The crystal structures of 2-*endo*-acetyl and 2-*endo*-carbomethoxy-1,4-epoxy-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalenes

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Crystals of 2-*endo*-acetyl-1,4-epoxy-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene are orthorhombic, a = 5.524(1), b = 8.929(1), c = 25.479(4) Å, Z = 4, space group $P2_12_12_1$; those of 2-*endo*-carbomethoxy-1,4-epoxy-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene are monoclinic, a = 10.878(2), b = 6.634(1), c = 18.224(4) Å, β = 92.76(2)°, Z = 4, space group $P2_1/c$. Both structures were solved by direct methods and refined by full-matrix least-squares methods to final R values of 0.041 and 0.036 for 875 and 1327 reflections with $I \geq 3\sigma(I)$ respectively.

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Les cristaux de l'acétyl-2 *endo* époxy-1,4 diméthoxy-6,7 tétrahydro-1,2,3,4 naphtalène sont orthorhombiques, a = 5,524(1), b = 8,929(1), c = 25,479(4) Å, Z = 4, groupe d'espace $P2_12_12_1$; ceux du carbométhoxy-2 *endo* époxy-1,4 diméthoxy-6,7 tétrahydro-1,2,3,4 naphtalène sont monocliniques, a = 10,878(2), b = 6,634(1), c = 18,224(4) Å, β = 92,76(2)°, Z = 4 et groupe d'espace $P2_1/c$. Les deux structures ont été résolues par des méthodes directes et affinées par la méthode des moindres carrés (matrice entière) jusqu'à des valeurs finales respectives de R de 0,041 et 0,036 pour 875 et 1327 réflexions avec $I \geq 3\sigma(I)$.

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Introduction

In the preceding paper (1) we described two general 5-*endo-trig* reversals of 7-oxabicyclo[2.2.1] heptenes and heptanes. Our rationalization of these processes as reverse-Michael and reverse-aldol reactions in general violation of Baldwin's rules (2) relied heavily upon the geometry of two benzo derivatives determined by X-ray crystallography. Diels–Alder adducts of isobenzofurans have not been previously subjected to X-ray analysis with the exception (3) of one rather exotic adduct of 1,3-diphenylisobenzofuran. In this paper we report the results of our analyses of the *endo* isomers of **1***a* and **1***c*.

Experimental

Crystals of *endo* **1***a* and **1***c* were obtained as described previously (4).

2-endo-*Acetyl-1,4-epoxy-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene (1*a*)*

A crystal of dimensions 0.22 × 0.40 × 0.41 mm was mounted in a general orientation. Unit cell parameters were refined from the 2θ values of 15 general reflections (20 < 2θ < 30°) measured with MoKα radiation (λ = 0.71069 Å). Crystal data at 21°C are:

$C_{14}H_{16}O_4$ fw = 248.48

Orthorhombic, a = 5.524(1), b = 8.929(1), c = 25.479(4) Å, V = 1256.7(3) Å^3, Z = 4, ρ_c = 1.312 g cm^{-3}, $F(000)$ = 528, μ(MoKα) = 1.034 cm^{-1}. Systematically absent reflections; $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$; space group $P2_12_12_1$ (D_2^4, No. 19).

Intensity data were measured with graphite-monochromated MoKα radiation on a Syntex $P2_1$ diffractometer using θ–2θ scans (3.2 < 2θ ≤ 50.0°) with a variable scan speed of 2.93–29.3° min^{-1} and a scan width of 1.0° below Kα$_1$ to 1.0° above Kα$_2$. Two standard reflections (120, 104) monitored after every 100 measurements fell by 4% during the data collection. These were used to scale the data to a common level. From a total of 1346 independent reflections measured, 875 (65.0%) with intensities $I \geq 3\sigma(I)$ were considered observed and used in the structure solution and refinement.

The structure was solved by direct methods (MULTAN 80), the positions of all non-hydrogen atoms being determined from an E-map. The structure was refined with anisotropic thermal parameters by full-matrix least-squares methods to an R of 0.079 ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$). At this stage, all the hydrogen atoms were located from a difference Fourier synthesis and included in the refinement which converged at R = 0.041. In the final cycles of refinement an empirical weighting scheme of $w^{-1} = 2.11 - 0.012|F_o| + 0.0008|F_o|^2$ was utilized to give constant error throughout the various ranges of F_o magnitude and a weighted residual R_w of 0.044 ($R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$). Scattering factors for non-hydrogen atoms were taken from ref. 5 and those for hydrogen from ref. 6. Programs used have been described elsewhere (7). On the final cycle of refinement, the mean and maximum parameter shifts were 0.05 and 0.21σ respectively. A final difference map was featureless with maximum residuals of 0.19 Å^{-3}. Final positional parameters are shown in Table 1. Anisotropic thermal parameters, carbon–hydrogen distances, and observed and calculated structure factors have been placed in the Depository of Unpublished Data.[1]

2-endo-*Carbomethoxy-1,4-epoxy-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene (1*c*)*

Experimental details are as above except where noted. Crystal dimensions were 0.32 × 0.33 × 0.42 mm. Crystal data are:

$C_{14}H_{16}O_5$ fw = 264.28

Monoclinic, a = 10.878(2), b = 6.634(1), c = 18.224(4) Å, β = 92.76(2)°, V = 1313.5(4) Å, Z = 4, ρ_c = 1.336 g cm^{-3}, $F(000)$ = 560, μ(MoKα) = 1.095 cm^{-1}. Systematically absent reflections: $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; space group $P2_1/c$ (C_{2h}^5, No.14).

During the data collection, the two standard reflections monitored (129, 500) showed only minor fluctuations (±2%). From a total of 2313 independent reflections measured (3.2 < 2θ ≤ 50°), 1327 (57.4%) with intensities $I \geq 3\sigma(I)$ were considered observed.

After direct methods solution, the structure was refined with anisotropic thermal parameters to an R of 0.090. Hydrogen atoms were located at this stage. The refinement converged at R = 0.036 with R_w = 0.036 ($w^{-1} = 2.39 - 0.032|F_o| + 0.0013|F_o|^2$). A final difference Fourier was featureless with maximum residuals of 0.18 eÅ^{-3}. Mean and maximum parameter shifts in the final refinement cycle were 0.09 and 0.33σ respectively. Final positional parameters are listed in Table 2. Anisotropic thermal parameters, carbon–hydrogen bond lengths, and observed and calculated structure factors have been placed in the Depository of Unpublished Data.[1]

[1] Structure factor tables, anisotropic thermal parameters (Table 5), and carbon–hydrogen distances (Table 6) are available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ont., Canada K1A 0S2.

TABLE 1. Final positional (fractional, × 10^4, hydrogen atoms, × 10^3) and isotropic thermal parameters (U × 10^3 Å) for the acetyl derivative **1***a*. $U_{eq} = \sqrt[3]{U_{11}U_{22}U_{33}}$

Atom	*x*	*y*	*z*	U_{eq}/U_{iso}
O(1)	4818(6)	4338(4)	2118(1)	59
O(2)	1374(7)	4473(4)	−44(1)	56
O(3)	−1749(7)	6152(4)	426(1)	60
O(4)	−380(6)	821(4)	1640(1)	61
C(1)	4684(9)	3108(5)	1751(2)	47
C(2)	2963(9)	2009(5)	2054(2)	46
C(3)	1300(11)	3119(6)	2338(2)	51
C(4)	2241(9)	4617(6)	2143(2)	52
C(5)	−112(9)	5562(5)	1290(2)	45
C(6)	−166(9)	5426(5)	745(2)	45
C(7)	1531(9)	4502(5)	493(1)	42
C(8)	3144(9)	3662(5)	777(2)	42
C(9)	3213(8)	3822(5)	1316(2)	40
C(10)	1637(9)	4778(5)	1565(2)	42
C(11)	3400(13)	3876(8)	−315(2)	65
C(12)	−3407(12)	7152(6)	668(2)	63
C(13)	1784(9)	871(5)	1709(2)	47
C(14)	3395(15)	−234(10)	1445(3)	85
H(1)	633(9)	278(4)	164(1)	51(13)
H(2)	405(8)	152(5)	232(2)	54(14)
H(3A)	−54(8)	294(4)	224(1)	36(11)
H(3B)	143(10)	306(5)	272(2)	72(15)
H(4)	190(8)	542(5)	236(2)	50(13)
H(5)	−108(7)	612(4)	147(1)	33(11)
H(8)	407(7)	309(4)	62(1)	34(12)
H(11A)	323(10)	408(5)	−66(2)	70(15)
H(11B)	505(10)	440(5)	−18(2)	78(16)
H(11C)	341(9)	262(5)	−28(2)	57(14)
H(12A)	−469(12)	652(7)	92(2)	116(21)
H(12B)	−432(10)	762(5)	40(2)	73(16)
H(12C)	−241(10)	805(7)	82(2)	96(21)
H(14A)	485(12)	−16(7)	153(2)	111(25)
H(14B)	312(16)	−30(10)	116(3)	152(32)
H(14C)	289(17)	−122(10)	159(3)	195(39)

TABLE 2. Final positional (fractional, × 10^4, hydrogen atoms, × 10^3) and isotropic thermal parameters (U × 10^3 Å^2) for the carboxymethoxy derivative **1***c*. $U_{eq} = \sqrt[3]{U_{11}U_{22}U_{33}}$

Atom	*x*	*y*	*z*	U_{eq}/U_{iso}
O(1)	8785(2)	2334(3)	2519(1)	84
O(2)	4612(1)	−1016(2)	776(1)	65
O(3)	3618(1)	1939(3)	1418(1)	69
O(4)	8063(2)	4798(4)	241(1)	122
O(5)	9026(2)	1846(4)	234(1)	93
C(1)	8744(2)	1615(5)	1772(1)	71
C(2)	9084(2)	3566(5)	1352(2)	74
C(3)	8496(3)	5203(5)	1821(2)	82
C(4)	7890(3)	3928(4)	2399(2)	76
C(5)	5573(2)	3104(4)	1968(1)	58
C(6)	4871(2)	1810(4)	1529(1)	53
C(7)	5415(2)	217(3)	1155(1)	51
C(8)	6682(2)	−16(4)	1185(1)	55
C(9)	7375(2)	1298(4)	1628(1)	56
C(10)	6834(2)	2797(4)	2023(1)	60
C(11)	5106(3)	−2759(4)	441(2)	67
C(12)	3034(3)	3694(5)	1677(2)	85
C(13)	8667(2)	3535(5)	552(2)	80
C(14)	8630(4)	1542(9)	−534(2)	117
H(1)	925(2)	43(4)	172(1)	67(7)
H(2)	997(2)	366(4)	135(1)	86(8)
H(3A)	790(2)	609(4)	150(1)	83(8)
H(3B)	910(2)	619(5)	209(1)	101(9)
H(4)	774(2)	464(4)	286(1)	72(8)
H(5)	524(2)	420(3)	222(1)	49(6)
H(8)	708(2)	−107(3)	90(1)	56(6)
H(11A)	439(2)	−350(4)	20(1)	75(7)
H(11B)	564(2)	−240(4)	5(1)	74(8)
H(11C)	553(2)	−373(4)	82(1)	83(8)
H(12A)	219(3)	359(5)	151(2)	113(11)
H(12B)	344(3)	499(5)	154(2)	111(11)
H(12C)	312(3)	361(5)	224(2)	152(13)
H(14A)	772(4)	175(6)	−60(2)	176(15)
H(14B)	897(4)	9(7)	−67(2)	184(15)
H(14C)	908(4)	252(7)	−76(2)	246(19)

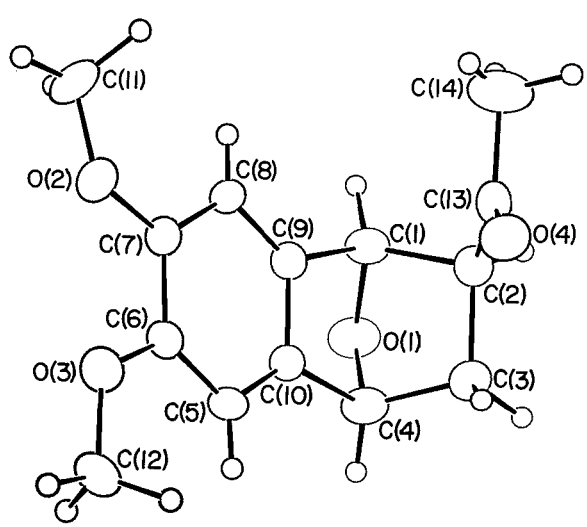
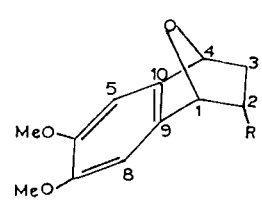
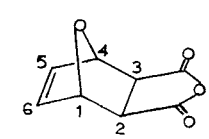


FIG. 1. ORTEP plot of **1***a*.



1



2

a (R = $COCH_3$)

c (R = CO_2CH_3)

Discussion

The molecular parameters determined for **1***a* and **1***c* are listed in Table 3 and an ORTEP plot of **1***a* is shown in Fig. 1. Most of the strain in these molecules resides in bond angle distortions; the angles at C(9) and C(10) in particular are severely distorted by C(1) and C(4) being pulled together (C(1) and C(4) are only 2.153(7) and 2.151(4) Å apart in **1***a* and **1***c* respectively) by the oxygen bridge. In general, the bond lengths and angles of the oxabicyclo moieties in **1***a* and **1***c* are comparable to those determined (8) for the furan – maleic anhydride adduct **2**. The only significant difference between the two systems is that the C(1)—O(1)—C(4) plane in **1***a* and **1***c* is tilted towards the benzene ring 7.4° more than the corresponding plane is tilted towards the 5,6-double bond in **2** (Table 4). Whether this discrepancy is a consequence of the

TABLE 3. Bond lengths (Å) and angles (°) for acetyl derivative **1***a* and carbomethoxy derivative **1***c*

Bond	Length **1***a*	Length **1***c*	Bond	Length **1***a*	Length **1***c*
C(1)—O(1)	1.446(6)	1.441(3)	C(1)—C(2)	1.569(7)	1.557(4)
C(1)—C(9)	1.514(6)	1.514(3)	C(2)—C(3)	1.534(7)	1.540(4)
C(2)—C(13)	1.492(6)	1.506(4)	C(3)—C(4)	1.518(7)	1.526(4)
C(4)—O(1)	1.446(6)	1.446(3)	C(4)—C(10)	1.518(6)	1.508(4)
C(5)—C(6)	1.394(6)	1.379(3)	C(5)—C(10)	1.382(6)	1.386(3)
C(6)—O(3)	1.358(6)	1.372(3)	C(6)—C(7)	1.405(6)	1.404(3)
C(7)—O(2)	1.370(5)	1.360(3)	C(7)—C(8)	1.372(6)	1.386(3)
C(8)—C(9)	1.381(6)	1.386(3)	C(9)—C(10)	1.373(6)	1.377(3)
O(2)—C(11)	1.420(7)	1.425(3)	O(3)—C(12)	1.419(7)	1.418(4)
C(13)—O(4)	1.209(6)	1.191(4)	C(13)—O(5)	—	1.329(4)
C(13)—C(14)	1.490(10)	—	O(5)—C(14)	—	1.459(4)

Bond	Angle **1***a*	Angle **1***c*	Bond	Angle **1***a*	Angle **1***c*
O(1)—C(1)—C(2)	100.8(2)	101.0(1)	O(1)—C(1)—C(9)	100.4(2)	101.2(1)
C(2)—C(1)—C(9)	107.3(2)	106.6(1)	C(1)—C(2)—C(3)	101.0(2)	101.5(1)
C(1)—C(2)—C(13)	113.6(2)	113.3(1)	C(3)—C(2)—C(13)	117.2(2)	115.6(1)
C(2)—C(3)—C(4)	102.1(2)	101.4(1)	O(1)—C(4)—C(3)	101.5(2)	101.5(1)
O(1)—C(4)—C(10)	101.0(2)	101.4(1)	C(3)—C(4)—C(10)	109.1(2)	107.9(1)
C(6)—C(5)—C(10)	118.3(2)	118.0(1)	C(5)—C(6)—C(7)	119.5(2)	121.1(1)
C(5)—C(6)—O(3)	124.6(2)	124.4(1)	C(7)—C(6)—O(3)	115.8(2)	114.5(1)
C(6)—C(7)—C(8)	120.8(2)	120.4(1)	C(6)—C(7)—O(2)	115.2(2)	115.1(1)
C(8)—C(7)—O(2)	123.9(2)	124.5(1)	C(7)—C(8)—C(9)	119.1(2)	117.7(1)
C(1)—C(9)—C(8)	134.3(2)	133.7(1)	C(1)—C(9)—C(10)	105.4(2)	104.5(1)
C(8)—C(9)—C(10)	120.3(2)	121.7(1)	C(4)—C(10)—C(5)	133.8(2)	133.6(1)
C(4)—C(10)—C(9)	104.4(2)	105.2(1)	C(5)—C(10)—C(9)	121.7(2)	120.9(1)
C(1)—O(1)—C(4)	96.2(2)	96.3(1)	C(7)—O(2)—C(11)	116.3(3)	117.3(1)
C(6)—O(3)—C(12)	117.1(3)	117.4(1)	C(2)—C(13)—O(4)	122.9(2)	125.8(1)
C(2)—C(13)—C(14)	117.1(3)	—	O(4)—C(13)—C(14)	120.0(3)	—
C(2)—C(13)—O(5)	—	110.7(1)	O(4)—C(13)—O(5)	—	123.5(1)
C(13)—O(5)—C(14)	—	117.2(2)			

TABLE 4. Least-squares planes
Equations of least-squares planes in the form $Ax + By + cz = D$
[Distances (Å) of the atoms from the planes]

Plane	Equation	Distances (Å)
Compound **1***a*		
Plane 1	$0.6738x + 0.7343y - 0.7642z = 3.4442$	[C(1) −0.002 C(4) 0.002 C(9) 0.004 C(10) −0.004]
Plane 2	$0.6236x + 0.0320y - 0.7811z = 5.1771$	[C(1) 0.009 C(2) −0.012 C(3) 0.013 C(4) −0.009]
Plane 3	$-0.0790x - 0.6437y + 0.7612z = 1.4050$	[C(1) 0 C(4) 0 O(1) 0]
Compound **1***c*		
Plane 1	$-0.0576x - 0.6166y + 0.7852z = 1.3365$	[C(1) −0.004 C(4) 0.004 C(9) 0.006 C(10) −0.006]
Plane 2	$0.8091x + 0.0728y + 0.5832z = 9.5192$	[C(1) 0.009 C(2) −0.012 C(3) 0.013 C(4) −0.009]
Plane 3	$0.7435x + 0.6344y \pm 0.2117z = 6.9524$	[C(1) 0 C(4) 0 O(1) 0]

	Dihedral angles (°) (**1***a*)	(**1***c*)	(**2**)*
Planes 1–2	112.6	111.5	114.6
Planes 1–3	125.8	126.9	131.3
Planes 2–3	121.7	121.6	114.2

*Reference 8.

different configurations (*endo* in **1***a* and **1***c* and *exo* in **2**) of the adducts is open to question.

Acknowledgements

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