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Acta Cryst. (1994). **C50**, 569–574

Stereochemistry of Transposition Reactions Involving Polycyclic Methylenecyclobutanol Derivatives

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(Received 23 June 1993; accepted 4 October 1993)

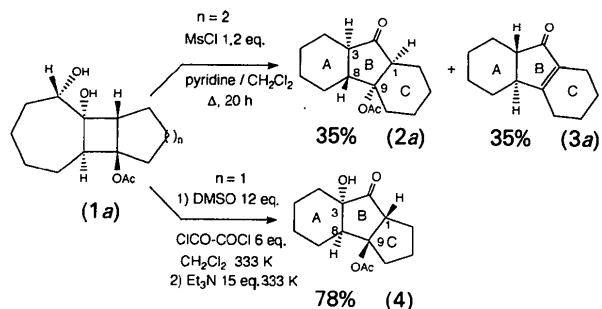
Abstract

The configurations at the junctions of tricyclic systems obtained by transposition reactions have been defined by crystal structure analyses of the compounds *trans,syn,cis*-1-acetoxycyclo[7.4.0.0^{2,7}]tridecan-8-one (**2a**); IUPAC name: 8-oxotricyclo[7.4.0.0^{2,7}]tridecan-1-yl acetate] and *cis,anti,cis*-1-acetoxycyclo[7.3.0.0^{2,7}]dodecan-8-one, [C₁₄H₂₀O₄, (**4**); IUPAC name: 7-hydroxy-8-oxotricyclo[7.3.0.0^{2,7}]dodecan-1-yl acetate]. This knowledge is important in our understanding of how these reactions occur. The geometries of the molecules in the crystal, found by X-ray diffraction, are compared with those calculated for the isolated molecules by molecular-mechanics methods.

Comment

During the study of the behaviour of the (**1a**) substrates with the purpose of synthesizing functionalized tricyclic

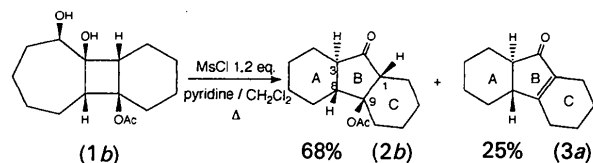
compounds such as (**2a**) and (**4**), according to the following scheme, it was found necessary to unambiguously define the stereochemistry of the transposition process.



For this purpose, although some information concerning the nature of the A/B junction could be obtained from the NMR spectrum of (**2a**), such information could not be obtained for the B/C junction. The same is true for this ring junction in compounds (**1a**) and (**4**), and therefore a correlation between the starting materials and the transposed products could not be established. Thus, the structures of compounds (**2a**) and (**4**) were studied by X-ray diffraction and the results are illustrated in the present paper. The structure of the starting product (**1a**) ($n = 3$) has been determined previously (Ianelli, Nardelli, Belletti, Brosse, Jamart-Grégoire & Caubère, 1993).

From the results of these analyses it appears that during transposition of (**1a**), regardless of conditions, the B/C junction is preserved in (**2a**) and (**4**), demonstrating that no epimerization occurs during this process. In the same way the relative position of the acetate group and the proton is also retained. The interesting point is that the transposition leading to an A/B *trans* junction in (**2a**), gives a *cis* junction in (**4**).

Compound (**1b**), whose crystal structure has also been determined recently (Ianelli *et al.*, 1993), was submitted to transposition leading to compounds (**2b**) and (**3a**), according to the process shown below.



The configuration at the A/B junction of compound (**3a**) has been defined previously (Jamart-Grégoire, Brosse, Ianelli, Nardelli & Caubère, 1993). The NMR spectrum of (**2b**) gives a coupling constant for the C3 and C8 protons identical to that of compound (**2a**), showing that a *trans* junction also exists. These results lead to the relevant conclusion that, in this series, transposition without oxidation occurs maintaining the configurations at C atoms, while transposition with oxidation seems to lead to the most thermodynamically stable compound.

Fig. 1 shows *ORTEP* (Johnson, 1965) drawings of the molecules of the two compounds. As shown by the data of Table 4, there are no significant differences between the two crystallographically independent molecules of compound (4); therefore, in Fig. 1, only one of the two molecules (molecule *A*) is represented. These molecules are built up by three rings in a rigid system, so it is not surprising that a satisfactory agreement is found between the values of bond distances, bond angles and torsion angles observed experimentally in the crystal and the corresponding quantities calculated by a molecular-mechanics optimization procedure (*PCMODEL-MMX* force-field; Serena Software, 1989) for isolated molecules, as shown in Tables 3 and 4. The largest differences for compound (2*a*) are 0.060 Å for the O2—C9 bond, 4.3° for the C9—O2—C14 bond angle and 5.5° for the C13—C1—C9—

C10 torsion angle, while for compound (4) the largest differences are 0.043 Å for the O2—C9 bond, 6.6° for the C9—O2—C13 bond angle of molecule *A* and 13.6° for the O1—C2—C3—C4 torsion angle of molecule *B*. There are no regular trends for the observed differences, so it is not possible to attribute them to packing effects or to some inadequacy of the theoretical model (only program default parameters were used in these calculations).

The optimized molecular structures were calculated starting from the atomic coordinates found experimentally in the crystal. The force-field energies and formation enthalpies (*H_f*) calculated for the two molecules are 109.5 kJ mol⁻¹ (26.2 kcal mol⁻¹) and 135.9 kJ mol⁻¹ (32.5 kcal mol⁻¹) for the *MMX* energy, and -665.7 kJ mol⁻¹ (-159.1 kcal mol⁻¹) and -605.9 kJ mol⁻¹ (-144.8 kcal mol⁻¹) for the *H_f* of compounds (2*a*) and (4), respectively.

Intramolecular steric hindering effects prevent rotation of the acetoxy group, as shown by the energy profile obtained by rotating this group about the C9—O2 bond, which presents a well defined minimum corresponding to the orientation found in the crystal for both compounds. With this orientation the O2—C14 [O2—C13 for compound (4)] bond is antiperiplanar to C8—C9 and synclinal to C1—C9 and C9—C10.

The conformation of the three-ring system is described by the dihedral angles and puckering parameters quoted in Table 5, which also shows the substantial agreement of the experimental data with those calculated by the molecular-mechanics optimization.

The orientation of the OH group in the two independent molecules of compound (4) is essentially determined by two hydrogen-bonding bifurcated interactions, one intramolecular [O4A···O1A = 2.806 (3), H4OA···O1A = 2.76 (3) Å, O4A—H4OA···O1A = 83 (2)°; O4B···O1B = 2.767 (3), H4OB···O1B = 2.37 (6) Å, O4B—H4OB···O1B = 114 (5)°] and the other intermolecular [O4A···O3Aⁱ = 2.882 (3), H4OA···O3Aⁱ = 2.01 (3) Å, O4A—H4OA···O3Aⁱ = 164 (3)°; O4B···O4Bⁱⁱ = 2.928 (3), H4OB···O4Bⁱⁱ = 2.47 (6) Å, O4B—H4OB···O4Bⁱⁱ = 121 (6)°; symmetry code: (i) 1 - x, y - 1/2, 1/2 - z; (ii) 2 - x, 1 - y, -z]. In both molecules the intermolecular interaction will predominate since the geometry of the intramolecular hydrogen-bond interaction is relatively strained.

Experimental

Compound (2*a*)

Crystal data

C₁₅H₂₂O₃
M_r = 250.34
 Orthorhombic
*P*2₁*cn*
a = 11.902 (6) Å
b = 11.952 (5) Å
c = 9.380 (6) Å

Mo *K*α radiation
 λ = 0.7107 Å
 Cell parameters from 30 reflections
 θ = 10.2–17.6°
 μ = 0.0795 mm⁻¹
T = 293 (2) K

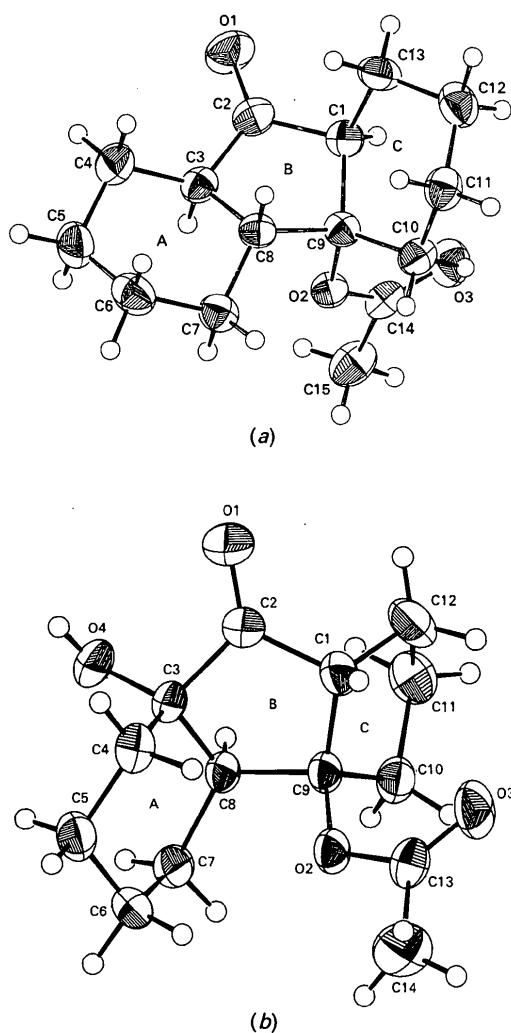


Fig. 1. *ORTEP* (Johnson, 1965) drawings of the molecules: (a) compound (2*a*), (b) molecule *A* of compound (4). Ellipsoids are drawn at the 50% probability level.

$V = 1334 (1) \text{ \AA}^3$	Small prisms	C3—C4	1.514 (4)	1.529
$Z = 4$	$0.61 \times 0.33 \times 0.29 \text{ mm}$	C3—C8	1.521 (4)	1.536
$D_x = 1.246 \text{ Mg m}^{-3}$	Colourless	C4—C5	1.526 (4)	1.540
		C5—C6	1.522 (4)	1.540
		C6—C7	1.530 (4)	1.541
<i>Data collection</i>		C7—C8	1.523 (4)	1.533
Enraf-Nonius CAD-4	$h = -2 \rightarrow 14$	C8—C9	1.531 (3)	1.546
diffractometer	$k = 0 \rightarrow 14$	C9—C10	1.524 (4)	1.537
θ - 2θ scans	$l = 0 \rightarrow 11$	C10—C11	1.516 (4)	1.533
4421 measured reflections	1 standard reflection	C11—C12	1.520 (4)	1.534
1368 independent reflections	frequency: 150 min	C12—C13	1.509 (4)	1.532
999 observed reflections	intensity variation:	C14—C15	1.493 (3)	1.515
[$I > 2\sigma(I)$]	within statistical	C9—O2—C14	122.6 (2)	126.9
$R_{\text{int}} = 0.0230$	fluctuation	C9—C1—C13	112.3 (2)	114.2
$\theta_{\text{max}} = 25.05^\circ$		C2—C1—C13	108.2 (2)	108.8
		C2—C1—C9	104.5 (2)	104.7
		O1—C2—C1	125.1 (2)	125.6
		C1—C2—C3	108.4 (2)	108.9
		O1—C2—C3	126.4 (2)	125.5
		C2—C3—C8	103.7 (2)	102.3
		C2—C3—C4	120.7 (2)	118.6
		C4—C3—C8	112.3 (2)	110.7
		C3—C4—C5	108.8 (2)	108.4
		C4—C5—C6	112.7 (2)	112.3
		C5—C6—C7	112.8 (3)	112.4
		C6—C7—C8	108.5 (2)	108.7
		C3—C8—C7	110.7 (2)	109.3
		C7—C8—C9	121.0 (2)	120.1
		C3—C8—C9	103.4 (2)	103.2
		C1—C9—C8	102.3 (2)	101.1
		O2—C9—C8	102.5 (2)	106.1
		O2—C9—C1	109.7 (2)	110.2
		C8—C9—C10	115.8 (2)	113.5
		C1—C9—C10	116.2 (2)	116.2
		O2—C9—C10	109.3 (2)	109.1
		C9—C10—C11	112.0 (2)	113.6
		C10—C11—C12	110.9 (3)	110.0
		C11—C12—C13	110.5 (2)	109.9
		C1—C13—C12	112.4 (2)	112.3
		O2—C14—O3	125.2 (2)	125.4
		O3—C14—C15	124.7 (3)	124.9
		O2—C14—C15	110.1 (2)	109.7
		C2—C3—C8—C9	-36.7 (3)	-39.9
		C3—C8—C9—C1	42.2 (2)	44.3
		C4—C3—C8—C7	60.4 (3)	63.8
		C8—C3—C4—C5	-56.5 (3)	-59.6
		C3—C4—C5—C6	53.2 (3)	54.2
		C4—C5—C6—C7	-54.3 (3)	-53.5
		C5—C6—C7—C8	54.8 (3)	55.1
		C6—C7—C8—C3	-57.1 (3)	-59.5
		C14—O2—C9—C1	62.5 (3)	62.7
		C14—O2—C9—C8	170.6 (2)	171.4
		C13—C1—C9—C10	-41.2 (3)	-35.7
		C1—C9—C10—C11	45.2 (3)	40.0
		C9—C10—C11—C12	-54.3 (3)	-53.1
		C10—C11—C12—C13	61.4 (3)	62.8
		C11—C12—C13—C1	-57.7 (3)	-59.1
		C9—C1—C13—C12	47.0 (3)	45.0

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for compound (2a)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
O1	0.92230	0.3802 (1)	0.2549 (2)	0.0623 (6)
O2	0.8321 (2)	0.6593 (1)	0.0331 (1)	0.0387 (5)
O3	0.9534 (2)	0.6357 (1)	-0.1497 (2)	0.0582 (6)
C1	0.8458 (3)	0.4532 (2)	0.0333 (2)	0.0376 (7)
C2	0.8584 (2)	0.4434 (2)	0.1943 (2)	0.0416 (7)
C3	0.7766 (3)	0.5225 (2)	0.2637 (2)	0.0387 (7)
C4	0.7183 (3)	0.4911 (2)	0.4015 (3)	0.0524 (9)
C5	0.6400 (3)	0.5864 (2)	0.4446 (3)	0.0575 (10)
C6	0.5594 (3)	0.6196 (2)	0.3259 (3)	0.0540 (10)
C7	0.6196 (3)	0.6482 (2)	0.1864 (3)	0.0442 (10)
C8	0.6938 (3)	0.5496 (2)	0.1450 (2)	0.0354 (7)
C9	0.7679 (3)	0.5542 (2)	0.0118 (2)	0.0341 (7)
C10	0.7058 (3)	0.5596 (2)	-0.1301 (3)	0.0422 (8)
C11	0.6552 (3)	0.4477 (2)	-0.1707 (3)	0.0466 (9)
C12	0.7439 (3)	0.3563 (2)	-0.1701 (3)	0.0521 (9)
C13	0.7935 (3)	0.3432 (2)	-0.0230 (3)	0.0480 (9)
C14	0.9193 (3)	0.6887 (2)	-0.0503 (2)	0.0424 (8)
C15	0.9695 (3)	0.7957 (2)	0.0013 (3)	0.0555 (9)

Table 2. Bond lengths (\AA), bond angles ($^\circ$) and selected torsion angles ($^\circ$) for compound (2a)

Observed values are from crystal structure analysis; calculated values are for an isolated molecule from MMX force-field optimized geometry.

	Observed	Calculated
O1—C2	1.213 (3)	1.208
O2—C9	1.484 (3)	1.424
O2—C14	1.346 (4)	1.350
O3—C14	1.198 (3)	1.210
C1—C2	1.522 (3)	1.525
C1—C9	1.535 (4)	1.550
C1—C13	1.548 (4)	1.538
C2—C3	1.505 (4)	1.514

Compound (4)

Crystal data

$\text{C}_{14}\text{H}_{20}\text{O}_4$

$M_r = 252.31$

Monoclinic

$P2_1/c$

$a = 10.769 (2) \text{ \AA}$

$b = 15.185 (2) \text{ \AA}$

$c = 15.849 (2) \text{ \AA}$

$\beta = 90.06 (1)^\circ$

$V = 2591.7 (7) \text{ \AA}^3$

$Z = 8$

$D_x = 1.293 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation

$\lambda = 1.5418 \text{ \AA}$

Cell parameters from 30 reflections

$\theta = 25-36^\circ$

$\mu = 0.730 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Small prisms

$0.43 \times 0.37 \times 0.33 \text{ mm}$

Colourless

Data collection

Siemens AED diffractometer	$h = -13 \rightarrow 13$
θ - 2θ scans	$k = 0 \rightarrow 18$
5218 measured reflections	$l = 0 \rightarrow 19$
4947 independent reflections	1 standard reflection
2782 observed reflections	monitored every 50 reflections
$[I > 2\sigma(I)]$	intensity variation:
$R_{\text{int}} = 0.0869$	within statistical fluctuation
$\theta_{\text{max}} = 70.1^\circ$	

Refinement

Refinement on F^2	Extinction correction:
$R(F) = 0.0472$	$F_c^* = kF_c[1 + (0.001\chi \times F_c^2 \lambda^3 / \sin 2\theta)]^{-1/4}$
$wR(F^2) = 0.1238$	Extinction coefficient:
$S = 0.989$	0.0053 (3)
4946 reflections	Atomic scattering factors
486 parameters	from <i>International Tables</i>
All H-atom parameters	for <i>X-ray Crystallography</i> (1974, Vol. IV, Tables
refined	2.2A, 2.3.1 for O and C,
$w = 1/[\sigma^2(F_o^2) + (0.0686P)^2]$	and 2.2C for H)
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{\text{max}} = 0.492$	
$\Delta\rho_{\text{max}} = 0.268 \text{ e } \text{\AA}^{-3}$	
$\Delta\rho_{\text{min}} = -0.223 \text{ e } \text{\AA}^{-3}$	

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for compound (4)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
O1A	0.5656 (2)	0.2077 (1)	0.3796 (2)	0.0810 (9)
O2A	0.3242 (2)	0.31686 (9)	0.16531 (9)	0.0410 (5)
O3A	0.3955 (2)	0.4550 (1)	0.1814 (1)	0.0620 (7)
O4A	0.3995 (2)	0.0768 (1)	0.3260 (1)	0.0487 (6)
C1A	0.4422 (2)	0.3148 (2)	0.3036 (2)	0.0404 (8)
C2A	0.4884 (2)	0.2236 (2)	0.3272 (2)	0.0445 (8)
C3A	0.4166 (2)	0.1549 (1)	0.2777 (1)	0.0372 (7)
C4A	0.4793 (3)	0.1353 (2)	0.1936 (2)	0.0441 (9)
C5A	0.3938 (3)	0.0810 (2)	0.1369 (2)	0.0516 (10)
C6A	0.2728 (3)	0.1293 (2)	0.1196 (2)	0.0529 (11)
C7A	0.2076 (3)	0.1556 (2)	0.2007 (2)	0.0461 (8)
C8A	0.2906 (2)	0.1997 (1)	0.2663 (1)	0.0343 (7)
C9A	0.3188 (2)	0.2998 (1)	0.2559 (1)	0.0353 (7)
C10A	0.2208 (3)	0.3567 (2)	0.2999 (2)	0.0430 (8)
C11A	0.2707 (3)	0.3660 (2)	0.3884 (2)	0.0600 (11)
C12A	0.4097 (3)	0.3745 (2)	0.3787 (2)	0.0610 (11)
C13A	0.3615 (3)	0.3962 (2)	0.1363 (2)	0.0466 (9)
C14A	0.3553 (5)	0.4001 (3)	0.0421 (2)	0.0717 (14)
O1B	1.0660 (2)	0.3033 (1)	-0.0615 (1)	0.0771 (9)
O2B	0.8253 (2)	0.19645 (9)	0.15470 (9)	0.0405 (5)
O3B	0.9049 (2)	0.0590 (1)	0.1451 (1)	0.0606 (6)
O4B	0.9027 (2)	0.4335 (1)	-0.0105 (1)	0.0536 (7)
C1B	0.9483 (2)	0.1956 (2)	0.0194 (2)	0.0395 (8)
C2B	0.9904 (2)	0.2861 (2)	-0.0073 (2)	0.0444 (8)
C3B	0.9163 (2)	0.3557 (1)	0.0393 (1)	0.0383 (7)
C4B	0.9767 (3)	0.3781 (2)	0.1239 (2)	0.0465 (9)
C5B	0.8892 (3)	0.4336 (2)	0.1779 (2)	0.0553 (10)
C6B	0.7689 (3)	0.3840 (2)	0.1952 (2)	0.0564 (10)
C7B	0.7060 (3)	0.3553 (2)	0.1141 (2)	0.0474 (9)
C8B	0.7908 (2)	0.3094 (1)	0.0503 (1)	0.0348 (7)
C9B	0.8223 (2)	0.2104 (1)	0.0639 (1)	0.0357 (7)
C10B	0.7289 (3)	0.1497 (2)	0.0197 (2)	0.0449 (9)
C11B	0.7845 (3)	0.1369 (2)	-0.0676 (2)	0.0614 (12)
C12B	0.9230 (3)	0.1310 (2)	-0.0531 (2)	0.0622 (11)
C13B	0.8659 (3)	0.1190 (2)	0.1871 (2)	0.0465 (8)
C14B	0.8570 (5)	0.1195 (3)	0.2809 (2)	0.0662 (14)

Table 4. Comparison of bond distances (\AA), bond angles ($^\circ$) and selected torsion angles ($^\circ$) for compound (4)

Observed values are from crystal structure analysis; calculated values are for an isolated molecule from *MMX* force-field optimized geometry.

	Observed		Calculated
	A	B	
O1—C2	1.199 (3)	1.213 (3)	1.209
O2—C9	1.459 (3)	1.454 (3)	1.416
O2—C13	1.351 (3)	1.355 (3)	1.349
O3—C13	1.200 (3)	1.204 (3)	1.210
O4—C3	1.423 (3)	1.429 (3)	1.414
C1—C2	1.519 (3)	1.508 (4)	1.515
C1—C9	1.545 (3)	1.547 (3)	1.542
C1—C12	1.536 (4)	1.535 (4)	1.536
C2—C3	1.516 (3)	1.516 (3)	1.518
C3—C4	1.524 (4)	1.529 (4)	1.535
C3—C8	1.529 (3)	1.533 (3)	1.537
C4—C5	1.527 (4)	1.527 (4)	1.534
C5—C6	1.520 (4)	1.524 (5)	1.534
C6—C7	1.519 (4)	1.516 (4)	1.536
C7—C8	1.525 (4)	1.531 (4)	1.538
C8—C9	1.559 (3)	1.556 (3)	1.550
C9—C10	1.533 (3)	1.533 (4)	1.540
C10—C11	1.509 (4)	1.521 (4)	1.536
C11—C12	1.510 (5)	1.511 (5)	1.536
C13—C14	1.496 (4)	1.490 (4)	1.515
C9—O2—C13	120.3 (2)	120.5 (2)	126.9
C9—C1—C12	105.6 (2)	106.2 (2)	106.3
C2—C1—C12	115.0 (2)	115.3 (2)	115.1
C2—C1—C9	105.5 (2)	105.1 (2)	105.9
O1—C2—C1	125.5 (2)	126.7 (2)	125.3
C1—C2—C3	109.5 (2)	109.9 (2)	110.3
O1—C2—C3	124.9 (2)	123.3 (2)	124.4
O4—C3—C2	111.2 (2)	111.2 (2)	111.3
C2—C3—C8	101.9 (2)	101.6 (2)	102.4
C2—C3—C4	111.2 (2)	111.0 (2)	109.8
O4—C3—C8	108.6 (2)	110.7 (2)	109.7
O4—C3—C4	111.4 (2)	110.1 (2)	109.9
C4—C3—C8	112.1 (2)	112.1 (2)	113.6
C3—C4—C5	110.7 (2)	110.6 (2)	111.3
C4—C5—C6	111.2 (2)	110.7 (2)	110.3
C5—C6—C7	111.8 (2)	111.7 (3)	111.4
C6—C7—C8	114.9 (2)	115.1 (2)	115.3
C3—C8—C7	113.9 (2)	113.2 (2)	113.6
C7—C8—C9	118.0 (2)	118.5 (2)	117.9
C3—C8—C9	105.9 (2)	105.5 (2)	106.9
C1—C9—C8	105.0 (2)	105.5 (2)	105.3
O2—C9—C8	106.6 (2)	106.4 (2)	109.4
O2—C9—C1	114.8 (2)	114.3 (2)	111.7
C8—C9—C10	111.5 (2)	112.0 (2)	111.9
C1—C9—C10	106.7 (2)	106.2 (2)	106.7
O2—C9—C10	112.1 (2)	112.3 (2)	111.6
C9—C10—C11	103.3 (2)	103.6 (2)	103.5
C10—C11—C12	105.4 (3)	105.0 (3)	103.9
C1—C12—C11	104.8 (3)	104.5 (3)	105.2
O2—C13—O3	123.5 (2)	124.0 (2)	125.3
O3—C13—C14	125.3 (3)	125.3 (2)	125.1
O2—C13—C14	111.2 (2)	110.7 (2)	109.6
C13—O2—C9—C1	-56.4 (3)	-55.5 (3)	-56.2
C1—C2—C3—O4	-146.0 (2)	-149.5 (2)	-142.4
C4—C3—C8—C7	47.2 (3)	47.5 (3)	44.0
C8—C3—C4—C5	-55.0 (3)	-55.7 (3)	-53.1
C3—C4—C5—C6	59.3 (3)	59.9 (3)	59.4
C4—C5—C6—C7	-55.0 (3)	-55.8 (3)	-56.8
C5—C6—C7—C8	47.5 (3)	48.5 (3)	48.8
C6—C7—C8—C3	-43.8 (3)	-44.4 (3)	-42.2
C1—C9—C10—C11	-25.6 (3)	-25.0 (3)	-26.8
C9—C10—C11—C12	37.6 (3)	37.9 (3)	37.8
C10—C11—C12—C1	-35.2 (3)	-35.9 (3)	-34.7
C9—C1—C12—C11	18.4 (3)	19.8 (3)	17.9
C12—C1—C9—C8	4.5 (3)	3.4 (3)	5.6
C2—C1—C9—C8	8.2 (2)	6.9 (2)	9.4
C9—C1—C2—C3	14.0 (3)	15.7 (3)	10.1

C1—C2—C3—C8	-30.5 (2)	-31.7 (2)	-25.2
C2—C3—C8—C9	34.9 (2)	34.9 (2)	30.6
C3—C8—C9—C1	-27.2 (2)	-26.5 (2)	-25.3

Table 5. Conformation of the rings and dihedral angles formed by their least-squares planes

Q_7 = total puckering amplitude (Cremer & Pople, 1975), CH = chair, HC = half chair, E = envelope. Values calculated from the *MMX* force-field optimized structure of the isolated molecule are given in square brackets.

Compound	Ring	Q_7 (Å)	Conformation	$A^{\wedge}B$ (°)	$B^{\wedge}C$ (°)
(2a)	A	0.574 (3) [0.601]	CH	6.3 (1) [7.3]	55.8 (1) [53.9]
	B	0.411 (3) [0.440]	HC-E		
	C	0.531 (3) [0.532]	CH		
(4)A	A	0.528 (3) [0.529]	CH	59.4 (1) [57.1]	58.9 (1) [61.6]
	B	0.341 (2) [0.298]	HC-E		
	C	0.364 (3) [0.374]	E-HC		
(4)B	A	0.537 (3) [0.529]	CH	59.7 (1) [57.1]	58.1 (1) [61.6]
	B	0.345 (2) [0.298]	HC-E		
	C	0.370 (3) [0.374]	E-HC		

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 no corrections were made for absorption. Extinction was considered only for compound (4) according to the procedure used in *SHELXL92* (Sheldrick, 1992).

No attempt was made to determine the absolute structure of compound (2a), the effects of anomalous scattering being too low. The configuration shown in Fig. 1 is that of one enantiomer. Both enantiomers are formed in the reaction and they are present in the same crystal related by the glides.

The diffraction pattern of compound (4) is metrically orthorhombic, but belongs to the monoclinic $2/m$ Laue class, the intensities of the hkl reflections being significantly different from those of $-hkl$. The presence of two independent molecules in the asymmetric unit of the crystals of this compound casts suspicion on the accuracy of the choice of the space group which was checked using the *TRACER* (Lawton & Jacobson, 1965), *NEWLAT* (Mugnoli, 1985), *LEPAGE* (Spek, 1988) and *MIS-SYM* (Le Page, 1987) programs. The relation between these two molecules was analysed by using the routine *SYMMOL* of the program *PARST* (Nardelli, 1983) and the projections of the unit-cell contents obtained using the program *PLUTO* (Motherwell & Clegg, 1976). The two independent molecules are related by a pseudo 2_1 axis parallel to x at about $(0, \frac{1}{4}, \frac{1}{6})$.

All the H atoms were found in a final $\Delta\rho$ synthesis and refined isotropically, except those of the C15 methyl group of compound (2a) which were placed in calculated positions using the *HFIX* 137 option of *SHELXL92*, with a common isotropic displacement parameter. For both compounds refinement was on F^2 for all reflections, except for one reflection of compound (4) which was flagged for possible systematic errors. The observed threshold $I > 2\sigma(I)$ is used only for calculating $R(\text{obs.})$ etc. given here for comparison with refinements on F .

It is interesting to consider the molecular 'thermal' motion in terms of the Schomaker & Trueblood (1968) LST rigid-body approximation. The results of this analysis, carried out using the *THMV* program (Trueblood, 1984), show that some internal motion (or disorder) involving mainly the O atoms and the Me groups in both compounds is present, the rigid-body model not

being very successful, as indicated by the following values of the wR_U index: 0.114 for compound (2a) and 0.146 for molecule A and 0.130 for molecule B of compound (4); the index improves to 0.072, 0.086 and 0.085, respectively, if the internal motions for those atoms are considered according to Dunitz & White (1973).

Data collection: local programs. Cell refinement: *LQPARM* (Nardelli & Mangia, 1984). Data reduction: local programs. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL92*. Molecular graphics: *ORTEP* (Johnson, 1965); *PLUTO*. Software used to prepare material for publication: *PARST*; *PARSTCIF* (Nardelli, 1991). The calculations were carried out on the ENCORE 91 computer of the Centro di Studio per la Strutturistica Diffratometrica del CNR, Parma, and on a COMPAQ 486c portable computer.

Financial support from the European Community Commission under contract No. SC1000657 is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71700 (67 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1073]

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1,3,5-Tris[3-(2,6,6-triméthyl-1-cyclohexen-1-yl)acryloyle]benzène

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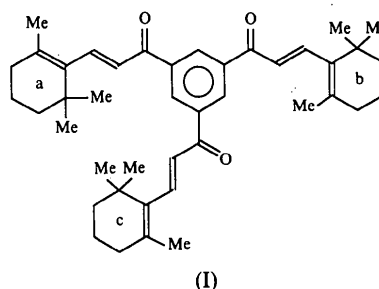
(Reçu le 12 juillet 1993, accepté le 18 octobre 1993)

Abstract

1,3,5-Tris[3-(2,6,6-triméthyl-1-cyclohexen-1-yl)acryloyle]benzene, C₄₂H₅₄O₃, contains three carbonyl groups at positions 1,3,5 on a benzene ring and three cyclohexene moieties. Disorder in the crystals arises from a 1:1 mixture of two possible puckered conformations of the cyclohexene rings. The triketone investigated is analogous to compounds isolated from two African plants used in traditional folk medicine against liver diseases and lesions.

Commentaire

Récemment, quatre tricétones benzéniques ont été isolées de deux plantes africaines utilisées dans la pharmacopée traditionnelle et appartenant à la famille des *Cochlospermaceae* (*C. tinctorium* et *C. planchonii*) (Addae-Mensah, Waibel & Achenbach, 1985; Diallo, Vanhaellen-Frastré & Vanhaelen, 1991). Les activités hépatoprotectrices de ces plantes ont été démontrées (Dalvi & Sere, 1988) et un brevet mentionne leur utilisation pour le traitement des hépatites virales et fulminantes (Wolga, 1987). L'obtention de quantités plus importantes de ces composés ainsi que de divers analogues, par synthèse mise au point au laboratoire (Valla, Andriamialisoa, Giraud & Ginderow, 1993) permettra d'effectuer une étude biologique approfondie. Les composés naturels, du fait de leur morphologie, ne se prêtaient pas à une étude cristallographique. Un analogue parfaitement cristallisé (I) nous a permis de réaliser cette étude.



La molécule est composée d'un groupement benzénique auquel est relié en position 1,3,5 trois groupements carbonyl, eux-mêmes liés à un groupement cyclohexène (Fig. 1). Le cycle benzénique est plan avec les groupements C=O au dessus du plan moyen pour C7A—O7A [0,019 (5), 0,388 (3) Å] et C7B—O7B [0,019 (5), 0,156 (3) Å] alors qu'il se trouve en dessous du même plan pour C7C—O7C [−0,056 (5), −0,028 (4) Å]. Les distances trouvées sont conformes avec celles du 1,3,5-triacétylbenzène (O'Connor, 1973). En ce qui concerne les trois groupements cyclohexène, il y a contraction des distances C13—C14 avec une distance C13A—C14A égale à 1,34 (1), C13B—C14B égale à 1,25 (1) et C13C—C14C égale à 1,19 (1) Å. Le cycle cyclohexène qui présente le gauchissement le plus prononcé est le cycle A. Le calcul des plans moyens passant par les différents cycles, montrent que C13A est à une distance du plan moyen de 0,342 (10) Å et C14A à 0,224 (9) Å alors que les cycles B et C se rapprochent de la planéité. Une valeur de 1,24 (2) Å a été trouvée pour le cyclohexène du 2,6-di-cis-4-hydroxyrétinoïc acid γ -lactone (Thackeray & Gafner, 1975). Les distances très courtes sont le résultat d'un désordre car ces atomes occupent une situation moyenne

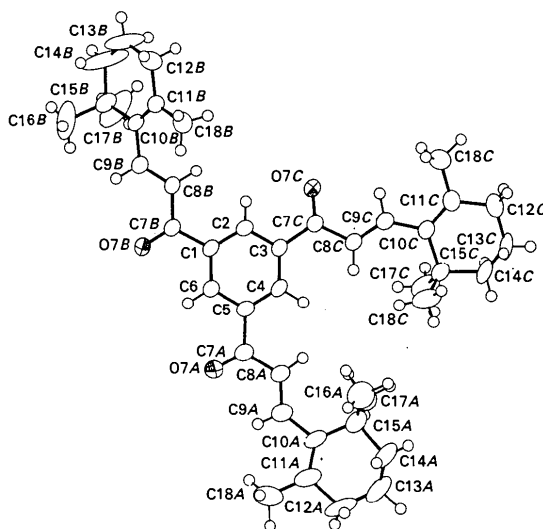


Fig 1. Désignation des atomes. Les ellipsoïdes correspondent à 50% de probabilité sauf pour les atomes d'hydrogène ou les diamètres sont arbitraires.