bromoperoxide falls into this category, it is perhaps noteworthy that two of these compounds[8-10] contain bromomethyl groups attached to the peroxide carbon atoms.

It is striking, on the other hand, that more than half of the 'long' O–O bonds are found in dioxetanes.[6,10,11] Furthermore, only two[10] of the nine[6,10-12] dioxetanes that have been examined have O–O distances significantly *less* than 1.49 Å, while the C–O–O–C dihedral angles vary from 0 to 30°. On this basis, it seems justifiable to conclude that bond angle strain can cause a significant lengthening of the O–O bond.

Of the remaining three structures containing 'long' O–O

Table 4. Crystal data

	$C_6H_9BrO_2$	$C_7H_{11}BrO_2$	$C_8H_{13}BrO_2$
M.W.	193.05	207.07	221.10
Crystal system	Monoclinic	Monoclinic	Monoclinic
$a/Å$	9.579(1)	8.870(1)	26.461(2)
$b/Å$	16.885(2)	5.441(1)	5.603(1)
$c/Å$	9.775(1)	16.845(2)	13.175(1)
$\beta/Å$	115.44(1)	91.547(8)	115.121(6)
$U/Å^3$	1 427.60	812.35	1 768.49
Space group	$P2_1/c$	$P2_1/c$	$C2/c$
Z	8	4	8
$D_c/g\ cm^{-3}$	1.80	1.69	1.66
$F(000)$	720	416	896
$\mu(Mo\text{-}K_\alpha)/cm^{-1}$	55.46	48.77	44.85
T/K	295	265	260
θ range (°)	1.5—25	1.5—25	1.5—25
Total unique data	2 498	1 428	1 562
Observed data	1 561	789	1 093
Significance test	$F > 3\sigma(F_o)$	$F > 4\sigma(F_o)$	$F > 3\sigma(F_o)$
No. of parameters	187	117	152
Weighting scheme coefficient g in $w = 1/[\sigma^2(F_o) + gF_o^2]$	0.0005	0.0001	0.000 45
Final $R = \Sigma\Delta F/\Sigma F_o$	0.0653	0.0484	0.0414
$R' = [\Sigma w \Delta F^2/\Sigma w F_o^2]^{\frac{1}{2}}$	0.0648	0.0502	0.0462

bonds, two of them, namely 1,4-diphenyl-2,3-dioxabicyclo-[2.2.1]heptane[3] and 3,5-dimethyl-8,9,10,11-tetraoxatricyclo-[5.2.1.1^{2,6}]undecan-4-one[13] (which contains a bicyclic [3.2.1] ozonide unit) have C–O–O–C dihedral angles (θ) of 0°. Given that our [3.2.1] bromoperoxide also has a 'long' O–O bond and θ 0°, it is tempting to suggest that maximisation of lone pair repulsions can also lead to lengthening of the O–O bond. However, there is also bond angle strain in the five-membered rings of all three examples. This is concentrated not at the peroxide oxygen atoms, where the angles are within 2° of the value [105.2(5)°] found for gaseous dimethyl peroxide,[14] but mainly at the single bridging atom (93° in the [2.2.1] peroxide,[3] 99° in the ozonide,[13] and 99° in our [3.2.1] peroxide). Furthermore, in the two [3.2.2] endoperoxides where the C–O–O–C dihedral angles are very small (4.9 and 5.9°) but where there is little or no bond angle strain, the O–O bond lengths are normal [1.473(5) and 1.472(7) Å]. Thus, the data collected so far suggest that bond angle strain is the major factor leading to 'long' O–O bonds.

Crystallographic Studies.—Crystal data for the compounds are listed in Table 4. Intensities were collected on a Nonius CAD4 diffractometer (Mo-K_α radiation) using standard procedures as outlined previously.[15] Monitoring of three standard reflections every hour during data collection revealed an isotropic decay of 10 and 17% for the [4.2.1] and [5.2.1] bromoperoxides, respectively, even though the data were collected at reduced temperatures. Intensity data, corrected for Lorentz and polarisation effects, were rescaled for decay and empirical absorption corrections applied.

Solution of all three structures was achieved by the heavy atom method. At the stage of isotropic refinement of all non-hydrogen atoms the DIFABS[16] method of absorption correction was applied. Following full-matrix least-squares refinement[17] with anisotropic thermal parameters, hydrogen atoms were located from difference maps. The [4.2.1] bromoperoxide exhibited high thermal motion consistent with conformational flexibility of the basal ring and hydrogens on C(4) and C(5) were not located or included, whereas those on all other carbons were located and refined with isotropic group thermal parameters. All hydrogens for the [5.2.1] bromoperoxide were refined with individual isotropic temperature

Table 5. Fractional atomic co-ordinates ($\times 10^4$) for the [3.2.1] bromo-peroxide

	x	y	z
Br(1)	−559(1)	5 735(1)	2 115(1)
Br(2)	−5 254(1)	4 550(1)	2 072(1)
O(11)	965(6)	4 286(4)	4 409(6)
O(12)	1 793(6)	4 286(4)	3 411(6)
O(21)	2 936(5)	6 202(4)	1 688(7)
O(22)	3 894(6)	6 340(4)	839(6)
C(11)	−764(8)	4 592(5)	1 951(8)
C(12)	−646(9)	4 210(5)	3 409(9)
C(13)	−1 123(10)	3 365(6)	3 128(12)
C(14)	−3(11)	2 914(6)	2 657(12)
C(15)	305(11)	3 359(6)	1 457(11)
C(16)	625(8)	4 209(5)	1 880(9)
C(21)	−4 710(8)	5 595(5)	2 968(9)
C(22)	−5 998(9)	5 982(5)	3 211(9)
C(23)	−5 373(10)	6 710(5)	4 200(10)
C(24)	−4 745(11)	7 308(5)	3 436(11)
C(25)	−3 771(9)	6 928(5)	2 772(10)
C(26)	−4 537(8)	6 177(5)	1 932(9)

Table 6. Fractional atomic co-ordinates ($\times 10^4$) for the [4.2.1] bromo-peroxide

	x	y	z
Br	1 225(1)	1 654(2)	1 060(1)
O(1)	−1 575(8)	5 323(12)	1 777(3)
O(2)	−1 538(9)	5 626(12)	925(4)
C(1)	−934(10)	1 629(21)	1 180(5)
C(2)	−1 685(10)	3 247(18)	579(5)
C(3)	−3 317(12)	2 653(28)	379(7)
C(4)	−4 393(13)	2 651(38)	1 057(9)
C(5)	−4 142(14)	1 213(31)	1 718(11)
C(6)	−2 838(13)	1 685(21)	2 296(7)
C(7)	−1 376(10)	2 716(16)	1 957(5)

Table 7. Fractional atomic co-ordinates ($\times 10^4$) for the [5.2.1] bromo-peroxide

	x	y	z
Br	382(.5)	1 439(1)	1 529(.5)
O(1)	1 032(2)	5 705(7)	619(3)
O(2)	1 584(2)	4 699(7)	1 290(3)
C(1)	905(2)	1 717(11)	822(4)
C(2)	1 481(2)	2 440(11)	1 700(4)
C(3)	1 948(2)	770(13)	1 807(5)
C(4)	2 148(3)	794(14)	883(5)
C(5)	1 719(3)	530(13)	−326(5)
C(6)	1 419(3)	2 785(13)	−946(5)
C(7)	832(3)	3 215(14)	−1 055(5)
C(8)	733(2)	3 684(11)	−25(4)

parameters whilst those of the [3.2.1] bromoperoxide were assigned idealized positions and refined with a damping factor.

Final fractional co-ordinates are in Tables 5—7. Thermal parameters are available as a Supplementary Publication (SUP No. 56552, 6 pp.). Observed and calculated structure factors are available on request from the editorial office.

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