

C2—C1—C10	114.7 (3)	C8—C14—O26	122.8 (4)
C1—C2—C3	112.7 (3)	C13—C14—O26	122.1 (4)
C2—C3—C4	110.2 (3)	C8—C15—C16	117.8 (4)
C2—C3—O1'	112.9 (3)	C15—C16—C17	113.2 (4)
C4—C3—O1'	107.0 (3)	C13—C17—C16	112.1 (3)
C3—C4—C5	113.4 (3)	C13—C17—C20	113.7 (3)
C4—C5—C6	109.9 (3)	C16—C17—C20	109.9 (3)
C4—C5—C10	113.4 (3)	C17—C20—C21	120.9 (4)
C6—C5—C10	110.5 (3)	C17—C20—C23	131.2 (4)
C5—C6—C7	111.2 (4)	C21—C20—C23	107.7 (4)
C6—C7—C8	114.6 (3)	C20—C21—O24	105.8 (4)
C7—C8—C9	111.8 (3)	C23—C22—O24	109.0 (4)
C7—C8—C14	110.6 (3)	C23—C22—O25	129.2 (5)
C7—C8—C15	106.5 (3)	O24—C22—O25	121.7 (5)
C9—C8—C14	111.3 (3)	C20—C23—C22	108.6 (4)
C9—C8—C15	110.3 (3)	C21—O24—C22	108.9 (4)
C14—C8—C15	106.1 (3)	C2'—C1'—O1'	109.6 (4)
C8—C9—C10	115.2 (3)	C2'—C1'—O5'	109.7 (4)
C8—C9—C11	110.8 (3)	O1'—C1'—O5'	111.9 (4)
C10—C9—C11	114.1 (3)	C1'—C2'—C3'	109.7 (4)
C1—C10—C5	106.3 (3)	C1'—C2'—O2'	110.5 (4)
C1—C10—C9	111.6 (3)	C3'—C2'—O2'	111.5 (4)
C1—C10—C19	105.4 (3)	C2'—C3'—C4'	109.3 (4)
C5—C10—C9	110.9 (3)	C2'—C3'—O3'	111.5 (4)
C5—C10—C19	110.2 (3)	C4'—C3'—O3'	106.9 (4)
C9—C10—C19	112.2 (3)	C3'—C4'—C5'	112.3 (4)
C9—C11—C12	116.3 (3)	C3'—C4'—O4'	110.9 (4)
C11—C12—C13	118.3 (4)	C5'—C4'—O4'	109.2 (4)
C12—C13—C14	108.4 (3)	C4'—C5'—C6'	112.4 (4)
C12—C13—C17	110.7 (3)	C4'—C5'—O5'	111.5 (4)
C12—C13—C18	108.4 (4)	C6'—C5'—O5'	105.1 (4)
C14—C13—C17	107.4 (3)	C3—O1'—C1'	115.4 (3)
C14—C13—C18	112.0 (4)	C3'—O3'—C7'	114.3 (4)
C17—C13—C18	110.0 (4)	C1'—O5'—C5'	113.2 (3)
C8—C14—C13	115.0 (3)		
C10—C1—C2—C3	55.2 (3)	C15—C16—C17—C13	-46.2 (4)
C1—C2—C3—C4	-51.6 (4)	C16—C17—C13—C14	55.0 (4)
C2—C3—C4—C5	52.8 (4)	C17—C13—C14—C8	-64.6 (4)
C3—C4—C5—C10	-56.3 (4)	C13—C14—C8—C15	58.8 (4)
C4—C5—C10—C1	53.6 (3)	C16—C17—C20—C21	116.7 (5)
C5—C10—C1—C2	-53.7 (3)	C16—C17—C20—C23	-57.2 (4)
C10—C5—C6—C7	-59.9 (4)	C4—C3—O1'—C1'	-146.4 (5)
C5—C6—C7—C8	55.8 (4)	C3—O1'—C1'—C2'	155.8 (5)
C6—C7—C8—C9	-46.1 (4)	O1'—C1'—C2'—C3'	62.2 (4)
C7—C8—C9—C10	42.8 (3)	C1'—C2'—C3'—C4'	56.0 (4)
C8—C9—C10—C5	-48.3 (3)	C2'—C3'—C4'—C5'	-51.0 (4)
C9—C10—C5—C6	56.0 (4)	C3'—C4'—C5'—O5'	50.4 (4)
C8—C9—C11—C12	-39.6 (3)	C4'—C5'—O5'—C1'	-55.7 (4)
C9—C11—C12—C13	38.2 (4)	C5'—O5'—C1'—C2'	61.4 (4)
C11—C12—C13—C14	-43.0 (4)	O5'—C1'—C2'—C3'	-61.0 (4)
C12—C13—C14—C8	55.1 (4)	O2'—C2'—C3'—O3'	-63.3 (4)
C13—C14—C8—C9	-61.2 (4)	C2'—C3'—O3'—C7'	93.2 (5)
C14—C8—C9—C11	50.1 (3)	O3'—C3'—C4'—O4'	65.7 (4)
C14—C8—C15—C16	-47.3 (4)	O4'—C4'—C5'—C6'	-68.4 (4)
C8—C15—C16—C17	43.8 (4)		

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71312 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1053]

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## Structural Studies of the Regioselectivity of Bishydroxylation of Polycyclic Methylene-cyclobutanol Derivatives

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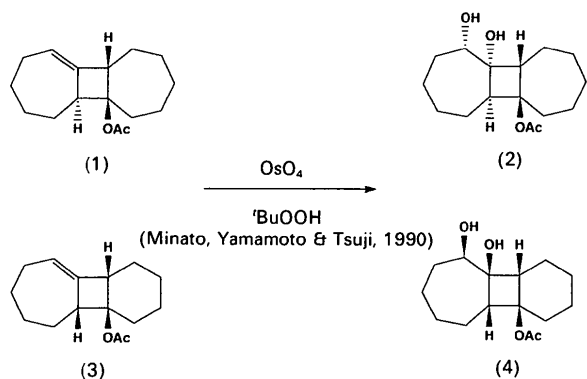
## Abstract

With tricyclic methylenecyclobutanols as starting materials, the following compounds were prepared and their crystal structures determined: *cis-transoid-cis*-7,8-dihydroxytricyclo[7.5.0.0<sup>2,8</sup>]tetradec-1-yl acetate (2) and *cis-cisoid-cis*-8,9-dihydroxytricyclo[6.5.0.0<sup>2,7</sup>]tridec-2-yl acetate (4). The stereochemistry at the ring junctions is retained during the reaction. The conformations of

these molecules and their hydrogen bonding in the crystals are discussed. The results of the  $F^2$  and  $F$  refinements are compared.

### Comment

In continuing our work on the synthesis of polycyclic derivatives (Jamart-Grégoire, Brosse, Ianelli, Nardelli & Caubère, 1991; Ianelli, Nardelli, Belletti, Jamart-Grégoire, Brosse & Caubère, 1993), the stereochemistry of the bis-hydroxylation of (1) and (3) was resolved.



Even though it is well known that the reagents used lead to bis-*cis*-hydroxylation (Lohray, 1992, and references therein), much less is known about the influence of steric parameters on the regioselectivity of such reactions with polycyclic derivatives. Moreover, it was also of paramount importance to determine if the stereochemistry of the ring was preserved during the reaction. As the classical spectroscopic methods were unable to answer these questions, the problem was solved by X-ray crystal structure analysis, which showed that (2) has a *cis-transoid-cis* structure while the structure of (4) is *cis-cisoid-cis*, as illustrated by the *ORTEP* (Johnson, 1965) drawings shown in Fig. 1.

There are two crystallographically independent molecules in the asymmetric unit of (4) related by a local pseudo  $c$  glide, approximately parallel to the (010) plane at about  $\frac{1}{2}b$ . There are no substantial differences between the structures of these two molecules.

Bond distances, bond angles and selected torsion angles are compared in Table 2, with the average values quoted where appropriate. Good agreement is observed generally for these values, except in a few cases (starred values) where atoms [C16 of (2) and C3, C4 and C16 of both molecules of (4)] affected by an exceptionally high thermal motion or disorder are involved (see  $U_{eq}$  values in Table 1). Worth noting is the value of the C2—C1—C14 angle, which is larger by about  $5^\circ$  in (4) as a consequence of the *syn (cisoid)* configuration of the tricyclic system which brings C3 and C14 to a contact distance of 3.262 (3) Å in molecule A and 3.240 (5) Å in molecule B.

Table 3 gives the relevant parameters that describe the conformation of the tricyclic system, which is characteristic of the molecules of these compounds. There are no significant differences in the conformational parameters of the two cycloheptane rings of (2), as with the two independent molecules of (4), while there are significant differences when comparing this ring between the two compounds. The average values of bond distances, endocyclic bond angles and torsion angles for this ring are as follows:  $\langle d(\text{C—C}) \rangle = 1.529$  (5),  $1.528$  (5) Å;  $\langle \alpha \rangle = 115.4$  (8),  $115.7$  (7) $^\circ$ ;  $\langle |\tau| \rangle = 61.7$  (97),  $61.0$  (99) $^\circ$ ;  $\Sigma\tau = 0.6$ ,  $-0.5^\circ$  for the two rings of (2), and  $\langle d(\text{C—C}) \rangle = 1.528$  (6),  $1.525$  (7) Å;  $\langle \alpha \rangle = 116.2$  (12),  $116.3$  (10) $^\circ$ ;  $\langle |\tau| \rangle = 64.6$  (78),  $63.5$  (80) $^\circ$ ;  $\Sigma\tau = -1.7$ ,  $1.5^\circ$  for (4). This is in good agreement with the parameters calculated by Hen-

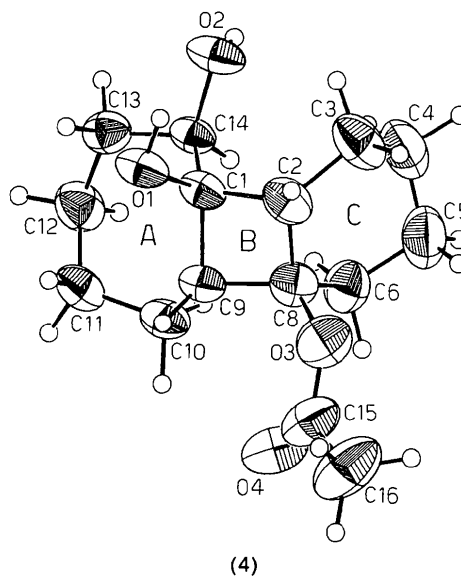
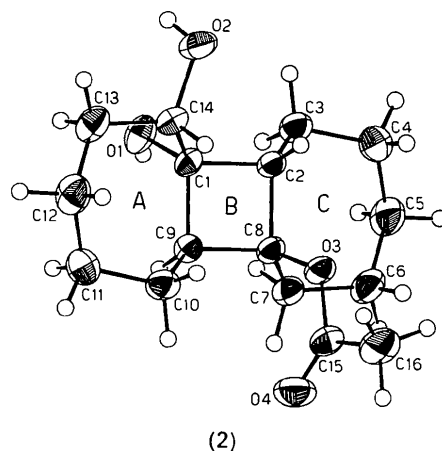


Fig. 1. *ORTEP* drawings of the molecules. Ellipsoids are at the 50% probability level.

drickson (1967) for the chair (C) and twist-chair (TC) conformations, respectively, of unsubstituted cycloheptane:  $\langle \alpha \rangle = 115.6^\circ$ ,  $\langle |\tau| \rangle = 61.0^\circ$ ,  $\Sigma\tau = 0^\circ$  and  $\Sigma E = 35.6 \text{ kJ mol}^{-1}$  for C, and  $\langle \alpha \rangle = 114.6^\circ$ ,  $\langle |\tau| \rangle = 64.8^\circ$ ,  $\Sigma\tau = 7.7^\circ$  and  $\Sigma E = 29.7 \text{ kJ mol}^{-1}$  for TC.

The orientation of the acetyl group is defined by the C2—C8—O3—C15 torsion angle, whose value (see Table 2) indicates that the O3—C15 bond is antiperiplanar to the C2—C8 bond in the molecules of both compounds. This conformation is imposed by intramolecular steric hindrance which prevents rotation about the C8—O3 bond, as indicated by the fact that the minimum of the non-bonded energy profile, obtained by rotating the group about the appropriate bond in the isolated molecule, corresponds to the conformation found in the crystal. The orientation of the carboxyl plane about the O3—C15 bond is determined by intramolecular interactions of the type C—H...O, which can be considered as weak hydrogen bonds (Taylor & Kennard, 1982; Berkovitch-Yellin & Leiserowitz, 1984): C7...O4 = 2.934 (2), H...O4 = 2.369 (2) Å and C7—H...O4 = 116.5 (2)° in (2); C10...O4 = 3.169 (3), H...O4 = 2.584 (3) Å and C10—H...O4 = 118.9 (4)° in (4), molecule A; C10...O4 = 3.229 (3), H...O4 = 2.653 (3) Å and C10—H...O4 = 118.4 (4)° in (4), molecule B.

The orientation of the hydroxyl groups is determined by the intermolecular hydrogen bonds that are involved: O1...O2<sup>i</sup> = 2.895 (2), H...O2<sup>i</sup> = 2.072 (4) Å and O1—H...O2<sup>i</sup> = 162.7 (5)° in (2); O2A...O1B = 2.750 (3), H...O1B = 1.90 (2) Å and O2A—H...O1B = 173 (3)°; O2B...O1A<sup>ii</sup> = 2.742 (3), H...O1A<sup>ii</sup> = 1.90 (2) Å and O2B—H...O1A<sup>ii</sup> = 175 (2)°; O1A...O2A<sup>iii</sup> = 2.712 (4), H...O2A<sup>iii</sup> = 1.90 (2) Å and O1A—H...O2A<sup>iii</sup> = 160 (2)°; O1B...O2B<sup>iv</sup> = 2.706 (4), H...O2B<sup>iv</sup> = 1.89 (2) Å and O1B—H...O2B<sup>iv</sup> = 162 (1)° in (4) [symmetry codes: (i) 1 + x, y, z; (ii) x, y, 1 + z; (iii) -x, 1 - y, -z; (iv) -x, 1 - y, 1 - z].

The structural analysis of (2) is clearly more accurate than that of (4), which is due to the quality of the intensity data that, in the case of (4), is low because of the high thermal motion (or disorder) that affects the atoms of this compound (see  $U_{eq}$  values in Table 1); the average values,  $\langle U_{eq} \rangle$ , are: 0.0432 Å<sup>2</sup> for (2) and 0.0758 and 0.0799 Å<sup>2</sup> for molecules A and B of (4), respectively.

It is interesting to consider the molecular 'thermal' motion in terms of the Schomaker & Trueblood (1968) TLS rigid-body approximation. The results of this analysis, carried out using the THMV program (Trueblood, 1984), show that particularly high internal motions (or disorder) are present in molecule B of (4), while the rigid-body model is satisfactory, particularly for molecule A, as indicated by the following values of the  $R_w(U)$  index (values from the  $F$  refinement in square brackets): 0.109 [0.111] for (2), 0.072 [0.078] for molecule A and 0.179 [0.184] for molecule B of (4), which indicate a small but systematically better agreement for the  $F^2$  refinement.

## Experimental

### Compound (2)

#### Crystal data

C<sub>16</sub>H<sub>26</sub>O<sub>4</sub>  
 $M_r = 282.38$   
 Triclinic  
 $P\bar{1}$   
 $a = 5.730 (1) \text{ \AA}$   
 $b = 15.767 (6) \text{ \AA}$   
 $c = 8.394 (1) \text{ \AA}$   
 $\alpha = 90.09 (1)^\circ$   
 $\beta = 104.50 (2)^\circ$   
 $\gamma = 90.63 (1)^\circ$   
 $V = 734.2 (3) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 1.277 \text{ Mg m}^{-3}$

#### Data collection

Siemens AED diffractometer  
 $\theta$ - $2\theta$  scans  
 Absorption correction: none  
 2779 measured reflections  
 2779 independent reflections  
 2098 observed reflections  
 $[I > 2\sigma(I)]$   
 $\theta_{\max} = 70.12^\circ$

#### Refinement

Refinement on  $F^2$   
 $R[F > 4\sigma(F)] = 0.0366$   
 $wR(F^2) = 0.0998$   
 $S = 1.128$   
 189 reflections  
 189 parameters  
 Only coordinates of H atoms refined  
 Calculated weights  
 $w = 1/[\sigma^2(F_o^2) + (0.0592P)^2 + 0.0184P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

### Compound (4)

#### Crystal data

C<sub>15</sub>H<sub>24</sub>O<sub>4</sub>  
 $M_r = 268.35$   
 Triclinic  
 $P\bar{1}$   
 $a = 14.172 (3) \text{ \AA}$   
 $b = 12.174 (2) \text{ \AA}$   
 $c = 11.105 (2) \text{ \AA}$   
 $\alpha = 65.36 (1)^\circ$   
 $\beta = 65.09 (12)^\circ$   
 $\gamma = 63.81 (1)^\circ$   
 $V = 1495 (1) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.192 \text{ Mg m}^{-3}$

Cu  $K\alpha_1$  radiation  
 $\lambda = 1.5405620 \text{ \AA}$   
 Cell parameters from 30 reflections  
 $\theta = 25.6 - 40.0^\circ$   
 $\mu = 0.691 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 Small prisms  
 $0.56 \times 0.45 \times 0.39 \text{ mm}$   
 Colourless  
 Crystal source: chemical synthesis

$h = -1 \rightarrow 6$   
 $k = -19 \rightarrow 19$   
 $l = -10 \rightarrow 10$   
 1 standard reflection monitored every 50 reflections  
 intensity variation: within statistical fluctuation

$\Delta\rho_{\max} = 0.231 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.163 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXL92 (Sheldrick, 1992)  
 Extinction coefficient: 0.0377 (21)  
 Atomic scattering factors from *International Tables for X-ray Crystallography* [1974, Vol. IV, Tables 2.2A, 2.3.1 (O, C) and 2.2C (H)]

Cu  $K\alpha_1$  radiation  
 $\lambda = 1.5405620 \text{ \AA}$   
 Cell parameters from 30 reflections  
 $\theta = 20 - 39^\circ$   
 $\mu = 0.656 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 Small prisms  
 $0.41 \times 0.32 \times 0.29 \text{ mm}$   
 Colourless  
 Crystal source: chemical synthesis

## Data collection

Siemens AED diffractometer	$h = -15 \rightarrow 17$
$\theta$ - $2\theta$ scans	$k = -13 \rightarrow 14$
Absorption correction:	$l = 0 \rightarrow 13$
none	1 standard reflection
5688 measured reflections	monitored every 50
5688 independent reflections	reflections
3483 observed reflections	intensity variation: within
$[I > 2\sigma(I)]$	statistical fluctuation
$\theta_{\max} = 70.31^\circ$	

## Refinement

Refinement on $F^2$	$\Delta\rho_{\max} = 0.279 \text{ e } \text{\AA}^{-3}$
$R[F > 4\sigma(F)] = 0.0492$	$\Delta\rho_{\min} = -0.364 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.1351$	Extinction correction:
$S = 1.104$	<i>SHELXL92</i> (Sheldrick,
5637 reflections	1992)
352 parameters	Extinction coefficient:
Only coordinates of H atoms	0.0063 (6)
refined	Atomic scattering factors
Calculated weights	from <i>International Tables</i>
$w = 1/[\sigma^2(F_o^2) + (0.0862P)^2]$	for X-ray Crystallogra-
where $P = (F_o^2 + 2F_c^2)/3$	phy [1974, Vol. IV, Tables
	2.2A, 2.3.1 (O, C) and
	2.2C (H)]

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )
$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

Compound (2)	x	y	z	$U_{\text{eq}}$
O1	0.2556 (2)	0.07866 (6)	0.9390 (1)	0.0441 (4)
O2	-0.2266 (2)	0.09323 (7)	0.9918 (1)	0.0464 (4)
O3	0.0598 (2)	0.35173 (6)	0.8507 (1)	0.0370 (3)
O4	0.2164 (2)	0.40786 (7)	0.6515 (2)	0.0596 (5)
C1	0.1042 (2)	0.15080 (8)	0.8922 (2)	0.0308 (4)
C2	0.1527 (2)	0.22592 (8)	1.0179 (2)	0.0309 (4)
C3	0.3250 (3)	0.21268 (9)	1.1855 (2)	0.0396 (5)
C4	0.3896 (3)	0.2947 (1)	1.2865 (2)	0.0489 (6)
C5	0.5948 (3)	0.3469 (1)	1.2479 (2)	0.0524 (6)
C6	0.5491 (3)	0.3817 (1)	1.0747 (2)	0.0490 (6)
C7	0.4924 (3)	0.31460 (9)	0.9380 (2)	0.0375 (5)
C8	0.2334 (2)	0.28268 (8)	0.8901 (2)	0.0305 (4)
C9	0.1810 (3)	0.20818 (8)	0.7627 (2)	0.0320 (4)
C10	0.0096 (3)	0.22054 (9)	0.5940 (2)	0.0415 (5)
C11	-0.0563 (3)	0.1378 (1)	0.4967 (2)	0.0498 (6)
C12	-0.2609 (3)	0.0869 (1)	0.5374 (2)	0.0500 (6)
C13	-0.2132 (3)	0.05207 (9)	0.7117 (2)	0.0464 (5)
C14	-0.1564 (3)	0.12014 (8)	0.8458 (2)	0.0346 (4)
C15	0.0699 (3)	0.40849 (9)	0.7318 (2)	0.0433 (5)
C16	-0.1286 (4)	0.4713 (1)	0.7138 (2)	0.0591 (7)

Compound (4)	x	y	z	$U_{\text{eq}}$
O1A	0.1080 (1)	0.5213 (2)	-0.2071 (1)	0.0610 (8)
O2A	0.0972 (1)	0.4945 (2)	0.0658 (1)	0.0655 (9)
O3A	0.1435 (2)	0.8818 (2)	-0.3949 (2)	0.0837 (10)
O4A	0.3139 (2)	0.8548 (2)	-0.5386 (2)	0.1012 (13)
C1A	0.1527 (1)	0.5889 (2)	-0.1775 (2)	0.0504 (10)
C2A	0.0786 (2)	0.7295 (2)	-0.1834 (2)	0.0651 (12)
C3A	0.0054 (2)	0.7849 (3)	-0.0606 (3)	0.0925 (18)
C4A	0.0680 (3)	0.8134 (3)	-0.0020 (3)	0.0987 (20)
C5A	0.1416 (3)	0.8885 (3)	-0.1145 (3)	0.0965 (22)
C6A	0.2282 (2)	0.8117 (2)	-0.2129 (3)	0.0739 (15)
C8A	0.1781 (2)	0.7734 (2)	-0.2805 (2)	0.0622 (11)
C9A	0.2383 (2)	0.6417 (2)	-0.3086 (2)	0.0529 (10)
C10A	0.3610 (2)	0.5780 (2)	-0.3275 (2)	0.0641 (12)
C11A	0.3996 (2)	0.4350 (2)	-0.3033 (2)	0.0718 (13)

C12A	0.3863 (2)	0.3588 (2)	-0.1506 (2)	0.0757 (14)
C13A	0.2682 (2)	0.3711 (2)	-0.0585 (2)	0.0654 (12)
C14A	0.1926 (1)	0.5045 (2)	-0.0501 (2)	0.0509 (10)
C15A	0.2171 (3)	0.9113 (3)	-0.5157 (3)	0.0880 (19)
C16A	0.1637 (3)	1.0224 (3)	-0.6178 (4)	0.1199 (27)
O1B	0.1111 (1)	0.5112 (1)	0.2969 (1)	0.0532 (7)
O2B	0.0811 (1)	0.5379 (2)	0.5547 (1)	0.0738 (9)
O3B	0.3629 (1)	0.1730 (2)	0.3059 (2)	0.0780 (10)
O4B	0.5216 (2)	0.2060 (2)	0.1596 (2)	0.1036 (13)
C1B	0.1953 (1)	0.4526 (2)	0.3642 (2)	0.0490 (10)
C2B	0.2104 (2)	0.3085 (2)	0.4410 (2)	0.0670 (12)
C3B	0.1781 (3)	0.2466 (4)	0.5948 (3)	0.1302 (21)
C4B	0.2539 (3)	0.1913 (5)	0.6620 (3)	0.1504 (32)
C5B	0.3737 (3)	0.1427 (3)	0.5904 (3)	0.0979 (20)
C6B	0.4053 (2)	0.2385 (2)	0.4523 (2)	0.0702 (13)
C8B	0.3331 (2)	0.2757 (2)	0.3632 (2)	0.0588 (11)
C9B	0.3112 (1)	0.4115 (2)	0.2607 (2)	0.0505 (10)
C10B	0.3900 (2)	0.4863 (2)	0.2059 (2)	0.0634 (12)
C11B	0.3398 (2)	0.6276 (2)	0.1471 (2)	0.0702 (14)
C12B	0.2769 (2)	0.7014 (3)	0.2542 (3)	0.0789 (15)
C13B	0.1715 (2)	0.6757 (2)	0.3559 (2)	0.0676 (14)
C14B	0.1805 (2)	0.5379 (2)	0.4428 (2)	0.0559 (11)
C15B	0.4570 (3)	0.1502 (3)	0.2043 (3)	0.0851 (16)
C16B	0.4681 (3)	0.0484 (3)	0.1527 (3)	0.1148 (23)

Table 2. Comparison of bond lengths ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and selected torsion angles ( $^\circ$ ) with e.s.d.'s in parentheses

	(2)	A	B	Average
O1—C1	1.433 (2)	1.432 (4)	1.431 (3)	1.432 (2)
O2—C14	1.445 (2)	1.431 (3)	1.434 (3)	1.439 (4)
O3—C8	1.464 (2)	1.467 (3)	1.455 (4)	1.464 (3)
O3—C15	1.354 (2)	1.329 (4)	1.339 (4)	1.347 (7)
O4—C15	1.201 (2)	1.199 (4)	1.196 (5)	1.200 (2)
C1—C2	1.560 (2)	1.554 (3)	1.558 (3)	1.558 (2)
C1—C9	1.559 (2)	1.559 (3)	1.559 (3)	1.558 (2)
C1—C14	1.519 (2)	1.524 (3)	1.516 (4)	1.520 (2)
C2—C3	1.519 (2)	1.532 (4)	1.506 (4)	1.519 (5)
C2—C8	1.552 (2)	1.530 (4)	1.529 (3)	1.543 (8)
C3—C4	1.535 (2)	1.508 (7)*	1.335 (6)*	-
C4—C5	1.528 (3)	1.509 (5)	1.494 (5)	1.517 (10)
C5—C6	1.516 (2)	1.511 (4)	1.518 (3)	1.516 (2)
C6—C7	1.531 (2)	-	-	-
C7—C8	1.517 (2)	-	-	-
C6—C8	-	-1.523 (5)	1.517 (4)	1.519 (3)
C8—C9	1.562 (2)	1.543 (3)	1.549 (3)	1.554 (6)
C9—C10	1.522 (2)	1.518 (3)	1.520 (4)	1.521 (2)
C10—C11	1.530 (2)	1.515 (4)	1.505 (3)	1.521 (8)
C11—C12	1.522 (3)	1.531 (3)	1.520 (4)	1.525 (3)
C12—C13	1.524 (2)	1.527 (4)	1.517 (4)	1.523 (2)
C13—C14	1.527 (2)	1.516 (3)	1.525 (3)	1.524 (3)
C15—C16	1.495 (3)*	1.493 (5)*	1.495 (6)*	-
C8—O3—C15	120.8 (1)	120.4 (4)	119.0 (4)	120.7 (3)
O1—C1—C14	108.3 (1)	108.6 (3)	109.1 (3)	108.4 (2)
O1—C1—C9	113.4 (1)	111.2 (3)	111.1 (3)	113.0 (6)
O1—C1—C2	115.3 (1)	112.9 (4)	112.4 (4)	115.0 (6)
C9—C1—C14	115.5 (1)	116.1 (4)	116.2 (4)	115.6 (1)
C2—C1—C14	113.8 (1)	119.0 (3)	118.6 (3)	-
C2—C1—C9	90.0 (1)	87.8 (3)	88.1 (3)	89.6 (6)
C1—C2—C8	90.0 (1)	89.4 (3)	89.7 (3)	89.9 (1)
C1—C2—C3	118.7 (1)	127.2 (3)*	127.7 (3)*	-
C3—C2—C8	119.2 (1)	118.4 (3)	117.4 (4)	119.0 (3)
C2—C3—C4	113.6 (1)	113.2 (4)	119.4 (5)	113.8 (8)
C3—C4—C5	114.8 (1)	111.5 (4)*	122.0 (4)*	-
C4—C5—C6	116.1 (2)	110.5 (4)*	110.5 (4)*	-
C5—C6—C7	114.8 (1)	-	-	-
C5—C6—C8	-	112.2 (4)	111.8 (4)	112.0 (2)
C6—C7—C8	115.4 (1)	-	-	-
C2—C8—C7	116.2 (1)	-	-	-
O3—C8—C7	112.5 (1)	-	-	-
C2—C8—C6	-	114.9 (3)	113.7 (3)	114.3 (6)
O3—C8—C6	-	109.4 (3)	110.5 (3)	110.0 (6)
O3—C8—C2	106.5 (1)	107.7 (4)	107.9 (4)	106.6 (3)

C7—C8—C9	115.4 (1)	-	-	-
C6—C8—C9	-	117.6 (4)	118.1 (4)	117.8 (3)
O3—C8—C9	113.9 (1)	116.5 (3)	115.1 (3)	114.2 (6)
C2—C8—C9	90.2 (1)	89.2 (3)	89.5 (3)	90.0 (2)
C1—C9—C8	89.7 (1)	88.8 (3)	88.9 (3)	89.5 (2)
C8—C9—C10	120.2 (1)	121.0 (4)	121.6 (4)	120.3 (2)
C1—C9—C10	119.9 (1)	121.5 (3)	120.9 (3)	120.1 (4)
C9—C10—C11	113.3 (1)	114.0 (5)	113.8 (5)	113.3 (1)
C10—C11—C12	115.0 (1)	113.5 (3)	114.3 (3)	114.8 (3)
C11—C12—C13	116.2 (1)	115.8 (4)	116.3 (4)	116.2 (1)
C12—C13—C14	114.0 (1)	116.5 (4)	117.0 (4)	114.3 (6)
C1—C14—C13	114.7 (1)	114.3 (3)	114.1 (3)	114.6 (1)
O2—C14—C13	111.6 (1)	108.6 (3)	108.4 (3)	111.0 (8)
O2—C14—C1	109.7 (1)	107.1 (4)	107.2 (4)	109.4 (6)
O3—C15—O4	124.7 (2)	123.8 (4)	124.4 (4)	124.5 (2)
O4—C15—C16	125.1 (2)	124.9 (5)	125.0 (5)	125.1 (2)
O3—C15—C16	110.3 (1)	111.3 (4)	110.6 (4)	110.4 (2)
C15—O3—C8—C2	-174.5 (1)	-156.8 (5)	162.5 (4)	-
C15—O3—C8—C6	-	77.8 (6)	-72.6 (6)	-
C15—O3—C8—C7	57.0 (2)	-	-	-
C15—O3—C8—C9	-76.7 (2)	-58.6 (6)	64.3 (6)	-
C14—C1—C2—C3	117.3 (1)	-23.8 (7)	20.9 (7)	-
C6—C8—C9—C10	-	-25.5 (7)	24.2 (6)	-
C7—C8—C9—C10	-116.4 (1)	-	-	-

\* Values affected by high thermal motion or disorder. The signs of the torsion angles refer to the coordinates of Table 1; the opposite signs are also valid, both enantiomorphs being present in the crystals.

Table 3. Conformation of the rings and dihedral angles ( $^{\circ}$ ) of ring planes

$Q_T$  = total puckering amplitude (Å) (Cremer & Pople, 1975).  $DAP$  = minimum displacement asymmetry parameter (Nardelli, 1983b). C = chair. TC = twisted chair.

Ring	$Q_T$	$DAP$	Conformation	A/B	B/C
Compound (2)					
A	0.807 (2)	$\Delta_1(C12) = 0.0408$ (6)	C	-	-
B	-0.0032 (4)	-	-	30.8 (1)	30.7 (1)
C	0.802 (2)	$\Delta_1(C5) = 0.0340$ (7)	C	-	-
Compound (4), molecule A					
A	0.791 (5)	$\Delta_1(C9) = 0.045$ (2)	TC	-	-
B	-0.058 (1)	-	-	33.2 (2)	53.6 (2)
C	0.503 (5)	-	C	-	-
Compound (4) molecule B					
A	0.790 (6)	$\Delta_1(C9) = 0.053$ (2)	TC	-	-
B	0.051 (1)	-	-	31.8 (2)	47.0 (2)
C	0.424 (4)	-	C	-	-

Table 4. Comparison of relevant refinement descriptors and regression parameters of half-normal probability plots

$N$  = number of reflections used in the refinement.  $P$  = number of refined parameters.  $w'R2 = \sum[w''(F_o^2 - F_c^2)^2] / \sum[w''(F_o^2)^2]^{1/2}$ .  $R1 = \sum|F_o - F_c| / \sum(F_o)$ .  $S2 = [\sum[w''(F_o^2 - F_c^2)^2] / (N - P)]^{1/2}$ .  $w'R = [\sum[w''(F_o - F_c)^2] / \sum[w''(F_o)^2]]^{1/2}$ .  $R = \sum|F_o - F_c| / \sum(F_o)$ .  $S = \sum[w''(F_o - F_c)^2] / (N - P)^{1/2} < \sigma(C-C) > = \text{average C-C bond e.s.d.}$   $d$  = comparison of all interatomic distances less than 4.65 Å.  $U_{ij}$  = comparison of atomic displacement parameters.  $xyz$  = comparison of positional coordinates.  $i$  = intercept.  $s$  = slope.  $r$  = correlation coefficient.  $n$  = number of points in the plot defining the regression line.

Refinement parameters	Refinement	$N$	$P$	$w'R2$	$R1$	$S2$	$\langle s(C-C) \rangle$
Compound (2)							
	$F^2$	2777	189	0.0998	0.0366	1.009	0.002
	$F$	2100	285	0.0631	0.0389	0.739	0.0025
Compound (4)							
	$F^2$	5637	352	0.1465	0.0492	0.924	0.004
	$F$	3483	475	0.0874	0.0561	0.809	0.008

Regression parameters	Plot	$i$	$s$	$r$	$n$
	$xyz$	0.003 (10)	0.570 (10)	0.991	60
	$U_{ij}$	-0.026 (5)	0.600 (5)	0.996	120
	$d$	-0.026 (5)	0.523 (5)	0.995	127
Compound (4)					
	$xyz$	-0.27 (2)	1.58 (3)	0.985	114
	$U_{ij}$	-0.052 (8)	0.806 (8)	0.989	228
	$d$	-0.146 (10)	1.399 (10)	0.993	275

Details of the preparation will be published elsewhere. The integrated intensities of both compounds were obtained by a modified version (Belletti, Uguzzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure. Refinement on  $F^2$  for all reflections except two for compound (2) and 51 for compound (4) 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  $F$ .

The accuracy of the choice of space group was checked using *TRACER* (Lawton & Jacobson, 1965), *NEWLAT* (Mugnoli, 1985), *LEPAGE* (Spek, 1988) and *MISSYM* (Le Page, 1987). [The conventional tri-obtuse unit (Niggli-reduced) cell for (4) is  $a = 11.105$  (2),  $b = 12.174$  (2),  $c = 13.842$  (22) Å,  $\alpha = 96.74$  (1),  $\beta = 111.78$  (12),  $\gamma = 114.64$  (1) $^{\circ}$ . The matrix transforming the given cell to the conventional one is  $(0\ 0\ 1 / 0\ -1\ 0 / 1\ 0\ -1)$ .]

The H atoms of the secondary CH<sub>2</sub> and tertiary CH groups were placed in calculated positions riding on the attached C atoms with an isotropic thermal parameter common to each kind of group. The methyl and hydroxyl H atoms were localized and refined by the *SHELXL92* (Sheldrick, 1992) commands HFIX 137 and 147, respectively, which look at the maximum electron density around the circle which represents the loci of possible H-atom positions (for a fixed X—H distance and Y—X—H angle).

For each compound, an independent refinement on  $F$  values was carried out starting from the same intensity data as the  $F^2$  refinement, using the *SHELX76* (Sheldrick, 1976) program and omitting the reflections having  $I < 2\sigma(I)$ , with the purpose of determining the influence of the 'unobserved' reflections. The percentage of omitted reflections is 24.4 and 38.2% for (2) and (4), respectively, corresponding to 0.2 and 0.4% of the total measured scattering power (sum of the measured intensities). The relevant refinement data obtained for the two analyses are collected in Table 4, together with the regression parameters of the half-normal probability plots (Abrahams & Keve, 1971) [calculated by the *ABRAHAMS* (Gilli, 1977) program], the non-H-atom coordinates ( $xyz$ ), the atomic anisotropic displacement parameters ( $U_{ij}$ ) and all the interatomic distances  $< 4.65$  Å (De Camp, 1973) not involving H atoms ( $d$ ).

From Table 4 it appears that, for both compounds, the agreement between  $F_o$  and  $F_c$  is better in the case of the  $F^2$  refinement ( $R1 < R$ ,  $S$  nearer to the expected value of 1), which gives lower e.s.d. values (see the average e.s.d.'s of the C—C bonds). The parameters of the linear regression through points of the half-normal probability plots indicate that no relevant systematic errors are present, particularly in the case of (2) for which overestimated e.s.d.'s are also observed, while for (4) positional parameters and interatomic distances show underestimated e.s.d.'s. For (4), only seven values of  $\Delta/\sigma$  are greater than 3 and these correspond to coordinates or distances involving the atoms affected by high thermal motion or disorder.

Throughout this paper, the average values are means weighted according to the reciprocal of the variances and the correspond-

ing e.s.d.'s are the largest of the 'external' and 'internal' standard deviations (Topping, 1960).

The calculations were performed on the ENCORE 91 computer of the Centro di Studio per la Strutturistica Diffraattometrica del CNR (Parma). Data collection: local programs. Cell refinement: *LQPARM* (Nardelli & Mangia, 1984). Data reduction: local programs. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986). Program(s) used to refine structure: *SHELXL92* (Sheldrick, 1992). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *PARST* (Nardelli, 1983a); *PARSTCIF* (Nardelli, 1991).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71327 (82 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1053]

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## Structure of a Cyclohexanone Derivative

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## Abstract

The crystal structure of 4-hydroxy-4,*N,N'*-trimethyl-2-(3-nitrophenyl)-6-oxo-1,3-cyclohexanedicarboxamide has been determined. The cyclohexane ring exhibits a chair conformation. The phenyl ring is planar and is approximately perpendicular to the cyclohexanone ring. The 3-nitro substituent on the phenyl ring is twisted about 10° out of the ring plane. The amide carbonyl groups are oriented in different directions with respect to the cyclohexanone ring. These orientations of the carboxamide groups facilitate the formation of an intramolecular O—H...O hydrogen bond. The molecules are packed such that chains are formed along the *b* axis. These chains are held together by N—H...O hydrogen bonds.

## Comment

The title compound was prepared by stirring an ethanol solution of *N*-methylacetamide with aromatic aldehyde in the presence of a catalytic amount of piperidine at room temperature (Shetty, 1987). Since it possesses potential pharmacological and pesticidal activity and is used as a key intermediate in the preparation of phenothiazines (Sadanandam & Leelavathi, 1991), it was considered interesting to establish its conformational details by an X-ray diffraction study.