Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	0.1467 (2)	0.3577 (3)	0.1873 (3)	0.0484
C(2)	0.2151 (2)	0.4397 (3)	0.3165 (4)	0.0563
O(3)	0.1746 (1)	0.2779 (2)	0.1028 (3)	0.0743
C(3)	0.0439 (2)	0.3756 (2)	0.1710 (3)	0.0438
C(4)	−0.0195 (2)	0.2926 (2)	0.0672 (4)	0.0546
C(5)	−0.1150 (2)	0.3032 (3)	0.0531 (4)	0.0626
C(6)	−0.1477 (2)	0.3969 (3)	0.1418 (4)	0.0645
C(7)	−0.0866 (2)	0.4819 (3)	0.2413 (4)	0.0609
C(8)	0.0096 (2)	0.4709 (2)	0.2566 (4)	0.0531
C(9)	0.3169 (2)	0.4175 (2)	0.3198 (3)	0.0458
C(10)	0.3632 (2)	0.4953 (3)	0.2291 (4)	0.0553
C(11)	0.4574 (2)	0.4779 (3)	0.2354 (4)	0.0610
C(12)	0.5043 (2)	0.3824 (3)	0.3341 (4)	0.0538
C(13)	0.4607 (2)	0.3033 (3)	0.4241 (4)	0.0623
C(14)	0.3663 (2)	0.3206 (3)	0.4163 (4)	0.0599
N(13)	0.6055 (2)	0.3662 (3)	0.3463 (4)	0.0839
O(14)	0.6480 (2)	0.2864 (3)	0.4448 (4)	0.1201
O(15)	0.6415 (2)	0.4368 (3)	0.2590 (4)	0.1316

Table 2. *Geometric parameters* (Å, °)

C(1)—C(2)	1.512 (3)	C(9)—C(10)	1.377 (4)
C(1)—O(3)	1.214 (4)	C(9)—C(14)	1.380 (4)
C(1)—C(3)	1.494 (3)	C(10)—C(11)	1.383 (4)
C(2)—C(9)	1.506 (4)	C(11)—C(12)	1.363 (4)
C(3)—C(4)	1.392 (3)	C(12)—C(13)	1.359 (4)
C(3)—C(8)	1.385 (4)	C(12)—N(13)	1.473 (4)
C(4)—C(5)	1.380 (4)	C(13)—C(14)	1.382 (4)
C(5)—C(6)	1.375 (4)	N(13)—O(14)	1.214 (4)
C(6)—C(7)	1.375 (4)	N(13)—O(15)	1.223 (5)
C(7)—C(8)	1.389 (4)		
O(3)—C(1)—C(3)	121.0 (2)	C(2)—C(9)—C(10)	120.5 (2)
C(2)—C(1)—C(3)	117.9 (2)	C(10)—C(9)—C(14)	118.7 (3)
C(2)—C(1)—O(3)	121.0 (2)	C(9)—C(10)—C(11)	121.0 (3)
C(1)—C(2)—C(9)	114.1 (2)	C(10)—C(11)—C(12)	118.8 (3)
C(1)—C(3)—C(8)	122.4 (2)	C(11)—C(12)—N(13)	118.9 (3)
C(1)—C(3)—C(4)	118.7 (2)	C(11)—C(12)—C(13)	121.8 (3)
C(4)—C(3)—C(8)	119.0 (2)	C(13)—C(12)—N(13)	119.3 (3)
C(3)—C(4)—C(5)	120.6 (3)	C(12)—C(13)—C(14)	119.2 (3)
C(4)—C(5)—C(6)	119.7 (3)	C(9)—C(14)—C(13)	120.6 (3)
C(5)—C(6)—C(7)	120.7 (3)	C(12)—N(13)—O(15)	117.3 (3)
C(6)—C(7)—C(8)	119.7 (3)	C(12)—N(13)—O(14)	118.3 (3)
C(3)—C(8)—C(7)	120.3 (3)	O(14)—N(13)—O(15)	124.4 (3)
C(2)—C(9)—C(14)	120.8 (2)		

min^{-1} in θ. The lattice parameters were determined from a symmetry-constrained least-squares fit. Refinement was based on full-matrix least-squares methods with H atoms in calculated positions (C—H 0.96 Å).

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates, and a stereoscopic view of the compound have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54995 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1007]

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Structural Aspects of Reactions Based on 'Aggregative Activation': Structures of 3-Oxatricyclo[6.3.0.0^{2,7}]undec-6-en-1-ol and 6,7-Epoxy-3-oxatricyclo[6.4.0.0^{2,7}]dodecan-1-ol

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Abstract

The preparation of the title compounds is described. The former was obtained by an 'aggregative activation' reaction of dehydrodihydropyran with bases, and the latter by epoxidation of one of the so-obtained alcohols. Structure analysis shows that complexation of the oxidizing agent by the hydroxyl group directs the stereoselectivity of epoxidation. The influence of epoxidation on the conformation of the three-ring system in these molecules is discussed. The rigidity of the molecules and hydrogen bonding explain the absence of significant anisotropies in the atomic displacements, so a satisfactory description of the displacements is obtained by the rigid-body model.

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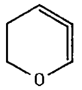
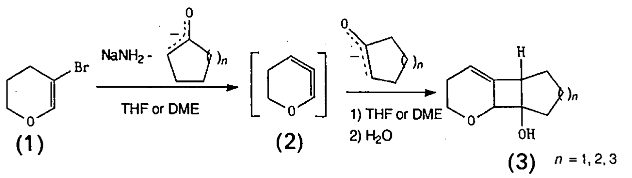
Comment

Dehydrodihydropyran (1) is a very interesting short-lived electrophilic intermediate.

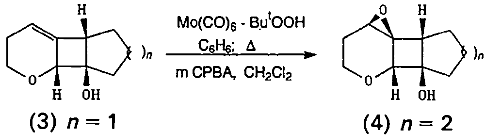


However, it has never been used in organic synthesis because it was very difficult to generate in a nucleophilic environment. Using the principle of 'aggregative activation' (Caubère, 1989, 1991), which covers all the phenomena occurring in complex bases and complex reducing agents, we were able to perform for the first time the reactions shown in the scheme below (THF = tetrahydrofuran, DME = dimethoxyethane).



Additionally, in order to establish the stereochemistry of this new family of compounds, we studied the crystal structure of (3) with $n = 1$. From the knowledge of this structure and the usual spectroscopic data, we were also able to deduce the structure of (3) with $n = 2$.

In order to use alcohols (3) as starting materials for further synthesis, the study of their epoxidation with peracids was carried out considering the oxidations given in the scheme below (the configurations shown were inferred from the crystal structure analysis).



The formation of only one isomer was observed and the crystal structure of (4) with $n = 2$ was determined. In the present paper the results of these structure analyses are reported; they show that epoxidation takes place on the same side of the double bond as the hydroxyl group. Thus, the regioselectivity of epoxidation could be explained by a complexation of the metal centre by the hydroxyl group. This hypothesis is in agreement with those given by Chong & Sharpless (1977) for epoxidation of allyl alcohol.

Fig. 1 shows *ORTEP* diagrams of the molecules of the two compounds and in Table 2 their bond distances and angles are compared. There are no significant differences between the two crystallographically independent molecules found in the crystal of compound (3), so in the following discussion their averaged values will be used.

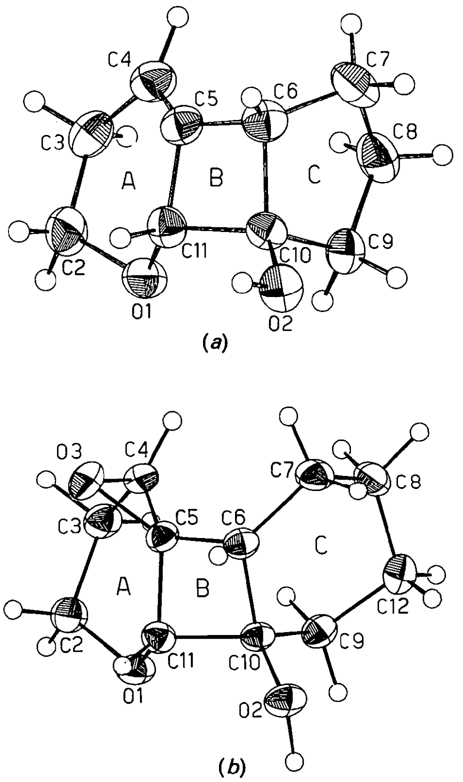


Fig. 1. *ORTEP* (Johnson, 1965) drawings of the molecules: (*a*) compound (3), molecule *B*; (*b*) compound (4). Ellipsoids at 50% probability.

In these molecules there are three chiral centres with the *S* (C6), *R* (C10), *R* (C11) configurations in compound (3) and *R* (C6), *R* (C10), *S* (C11) configurations in compound (4) (the changes are due to epoxidation, which inverts the priority of C5 with respect to C10 in the two compounds). The enantiomers are, of course, also present, the space groups of both compounds being centrosymmetric.

The epoxidation and the different number of C atoms in the cycloalkane rings influence the conformations of the molecules of the two compounds; in particular, the dihedral angles between the mean least-squares planes through the rings are affected: that between rings *A* and *B* is narrowed, while that between rings *B* and *C* is enlarged, the first as a consequence of the addition of the epoxy O atom, the second due to the enlargement of the ring (Table 3).

A better comparison of the conformations about the cyclobutane bonds is given by the Newman projections of Fig. 2, which show that epoxidation causes the C5–C4 bond to be more eclipsed with respect to the C11–O1 and C6–C7 bonds. Increasing the number of the C atoms in the C6...C10 cycloalkane ring causes an enlargement of the C7–C6–C10–C9 torsion angle which increases from 13.5(3)° in compound (3) to 32.4(2)° in compound (4).

The geometry of the epoxy ring agrees well with average values from the literature: C–C = 1.473(2), C–O

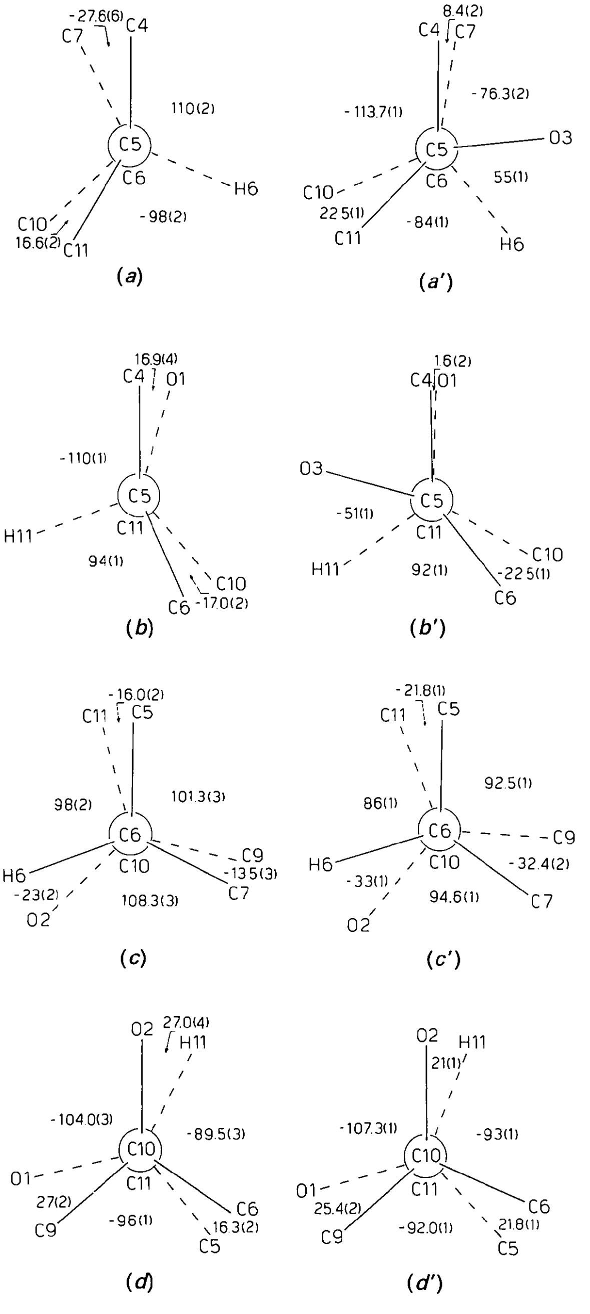


Fig. 2. Newman projections along the cyclobutane bonds: (*a*)–(*d*) compound (3), (*a'*)–(*d'*) compound (4).

= 1.451(1) Å, C–C–O = 59.48(8), C–O–C = 61.0(1)° (Adovasio, Nardelli & Saba, 1991). Its orientation is defined by the C11–C5–C4–O3 = 114.8(1) and C2–C3–C4–O3 = −50.2(2)° torsion angles. It is worth noting that epoxidation occurs at the *exo* side of the ring system and is directed by the hydroxyl group in the same way as for allylic alcohols. The chemistry of these epoxy alcohols will be actively pursued.

Despite epoxidation, the puckering of ring *A* (Table 3) does not change significantly, while the conformation becomes intermediate between half-chair and sofa. The two C–O distances show a systematic difference: O1–C11 = 1.422(1) av. is significantly shorter than O1–C2 = 1.442(2) Å av. ($\Delta/\sigma = 8.94$).

Epoxidation slightly increases the puckering of the cyclobutane ring and slightly influences the endocyclic angles at C5 and C11, which become narrower by 1.5 and 2.0°, respectively. The endocyclic angles at C6 and C10 are not affected by epoxidation nor by the change of the C ring size. This change does not seem to have a significant influence on the length of the C6–C10 bond ($\Delta/\sigma = 2.79$).

An analysis of the anisotropic atomic displacements, carried out in terms of the **TLS** rigid-body approximation according to Schomaker & Trueblood (1968) and Trueblood (1984), gives satisfactory agreements between the calculated and observed tensor matrix elements (Table 4), indicating that the internal motions are not very important. This can also be seen from the atomic ellipsoids of Fig. 1 and from the values of the ratios of the principal axes of these ellipsoids (deposited). This rigidity of the structure is probably due to the absence in the molecules of moieties possessing conformational freedom, the only one being the OH group (it shows the greatest anisotropy) which is restrained by the following hydrogen bonds with adjacent molecules: compound (3) O2*A*–H2O*A* = 0.88(4), O2*A*···O2*B* = 2.875(3), H2O*A*···O2*B* = 2.01(3) Å, O2*A*–H2O*A*···O2*B* = 167(3)°, O2*B*–H2O*B* = 0.82(4), O2*B*···O1*A*^{i} = 2.775(3), H2O*B*···O1*A*^{i} = 2.07(4) Å, O2*B*–H2O*B*···O1*A*^{i} = 145(4)° [(i) = $x-1$, y, z]; compound (4) O2–H2O = 1.00(2), O2···O1^{ii} = 2.807(2), H2O···O1^{ii} = 1.81(4) Å, O2–H2O···O1^{ii} = 173(4)° [(ii) = $-x$, $1-y$, $-z$].

The packing of the two independent molecules in the unit cell of compound (3) is illustrated in the *PLUTO* drawing of Fig. 3 which shows that the two molecules

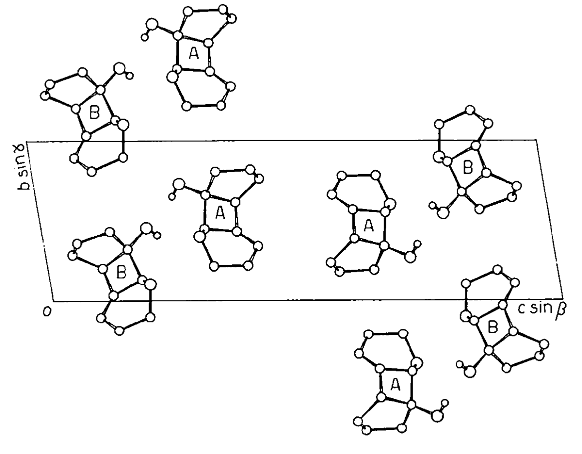


Fig. 3. Packing of the two independent molecules in the unit cell of the crystals of compound (3).

are related by a local pseudo-twofold screw axis approximately parallel to the *bc* plane running along *b* at *ca* 1/4*c*. It is important to note that there is no approximate symmetry for the hydrogen bonds molecules *A* and *B* form in the crystal.

Experimental

Compound (3)

Crystal data

$C_{10}H_{14}O_2$
$M_r = 166.22$
Triclinic
$P\bar{1}$
$a = 5.493$ (4) Å
$b = 7.262$ (5) Å
$c = 22.459$ (15) Å
$\alpha = 98.51$ (3)°
$\beta = 93.75$ (3)°
$\gamma = 102.53$ (2)°
Cell parameters from 30 reflections
$\theta = 9–19°$

$V = 860.5$ (1.0) Å^3
$Z = 4$
$D_x = 1.283$ Mg m^{-3}
Mo $K\alpha_1$
$\lambda = 0.709300$ Å
$\mu = 0.0820$ mm^{-1}
$T = 293$ (2) K
Small prisms
0.51 × 0.39 × 0.23 mm
Colourless
Crystal source: chemical synthesis (see text)

Data collection

Siemens AED diffractometer
θ–2θ scans
Absorption correction: none
3052 measured reflections
1638 observed reflections [$I > 2\sigma(I)$]
$\theta_{\max} = 25°$

$h = -6 \rightarrow 6$
$k = -8 \rightarrow 8$
$l = 0 \rightarrow 26$
1 standard reflection monitored every 50 reflections
intensity variation: none

Refinement

Refinement on F
Final $R = 0.0351$

All H-atom parameters refined

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Compound (3)				
O1*A*	0.6234 (3)	−0.3994 (3)	−0.30823 (7)	0.0426 (6)
O2*A*	0.0797 (4)	−0.7315 (3)	−0.28575 (9)	0.0522 (8)
C2*A*	0.7121 (6)	−0.2152 (4)	−0.3261 (1)	0.0507 (11)
C3*A*	0.6616 (6)	−0.2176 (5)	−0.3930 (1)	0.0492 (11)
C4*A*	0.4062 (5)	−0.3378 (4)	−0.4184 (1)	0.0458 (10)
C5*A*	0.2666 (5)	−0.4324 (4)	−0.3826 (1)	0.0378 (9)
C6*A*	0.0619 (5)	−0.6134 (4)	−0.3891 (1)	0.0426 (9)
C7*A*	0.0732 (6)	−0.7640 (5)	−0.4430 (1)	0.0534 (11)
C8*A*	0.3208 (6)	−0.8199 (5)	−0.4289 (1)	0.0533 (12)
C9*A*	0.3500 (6)	−0.8081 (4)	−0.3602 (1)	0.0437 (11)
C10*A*	0.2113 (5)	−0.6608 (4)	−0.3331 (1)	0.0379 (9)
C8*B*	0.2751 (6)	−0.3589 (5)	−0.0659 (1)	0.0527 (12)
C11*A*	0.3575 (4)	−0.4487 (3)	−0.3201 (1)	0.0350 (9)
O1*B*	0.4556 (3)	−0.1029 (2)	−0.19615 (8)	0.0480 (7)
O2*B*	−0.1039 (4)	−0.4550 (3)	−0.20662 (8)	0.0455 (7)
C2*B*	0.5616 (7)	0.1009 (4)	−0.1852 (1)	0.0517 (11)
C3*B*	0.5798 (5)	0.1880 (4)	−0.1191 (1)	0.0470 (11)
C4*B*	0.3540 (5)	0.1053 (4)	−0.0887 (1)	0.0456 (10)
C5*B*	0.1779 (5)	−0.0343 (4)	−0.1201 (1)	0.0385 (9)
C6*B*	−0.0204 (5)	−0.2027 (4)	−0.1084 (1)	0.0430 (10)
C7*B*	0.0388 (6)	−0.2860 (5)	−0.0527 (1)	0.0548 (11)
C9*B*	0.2405 (5)	−0.4317 (4)	−0.1337 (1)	0.0409 (10)
C10*B*	0.0718 (4)	−0.3219 (3)	−0.1629 (1)	0.0345 (9)
C11*B*	0.2041 (5)	−0.1319 (4)	−0.1814 (1)	0.0383 (9)
Compound (4)				
O1	0.0633 (1)	0.59867 (4)	0.0160 (2)	0.0380 (3)
O2	−0.1743 (2)	0.48968 (5)	−0.3575 (2)	0.0403 (4)
O3	0.0124 (2)	0.69645 (5)	−0.4180 (2)	0.0430 (4)
C2	0.1400 (2)	0.66087 (7)	0.0536 (3)	0.0412 (4)
C3	0.0044 (2)	0.71272 (6)	−0.0074 (2)	0.0388 (5)
C4	−0.0942 (2)	0.70534 (6)	−0.2416 (2)	0.0347 (4)
C5	−0.0821 (2)	0.64359 (6)	−0.3478 (2)	0.0306 (4)
C6	−0.2173 (2)	0.60088 (6)	−0.4830 (2)	0.0312 (4)
C7	−0.4058 (2)	0.62221 (7)	−0.5609 (2)	0.0382 (5)
C8	−0.5130 (2)	0.62744 (7)	−0.3704 (3)	0.0408 (5)
C9	−0.2998 (2)	0.56211 (6)	−0.1113 (2)	0.0338 (4)
C10	−0.1773 (2)	0.55347 (5)	−0.2830 (2)	0.0290 (4)
C11	0.0024 (2)	0.58755 (6)	−0.2154 (2)	0.0315 (4)
C12	−0.4900 (2)	0.56851 (7)	−0.2217 (3)	0.0390 (4)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	Compound (3)			Compound (4)
	Mol. *A*	Mol. *B*	Av.	
O1—C2	1.446 (4)	1.446 (3)	1.446 (3)	1.439 (2)
O1—C11	1.424 (3)	1.420 (3)	1.422 (3)	1.422 (2)
O2—C10	1.420 (3)	1.421 (3)	1.420 (3)	1.417 (2)
O3—C4	-	-	-	1.464 (2)
O3—C5	-	-	-	1.433 (2)
C2—C3	1.507 (4)	1.512 (4)	1.510 (4)	1.516 (2)
C3—C4	1.507 (4)	1.508 (4)	1.508 (4)	1.504 (2)
C4—C5	1.311 (4)	1.317 (3)	1.314 (3)	1.459 (2)
C5—C6	1.515 (3)	1.518 (4)	1.516 (3)	1.513 (2)
C5—C11	1.490 (4)	1.485 (4)	1.488 (4)	1.512 (2)
C6—C7	1.522 (4)	1.514 (5)	1.518 (4)	1.526 (2)
C6—C10	1.579 (4)	1.569 (4)	1.574 (4)	1.559 (2)
C7—C8	1.528 (5)	1.534 (5)	1.531 (5)	1.531 (2)
C8—C9	1.529 (4)	1.521 (4)	1.525 (4)	-
C8—C12	-	-	-	1.525 (2)
C9—C10	1.522 (4)	1.523 (4)	1.522 (4)	1.528 (2)
C9—C12	-	-	-	1.520 (2)
C10—C11	1.550 (3)	1.543 (4)	1.546 (3)	1.558 (2)
C2—O1—C11	107.5 (3)	107.5 (3)	107.5 (3)	111.5 (1)
C4—O3—C5	-	-	-	60.5 (1)
O1—C2—C3	113.4 (3)	112.6 (3)	113.0 (3)	111.4 (1)
C2—C3—C4	112.2 (3)	112.6 (3)	112.4 (3)	112.3 (1)
O3—C4—C3	-	-	-	116.1 (1)
C3—C4—C5	118.9 (3)	118.7 (3)	118.8 (3)	116.6 (1)
O3—C4—C5	-	-	-	58.7 (1)
O3—C5—C4	-	-	-	60.8 (1)
C4—C5—C11	123.6 (3)	123.3 (3)	123.4 (3)	120.9 (1)
C4—C5—C6	137.1 (3)	138.2 (3)	137.6 (3)	132.7 (1)
O3—C5—C11	-	-	-	124.4 (1)
O3—C5—C6	-	-	-	129.9 (1)
C6—C5—C11	93.0 (2)	92.6 (3)	92.8 (2)	91.4 (1)
C5—C6—C10	86.1 (2)	86.0 (2)	86.0 (2)	85.9 (1)
C5—C6—C7	114.3 (3)	115.5 (3)	114.9 (3)	122.3 (1)
C7—C6—C10	106.8 (3)	106.6 (3)	106.7 (3)	119.1 (1)
C6—C7—C8	103.9 (3)	103.7 (3)	103.8 (3)	113.4 (1)
C7—C8—C12	-	-	-	111.1 (1)
C10—C9—C12	-	-	-	112.1 (1)
C7—C8—C9	105.1 (3)	104.8 (3)	105.0 (3)	-
C8—C9—C10	107.7 (3)	107.8 (3)	107.8 (3)	-
C6—C10—C9	104.8 (2)	104.8 (2)	104.8 (2)	112.7 (1)
O2—C10—C9	108.7 (3)	107.8 (3)	108.2 (3)	111.9 (1)
O2—C10—C6	119.7 (3)	120.4 (3)	120.0 (3)	111.7 (1)
C9—C10—C11	117.2 (3)	116.3 (3)	116.8 (3)	113.2 (1)
C6—C10—C11	88.3 (2)	88.5 (2)	88.4 (2)	88.0 (1)
O2—C10—C11	116.8 (3)	117.8 (3)	117.3 (3)	117.3 (1)
C5—C11—C10	88.0 (2)	88.1 (2)	88.0 (2)	86.0 (1)
O1—C11—C10	120.9 (3)	120.7 (3)	120.8 (3)	118.2 (1)
O1—C11—C5	113.5 (3)	113.7 (3)	113.6 (3)	116.0 (1)
C8—C12—C9	-	-	-	110.0 (1)

Table 3. *Puckering parameters and dihedral angles of the least-squares planes through the rings*

Q_T = total puckering amplitude (Cremer & Pople, 1975), DAP = displacement asymmetry parameter (Nardelli, 1983*b*).

	Ring	Compound (3) Mol. *A*	 Mol. *B*	Compound (4)
Q_T	*A*	0.500 (3)	0.506 (3)	0.510 (1) Å
	B	0.057 (1)	0.057 (1)	0.078 (1)
	C	0.335 (4)	0.342 (4)	0.520 (2)
DAP	*A*	D_2(C2–O1) = 0.0444 (14)	D_2(C2–O1) = 0.0502 (13)	D_2(C2–O1) = 0.0634 (6) D_S(C5) = 0.0829 (7)
	C	D_2(C10) = 0.0091 (13) D_S(C7) = 0.0685 (17)	D_2(C10) = 0.0208 (14) D_S(C7) = 0.0549 (18)	D_S(C12) = 0.0076 (8) D_2(C6–C10) = 0.0541 (7) D_2(C9–C12) = 0.0649 (7)
Conf.*n*	*A*	Half-chair	Half-chair	Half-chair/sofa
	C	Half-chair	Half-chair	Sofa/half-chair
	AB	153.4 (1)	154.0 (1)	139.4 (1)°
	AC	107.1 (1)	107.2 (1)	119.5 (1)°

$wR = 0.0452$
$S = 0.5248$
1638 reflections
329 parameters

$w = k[\sigma^2(F_o)+0.005F_o^2]$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.07$ e Å^{-3}
$\Delta\rho_{\min} = -0.09$ e Å^{-3}
Extinction correction: none

Compound (4)

Crystal data

$C_{11}H_{16}O_3$
$M_r = 196.25$
Monoclinic
$P2_1/a$
$a = 7.741$ (1) Å
$b = 21.032$ (11) Å
$c = 6.050$ (1) Å
$\beta = 99.43$ (1)°
Cell parameters from 30 reflections
$\theta = 37$–51°
$V = 971.7$ (6) Å^3

$Z = 4$
$D_x = 1.342$ Mg m^{-3}
Cu $K\alpha_1$
$\lambda = 1.540562$ Å
$\mu = 0.7472$ mm^{-1}
$T = 293$ (2) K
Small prisms
$0.50 \times 0.26 \times 0.19$ mm
Colourless
Crystal source: chemical synthesis (see text)

Data collection

Siemens AED diffractometer
θ–2θ scans
Absorption correction: none
3306 measured reflections
1700 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0335$

$\theta_{\max} = 70°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 25$
$l = 0 \rightarrow 7$
1 standard reflection monitored every 50 reflections intensity variation: none

Refinement

Refinement on F
Final $R = 0.0475$
$wR = 0.0787$
$S = 1.0944$
1700 reflections
191 parameters

$w = 1/[\sigma^2(F_o)+0.005F_o^2]$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}
Extinction correction: none

For both compounds, the integrated intensities were measured using a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure. Corrections for Lorentz and polarization effects were applied but not for absorption, while extinction was considered according to Zachariasen (1963) for compound (4).

Table 4. *Relevant results of the rigid-body analysis of atomic anisotropic displacements (Trueblood, 1984)*

$\langle\Delta\rangle$ = mean difference of the mean-square vibrational amplitudes along the interatomic directions for pairs of atoms. $\Delta U = U_{ij}(\text{obs.}) - U_{ij}(\text{calc.})$. $\sigma(w\Delta U) = [\Sigma(w\Delta U)^2/\Sigma w^2]^{1/2}$. $R_{wU} = [\Sigma(w\Delta U)^2/\Sigma(wU_o)^2]^{1/2}$. L_1, L_2, L_3 = root-mean square of the **L**-tensor eigenvalues. T_1, T_2, T_3 = root-mean square of the **T**-tensor eigenvalues.

	Compound (3) Mol. *A*	 Mol. *B*	Compound (4)
$\langle\Delta\rangle$ (Å^2)	0.0028 (35)	0.0025 (32)	0.0015 (20)
$\sigma(w\Delta U)$ (Å^2)	0.0021	0.0023	0.0014
$\langle\sigma(U_{\rm obs})\rangle$ (Å^2)	0.0014	0.0014	0.0006
R_{wU}	0.072	0.083	0.065
L_1 (°)	4.82	5.61	4.29
L_2 (°)	3.81	2.92	2.93
L_3 (°)	3.08	2.48	2.43
T_1 (Å)	0.194	0.195	0.180
T_2 (Å)	0.178	0.182	0.160
T_3 (Å)	0.170	0.173	0.149

The structures were determined by direct methods with *SHELX*86 (Sheldrick, 1986) and refined by anisotropic full-matrix least squares on F, using *SHELX*76 (Sheldrick, 1976). The H atoms were localized from final difference Fourier syntheses and refined isotropically. Final atomic coordinates of non-H atoms are given in Table 1.

There are no significant differences between the two crystallographically independent molecules in compound (3). From the *PLUTO* (Motherwell & Clegg, 1976) drawing of the cell contents, shown in Fig. 3, and from the non-bonded contacts calculated by *PARST* (Nardelli, 1983*a*), it appears that the two independent molecules have different environments. The correctness of the space-group choice was checked by using *TRACER* (Lawton & Jacobson, 1965), *NEWLAT* (Mugnoli, 1985), *LEPAGE* (Spek, 1988) and *MISSYM* (Le Page, 1987).

The atomic scattering factors and the anomalous-scattering coefficients are from *International Tables for X-ray Crystallography* (1974, Vol. IV). Throughout the paper the averaged values are means weighted according to the reciprocals of the variances and the corresponding e.s.d.'s are the largest of the values of the 'external' and 'internal' standard deviations (Topping, 1960).

The calculations were carried out on the ENCORE–GOULD–POWERNODE 6040 computer of the 'Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma)'. In addition to the quoted programs, *LQPARM* (Nardelli & Mangia, 1984) and *ORTEP* (Johnson, 1965) have been used.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, principal axes of thermal ellipsoids and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54997 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1000]

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